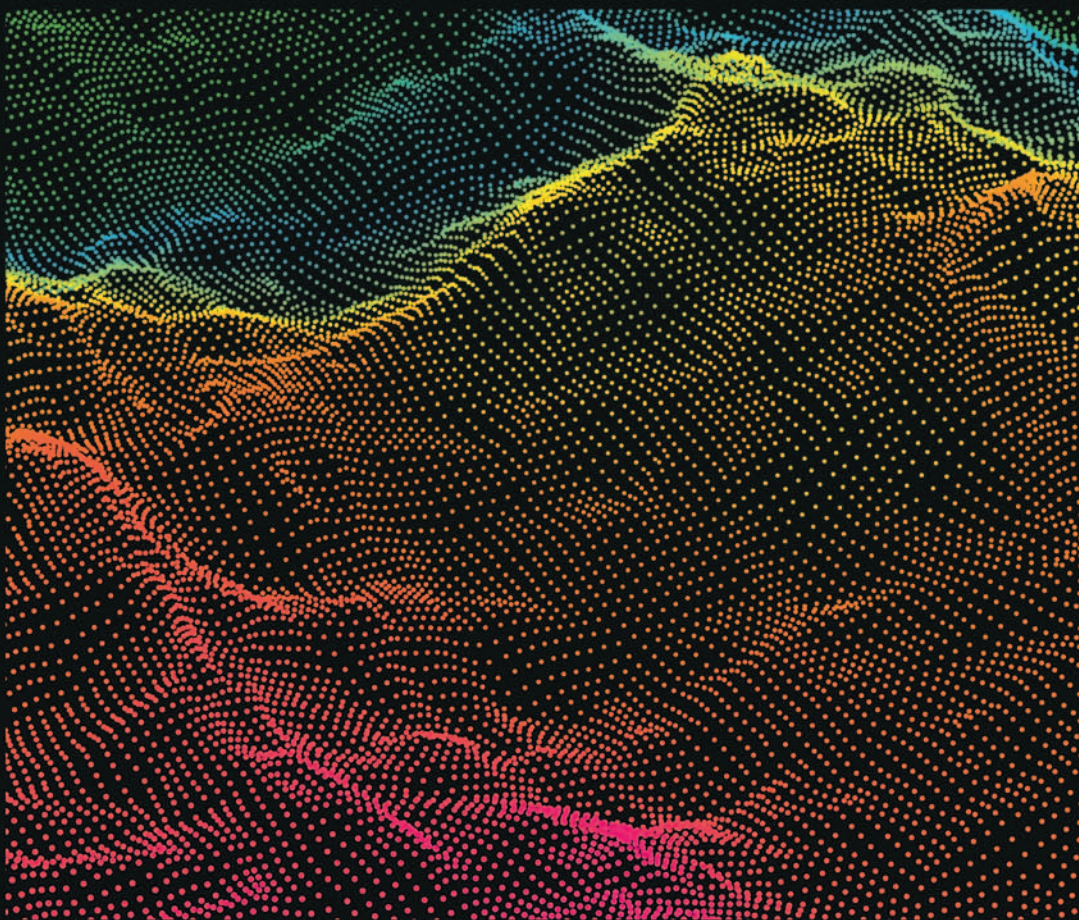


ELSEVIER SERIES IN **MECHANICS OF ADVANCED MATERIALS**

UNCERTAINTY QUANTIFICATION IN MULTISCALE MATERIALS MODELING



Edited by
YAN WANG
DAVID L. MCDOWELL

Uncertainty Quantification in Multiscale Materials Modeling

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Uncertainty Quantification in Multiscale Materials Modeling

Edited by

Yan Wang and

David L. McDowell

**Georgia Institute of Technology, Atlanta, GA,
United States**



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Preface

Human history shows evidence of epochs defined by new material discovery and deployment, which in turn have led to technology innovation and industrial revolutions. Discovery and development of new and improved materials has accelerated with the availability of computational modeling and simulation tools. Integrated Computational Materials Engineering has been widely pursued over the past decade to understand and establish the process—structure—property relationships of new materials. Yet the deployment of computational tools for materials discovery and design is limited by the reliability and robustness of simulation predictions owing to various sources of uncertainty.

This is an introductory book which presents various uncertainty quantification (UQ) methods and their applications to materials simulation at multiple scales. The latest research on UQ for materials modeling is introduced. The book reflects a range of perspectives on material UQ issues from over 50 researchers at universities and research laboratories worldwide. The target audience includes materials scientists and engineers who want to learn the basics of UQ methods, as well as statistical scientists and applied mathematicians who are interested in solving problems related to materials.

The book is organized as follows. Chapter 1 provides an overview of various UQ methods, both nonintrusive and intrusive, the sources of uncertainty in materials modeling, and the existing research work of UQ in materials simulation and design at different length scales. Chapters 2–5 describe the existing research efforts on model error quantification for quantum mechanical simulation to predict material properties via density functional theory. Chapters 6–7 provide state-of-the-art examples of Bayesian model calibration of interatomic potentials, the major source of errors in molecular dynamics simulation, and sensitivity analyses of their effects on physical property predictions. Chapters 8–10 provide examples of UQ methods developed for mesoscale simulations of materials, including kinetic Monte Carlo and phase field simulations. Chapters 11–13 discuss recent research of random fields and their applications to materials modeling in the higher length scale (mesoscopic) continuum regime, such as uncertainty propagation between scales in composites for mechanical property prediction and damage detection. Chapters 14 and 15 illustrate some of the unique UQ issues in multiscale materials modeling, including Bayesian model calibration based on information obtained from different scales, and reliability assessment based on stochastic reduced-order models with samples obtained using multifidelity simulations. Chapter 16 provides insight regarding materials design and optimization under uncertainty for cases in which Bayesian optimization and surrogate models can

play a major role. Chapter 17 highlights the challenges in metamaterial property and behavior predictions, where the variability induced by additive manufacturing processes needs to be quantified in simulations and incorporated in the material database.

We would like to thank all authors of the chapters for their contributions to this book and their efforts to advance the frontiers of the emerging field of UQ for materials. We are also in debt to our reviewers who rigorously examined the submissions, provided helpful feedback during manuscript selection, and improved the quality of the included chapters. This volume would not have been possible without the tireless efforts and devotion of Ms. Ana Claudia Abad Garcia, our Elsevier publishing editor and project manager, as well as the encouragement from the book series editor-in-chief Prof. Dr. Vadim Silberschmidt.

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Uncertainty quantification in materials modeling

1

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1.1 Materials design and modeling

New and improved materials have long fostered innovation. The discovery of new materials leads to new product concepts and manufacturing techniques. Historically, materials discovery emerges from exploratory research in which new chemical, physical, and biological properties of new materials become evident. Then their potential applications are identified. This discovery pathway is typically lengthy and has largely relied on serendipity. In contrast, intentional materials design is an application requirement—driven process to systematically search for solutions. In general, design involves iterative searching aimed at identifying optimal solutions in the design space, which is formed by the material composition and hierarchical structure (e.g., micro-structure). The goal thus is to find compositions and structures that achieve the most suitable chemical and physical properties subject to various constraints, including cost, time, availability, manufacturability, and others.

A transformational trend in early 21st century is to incorporate computational modeling and simulation of material process—structure and structure—property relations to reduce materials development cycle time and its reliance on costly and time-consuming empirical methods. The Integrated Computational Materials Engineering (ICME) initiative [1,2] has been embraced by various industry sectors as a viable path forward to accelerate materials development and insertion into products by employing more comprehensive management of data, process monitoring, and integrated computational modeling and simulation. This has led more recently to the development of the US Materials Genome Initiative (MGI) [3], as well as companion thrusts in Europe and Asia [4], which aim to accelerate discovery and development of new and improved materials via a strategy of fusing information from experiments, theory, and computational simulation, aided by the tools of uncertainty quantification (UQ) and data science with the emphasis on high throughput protocols.

An accurate measurement to evaluate the role of ICME is the extent that it principally provides decision support for materials design and development. In other words, a metric for measuring the success of ICME is the increase of the fraction of decisions made in the critical path of materials development, optimization, certification, and deployment, where decision makers are informed via modeling and simulation as opposed to experiments. The same is true for the discovery of new materials as per objectives of the MGI.

To design material systems [5] by tailoring the hierarchical material structure to deliver required performance requires that we go beyond the aims of basic science to explain phenomena and governing mechanisms, namely to understand and quantify these phenomena and mechanisms to the extent necessary to facilitate control and to manipulate structure at individual scales in a way that trends toward desired properties or responses. This change of emphasis toward connecting process to structure and structure to properties or responses undergirds much of the science base supporting ICME goals of materials design and development. The multiscale nature of material structure and responses is essential; multiscale modeling of utility to ICME must address the spatial- and temporal-scale hierarchies in order to

- Understand interaction mechanisms across length and time scales that affect cooperative properties arising from the hierarchical material structure;
- Improve materials by addressing both unit processes at fine scale and couplings of mechanisms across scales.

These two needs call for the application of systematic methods to search material structures and microstructures that deliver the required sets of properties or responses at various scales of interests. Multiscale modeling captures the responses and interactions of collective structures at various levels of material structure hierarchy. Further advances in multiscale modeling are necessary to understand the modes of materials synthesis in processing, as well as degradation or evolution in service.

Understanding the cause–effect relationship between material structure and properties or responses is a key element of materials design. The structure–property linkages can be regarded as “input–output” relations to facilitate engineering systems design of materials. Similarly, it is necessary to understand and quantify the relationship between fabrication and materials processing and resulting material structure. Physical realization of optimal material microstructures may be restricted by the limitations of available processing techniques. In many cases, available process–structure linkages are considered as constraints on accessible materials. As a result, the central task of materials design is to establish the process–structure–property (P–S–P) relationship based on the needs of properties or responses.

An example of P–S–P relationship is illustrated in Fig. 1.1 [6] for ultrahigh strength, corrosion-resistant steels. Each of the lines between boxes indicates a linkage from process to structure or from structure to property. We note that these mappings often involve phenomena that occur at multiple length and time scales, but these phenomena can manifest anywhere within the chain of P–S–P relations.

Modeling and simulation is an efficient means to augment physical experiments to identify P–S–P linkages. ICME tools at different scales have been developed to predict microstructures from fabrication processes and predict chemical and physical properties of microstructures. The major paradigm shift of ICME is to develop data-enhanced and simulation-based tools to inform decisions in materials design and development. However, there are tremendous challenges in predicting P–S–P relationships. The first challenge pertains to the quantitative representation of the hierarchical nature of material structures at various length scales. Advancement in multiscale computational modeling as required to bridge the length and time scale

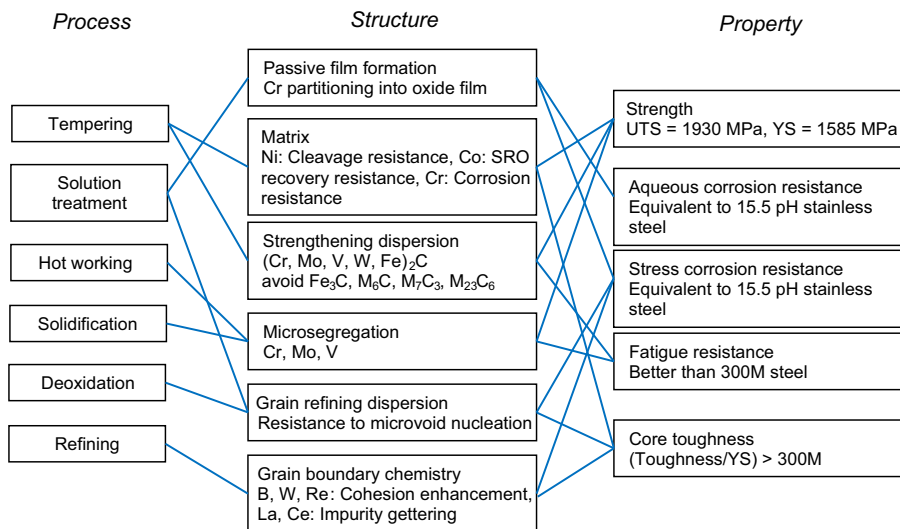


Figure 1.1 An example of process—structure—property relationship in designing ultrahigh strength, corrosion-resistant steels.

Adapted from G.B. Olson, Genomic materials design: the ferrous frontier. *Acta Mater.*, 61(3) (2013) 771–781.

gaps is the second major challenge. The third challenge is the reliability and credibility of predictions from these models in the face of uncertainty from various sources.

The ultimate goal of ICME tools is to provide assistance to identify the P–S–P relationships and to inform decisions in materials selection and design processes under uncertainty. For centuries, uncertainty has been a key component underlying the domains of philosophy, mathematics, and statistical and physical sciences. The study of uncertainty led to a new branch of mathematics in the 17th century, known as probability. Although different interpretations of probability coexist and debates between scholars from these different schools persist for centuries, it has been generally accepted by all that the source of uncertainty is our lack of knowledge about future. In the domains of physical sciences, two sources of uncertainty are differentiated. One is the lack of perfect knowledge and the other is the random fluctuation associated with finite temperature processes. The former is referred to by many as *epistemic*, whereas the latter is *aleatory*. Any uncertainty phenomenon we observe is the conflated effect of these two components. The differentiation of these two components is pragmatic and mainly for decision-making practitioners. Epistemic uncertainty often appears as bias or systematic error in data or simulation results and is regarded as reducible; increasing our level of knowledge can reduce the epistemic component of uncertainty. In contrast, aleatory uncertainty appears as random error and is irreducible. Random fluctuation inherently exists in position of atoms and electrons at temperatures above absolute zero and is manifested as uncertainty of material structure at various scales. When decision makers can differentiate the sources of uncertainty,

the risk of a go/no-go decision is more readily managed. Gaining more knowledge to reduce the epistemic component of uncertainty will generally lead to more precise estimation of the risk.

ICME tools, such as density functional theory (DFT), molecular dynamics (MD), coarse-graining atomistic modeling methods, kinetic Monte Carlo (kMC), dislocation dynamics (DD), microscopic and mesoscopic phase field (PF), and finite-element analysis (FEA), predict physical phenomena at different length and time scales. The sources of uncertainty associated with these tools should be identified if we would like to make robust decisions based on the results of these computational tools.

All models require certain levels of abstraction. Simplification can be related to dimensional reduction in parameter space when too many factors are involved, separation of size or time scales, and separation of physical domains when tightly coupled physics confers complexity to models. Assumptions of independence between factors, temporally or spatially, are often made to reduce model complexity. Approximation error is always involved, and truncation is inevitable when functional analysis is applied in modeling and experimental data analysis. Numerical discretization or linearization is regularly applied during computation. Furthermore, the choice of model forms from domain experts is typically subjective and based on user preference. The subjectivity of model choice also includes the unintended bias or convenient shortcuts in the modeling process of each expert based on their own scope of knowledge and understanding. As a result of simplification, approximation, and subjectivity, all models have *model form uncertainty* and it affects the predictions.

In addition, the parameters of models need to be calibrated for accurate prediction. Calibration-related model errors are called *parameter uncertainty*. Typically, model predictions are compared with experimental observations, and the parameters are adjusted to match with the observations. Data fitting or optimization procedures are pursued in the calibration process. All experimental measurements have systematic errors stemming from instruments or human operators. This leads to bias in the parameters of the fitted empirical model. Random errors from experimental measurements, especially with a small dataset, are also propagated to models. All sensors that are used to collect data rely on certain mathematical or physical models to map the collected signals to quantities of interest. These sensor models also have model form and parameter uncertainties. These errors associated with the underlying sensor models are in turn propagated to the models that are being calibrated. In first principles modeling, model parameters are calibrated based on first principles calculations and seek consistency with higher scale observations. The model form and parameter uncertainties of the first principles models also propagate through model calibration.

Model form uncertainty and parameter uncertainty are the major components of epistemic uncertainty. An overview of model form and parameter uncertainties in multiscale modeling is listed in [Table 1.1](#). Lack of perfect knowledge about the physical phenomena also contributes to the discrepancy between the models and actual physics. Needless to say, bias also exists in the data archived in ICME databases that are produced either via experiment or simulation [7].

Model form and parameter uncertainties affect the accuracy of the predictions of ICME tools. The reliability of P–S–P linkages can be problematic. The errors

Table 1.1 An overview of model form and parameter uncertainties in multiscale modeling.

Category	Source	Examples
Model form uncertainty	Simplification	Dimension reduction Separation of scales Separation of physics Independence assumption
	Approximation	Truncation Numerical treatment
	Subjectivity	Model preference Knowledge limitation
Parameter uncertainty	Experiment data	Systematic error Random error Sensor model
	First principles models	Model form uncertainty Parameter uncertainty

associated with the predictions need to be quantified so that the robustness of design can be assessed. UQ is the exercise of applying quantitative methods to measure and predict uncertainty associated with experimental data and model predictions. The predicted uncertainty is used to support risk analysis and decision making in materials design and development. Various UQ methods, including probabilistic and nonprobabilistic approaches, have been developed in the areas of statistics and applied mathematics and have been widely applied in engineering and science domains. Uncertainty is usually quantified in terms of probability distributions, confidence intervals, or interval ranges. In modeling and simulation, uncertainty is associated with model inputs, e.g., initial and boundary conditions, which comes from the sources of data. Uncertainty propagates to the output of simulation, spatially and temporally, confounded with model form and parameter uncertainties associated with the simulation model(s).

It is particularly challenging to estimate uncertainty propagation in UQ methods for materials modeling because materials modeling often relies on application of multiple tools at different length and time scales that range from discrete to continuous, with a large number of design variables. Formal application of model order reduction concepts across these disparate models differs substantially from traditional applications of continuum modeling for solids and fluids where the discrete character of defects and structures that controls responses of materials at fine scales is not considered. Reduced-order models themselves introduce model-form errors. Traditional stochastic modeling is typically confined to a single class of models with a given set of governing differential equations to address parametric uncertainty associated with variability of fields. Each simulation tool, such as DFT, MD, kMC, DD, PF,

and FEA, has a unique basis and set of assumptions and is limited to a particular range of length and time scales. Given the hierarchical nature of materials, sufficient understanding of material behavior often requires multiple tools to be applied. The outputs of a lower scale model are usually used as inputs to a higher scale model, whether operating sequentially (hierarchical modeling) or concurrently. Moreover, materials often exhibit a very strong sensitivity of response to change of configuration of structure and/or defects that is not smooth and continuous, which challenge the coarse-graining and model order reduction approaches that attempt to address material response over many length and perhaps time scales. Hence, propagation of uncertainty arises not only from individual scales in the hierarchy of material structure but also from the way in which information from different models is interpreted to inform the application of models at other scales (so-called scale-bridging or linking). Cross-scale propagation is one of the unique issues in UQ for materials modeling.

The purpose of this first chapter is to provide an overview of the sources of uncertainty in materials modeling, as well as the major classes of UQ methods that have been developed in the past few decades. As the ICME paradigm is adopted by researchers in materials science and engineering, understanding the sources of uncertainty in materials modeling and choosing appropriate UQ methods to assess the reliability of ICME prediction become important in materials design and development, as well as in deployment of materials into products.

1.2 Sources of uncertainty in multiscale materials modeling

We focus here on uncertainty in materials modeling across length and time scales. Reliable simulation requires that uncertainty to be quantified and managed. The first step of UQ is to identify the sources of uncertainty in the model. Based on the sources, epistemic and aleatory components of uncertainty are differentiated. The differentiation is helpful for us to apply different quantification and management strategies to the two components. For the epistemic component, which is due to the lack of knowledge, increasing the level of knowledge about the system under study can help reduce the uncertainty. Examples of strategies to reduce epistemic uncertainty include (i) building a more accurate physical model with better understanding of the physics and cause–effect relationships, (ii) controlling the most sensitive factors that cause the variations in model predictions or experimental observations, (iii) performing model calibration with a larger amount of data collection for targeted sensitive parameters, and (iv) conducting instrument calibration based on more precise standard references to reduce the systematic error. In contrast to epistemic uncertainty, aleatory uncertainty owes to the inherent randomness due to fluctuation and perturbation, which cannot be reduced. To cope with it, we typically perform multiple measurements or multiple runs of simulations and use the average values, with the notion of variance, to predict the true but unknown quantities of interest subject to variability.

1.2.1 Sources of epistemic uncertainty in modeling and simulation

The major sources of epistemic uncertainty in the general scheme of modeling and simulation are illustrated in Fig. 1.2, which can be categorized as data related and model related. They are summarized as follows.

The data-related epistemic uncertainty is due to

- Lack of data or missing data. The parameters of models, probability distributions, and distribution types are uncertain when the sample size is small. The availability of high-quality experimental data is critical for fitting data during model calibration and for comparison in model validation. In materials modeling, the additional challenge is that it may not be possible to directly measure the quantity of interest (QoI) because of experimental techniques. A different quantity, sometime at a different scale, is measured and used to infer the value of the QoI. Lack of sufficient information will introduce errors in models and requires the analyst to find new ways to describe the associated uncertainty more rigorously.
- Measurement errors. Systematic errors can be introduced because of the limitation of measurement environment, measurement procedure, and human error. In addition, most sensing protocols in measurements rely on some type of sensor models that relate QoIs to electrical signals. Model form and parameter uncertainty associated with these sensor models also contribute to measurement error.

The model-related epistemic uncertainty is due to

- Conflicting information. If there are multiple sources of information, the analyst may face conflicts among them in model selection. For instance, it is not appropriate to draw a simple conclusion regarding distributions from several pieces of contradictory evidence. The inconsistency results in potentially inaccurate types of distributions.

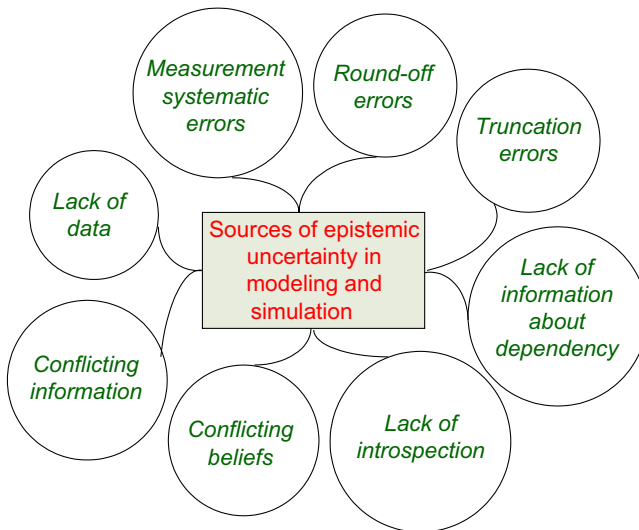


Figure 1.2 Major sources of epistemic uncertainty in modeling and simulation.

- **Conflicting beliefs.** When data are not available or are limited, the analyst usually relies on expert opinions and beliefs to determine the model forms. Information obtained from the experts is subjective due to the diversity of their past experiences and their own understanding of relevant phenomena, which can easily lead to inconsistent model predictions. This is particularly true of assigning phenomena to consider in multiscale modeling and can arise from differing perspectives of materials science and structural mechanics communities, for example.
- **Lack of introspection.** In some cases, the analyst cannot afford the necessary time to think deliberately about an uncertain process or event, derive more accurate description of physical systems, perform more sensitivity studies, or run additional simulations. The lack of introspection increases the risk of using inaccurate model.
- **Lack of information regarding dependencies.** Given the limitation of modeling and simulation techniques, a complex system is usually decomposed into subsystems, which are assumed to be independent from each other to mitigate complexity. Lack of knowledge about the correlations among factors and variables, as well as unknown time dependency of these factors, contribute to the error and bias in model predictions.
- **Truncation errors.** Functional analysis is the foundation for modeling and simulation which enables numerical methods to solve differential equations and model stochastic processes. It is also widely applied in spectral analysis of experimental data. Truncation is inevitably applied in the analysis for affordable computational expenses.
- **Round-off errors.** Floating-point representation is essential for digital computers to represent real numbers. The errors can become prominent when the number of arithmetic operations increases, e.g., system dynamics simulation with a very short time step but for a long period of time.

In modeling and simulation, epistemic uncertainty is the result of the errors mainly associated with the models and input data. Since aleatory and epistemic uncertainties stem from separate sources and have very different characteristics, they are ideally distinguished and modeled in different forms. Aleatory uncertainty is traditionally and predominantly modeled using probability distributions. Epistemic uncertainty however has been modeled in several ways, including probability, interval or convex bounds, random sets, etc.

1.2.2 Sources of model form and parameter uncertainties in multiscale models

1.2.2.1 Models at different length and time scales

Model form and parameter uncertainties are major epistemic components of error in modeling and simulation. These are elaborated next in commonly used ICME materials modeling tools at various scales.

In DFT simulations, the major source of model form uncertainty is the exchange-correlation potential functionals, where many-particle interactions are approximated and simplified in the data fitting procedure. The so-called rungs in Jacob's ladder, varying from local spin-density approximation to generalized gradient approximation (GGA), meta-GGA, hyper-GGA, and higher-order approximations, lead to different accuracy levels. In addition, the Born-Oppenheimer approximation assumes that the

lighter electrons adjust adiabatically to the motion of the heavier atomic nuclei, and thus their motions can be separated. Zero-temperature ground state of the system is also assumed in DFT calculation. In addition, the pseudopotentials are typically used to replace the Coulomb potential near each nucleus in the calculation to reduce computational load, which also introduces approximation error. Error is also introduced in the trade-offs between long-range and short-range dispersions and between efficiency and accuracy during the approximation. Numerical treatments such as k-point sampling and orbital basis selection also introduce model form uncertainty. In the self-consistent calculation of ground state energy, the chosen threshold for convergence introduces additional numerical errors.

In MD simulations, the major sources of model form and parameter uncertainty are associated with the interatomic potential functions, most of which are obtained empirically. The choice of analytical forms, number of parameters, and the calibration process introduce approximation errors. The systematic error in measurement data can be inherited through calibration. The errors associated with the interatomic potentials propagate to the output prediction through the simulation process. Prediction errors of extrapolative nature emerge when interatomic potentials are calibrated with one property but used to predict another property. Other sources of uncertainty include the cut-off distance in simulation for ease of computation, the type of imposed boundary conditions (e.g., periodic) that may introduce artificial effects, small simulation domain size that is not representative of realistic defect structures and may lead to image stresses, deviation of microstructure from the physical case, and use of short simulation times to estimate statistical ensemble behavior. To overcome the time scale limitation of MD, errors are introduced in accelerating simulations by use of larger time steps, modified interatomic potentials to simulate transitions, high temperatures, parallel replicates for rare events, or the application of physically unrealistic high strain rates due to mechanical and/or thermal loading. Computational errors with different computer architectures arise due to round-off in floating-point numbers as well as task distribution and sequencing in parallel computation.

In kMC simulation, the major sources of epistemic uncertainty are incomplete event catalogs and imprecise associated rates or propensities. The accuracy of kMC simulation depends on the validity of complete knowledge of all possible events, which is impossible. Furthermore, the actual kinetic rates can vary with time. They also depend on the state of the system. For instance, external loads can alter the diffusion of defects. The crowding effect reduces reaction rates when molecules or reaction products block reaction channels. The assumption of constant rates is unreasonable in such cases. In kMC, events are also assumed to be independent from each other, and the interarrival times between events are assumed as random variables that follow exponential distributions. These assumptions simplify computation. In reality, the events may be correlated, and memory effects in evolution of material structure also violate the assumption of exponential distributions. These assumptions and simplifications lead to model form uncertainty, in addition to parameter uncertainty arising from calibration with experimental data.

In discrete DD simulation models, the major approximations include the modeling of the stress field and phenomenological rules for dislocation–dislocation interactions,

neglect of dislocation core spreading and partial dislocations, interactions of dislocations with precipitates or other second phases, and interfaces. Simple mobility relations are assumed with considerable uncertainty. Numerical errors are introduced with the piecewise linear approximations of dislocation curves during discretization, and numerical solutions of ordinary differential equations. Similarly, in continuous DD simulations, the major sources of uncertainty include the approximation of dislocation density evolution with the associated partial differential equations over ensembles. Numerical errors are introduced in the solving process based on spectral analysis with truncation and calculating integrals.

In PF simulation, the major source of model form and parameter uncertainty is the empirical model of the free energy functional, which is usually derived from principles of thermodynamics with assumptions of constant temperature, pressure, or volume, with approximation errors from truncation and pure empirical data fitting. The additional numerical treatment in solving the partial differential equations of Cahn–Hilliard and Allen–Cahn also introduces errors. This includes the antitrapping current to eliminate the solution trapping during interface diffusion when an interface larger than the physical one is modeled in order to improve computational efficiency. Some other parameter uncertainty is caused by assumptions such as temperature-independent interface mobility and location-independent diffusion coefficient.

In FEA simulations, besides the model form uncertainty inherited in partial differential equations and material constitutive laws, approximation errors are the result of domain discretization with meshes, interpolation with limited numbers of basis functions, truncation with low-order approximations, numerical methods to solve linear equations, and others.

In summary, incomplete description of physics, experimental data, and numerical treatment introduce epistemic uncertainty into simulation models. As a result, the prediction of QoI as the simulation output is inherently inaccurate. When QoIs are statistical ensembles that depend on temperature, the output is also imprecise and contains variability. Therefore, the simulation output usually contains the confounded effects of model form, parameter, and aleatory uncertainties.

1.2.3 *Linking models across scales*

UQ for ICME has the distinct need to consider uncertainty propagation between multiple length and time scales in material systems. Uncertainty observed at a larger scale is the manifestation of the collective uncertainties exhibited at smaller scales. For instance, the nondeterministic strengths of material specimens are due to the statistical distributions of grain boundaries and defects. The randomness of molecular movement known as Brownian motion arises from the stochasticity of physical forces and interactions among electrons at the quantum level. The ability to model the propagation of uncertainty between scales is essential to obtain useful information from multiscale modeling as necessary to inform understanding of higher-scale material response and to support decision making in materials design and development. Existing ICME tools simulate material systems over a range from nanometers to micrometers. The major challenge of UQ in these tools is the information exchange between

different models, where assumptions of scales and boundaries are made a priori. For purposes of model validation, not all physical quantities predicted in simulation can be directly observed, especially those at small length and short time scales. Measurable quantities at larger scales are typically used to validate models. This is based on some assumed, implied, and/or derived correlation between measured quantities and unobservable quantities, which introduces model form uncertainty as part of sensing or measurement errors. In other words, even physical measurements appeal to some model construct to interpret. As a result, model calibration and model validation face new challenges in multiscale modeling.

Another pervasive and understated challenge for multiscale materials modeling is the common lack of “smoothness” between material response functions and microstructure. The structure–property relationships can be highly nonlinear. For example, phase transformations confer distinct jumps of structure and properties. Moreover, the nature of the interaction of defects with interfaces in crystals depends substantially on the structure of the interface and character of the applied stress state. Strong temperature dependencies in kinetics of evolution can lead to evolution of local microstructure states that differ from assumed isothermal conditions. In many cases, applications involving uncertainty propagation in mechanics of structures based on finite-element modeling, for example, do not address these kinds of common, material-specific nonlinearity or discontinuities in material structure evolution and associated responses. Such cases require the identification of these complex mechanisms, in addition to a multifidelity modeling capability capable of resolving or addressing them.

This latter point brings us to a distinction between so-called hierarchical and concurrent multiscale modeling [8]. Models pertaining to different levels of the material structure hierarchy are typically related to each other or exercised in one of two ways: hierarchical (one-way, bottom up) or concurrent (two-way) multiscale schemes. *Concurrent multiscale modeling* schemes exercise simultaneous simulations for models with different fidelities or spatial resolutions over the same temporal duration, necessitated in cases where (i) time scales are not separable for phenomena that occur at several length scales of interest or (ii) the collective, higher-scale responses of interest relate inextricably to certain fine-scale features or mechanisms that differ from one problem to the next. An example is a specific type of failure mechanism solicited by a specific higher-scale component geometry (e.g., notch) or loading condition (e.g., low velocity impact). These models can be either applied to the same spatial domain with different spatial resolution and degrees of freedom or pursued with different fidelity in adjacent, abutting, or overlapping domains; the latter requires schemes for communication of model responses between these regions and are typically referred to as domain decomposition methods. *Hierarchical multiscale modeling schemes* typically pass information from models exercised at each successive length and/or time scale to the next higher scale(s), with the intent to instruct model form and/or parameters of the latter. In some cases, they can pass information to models framed at much higher scales. For example, elastic constants and diffusion coefficients computed using DFT or other atomistic simulations can be employed in crystal plasticity models or macroscale plasticity models. They may be hierarchical in length and time, adding additional flexibility to the framing of the multiscale modeling problem. Most

multiscale modeling work to date has focused more on hierarchical multiscale models that are linked by handshaking or passing of information from the outputs of one model to the inputs of the next. Formulation of concurrent multiscale models, particularly for a heterogeneous set of models at various scales, is quite challenging if there is an attempt to identify and track the sources of uncertainty.

As another special challenge of UQ in multiscale modeling, uncertainty propagation between scales needs to be carefully treated. Simply regarding these models as series of “black boxes” with simple input–output functional relations has the tendency to overestimate uncertainty. The QoIs between scales are intrinsically correlated. As a result, uncertainty is not necessarily always worsened or amplified through propagation. Understanding of the physics assists to more accurately estimate uncertainty.

1.3 Uncertainty quantification methods

Various UQ methods have been developed in the past half century. Most UQ approaches have been based on probability theory. Alternative approaches [9] such as evidence theory, possibility, interval analysis, and interval probability have also been developed, differentiating between aleatory and epistemic uncertainty. With respect to the application of modeling and simulation, UQ methods can be categorized as either intrusive or nonintrusive. Nonintrusive UQ methods do not require an internal representation of uncertainty in the simulation models. The original simulation tools are treated as “black boxes” and the UQ methods are implemented as parent processes to call upon the simulation tools to conduct the necessary evaluations. In contrast, intrusive UQ methods require the modification of the original simulation software tools so that uncertainty can be represented internally. This distinction is very important in light of the nature of hierarchy of length and time scales in the heterogeneous cascade of multiscale models. Specifically, intrusive methods require that uncertainty propagates internal to the entire system of models, including linking formalisms between models; this is quite challenging in view of the need to adaptively refine and make decisions regarding treatment of scales within each of the distinct models. Nonintrusive methods might be attractive in such cases owing to their more modular character in assisting to construct flexible workflows; however, they likely do not scale well for solving high-dimensional problems and the implementation in high-performance computing architectures.

Commonly used nonintrusive UQ methods include Monte Carlo (MC) simulation, global sensitivity analysis (GSA), surrogate models, polynomial chaos, and stochastic collocation. Common intrusive UQ methods include local sensitivity analysis (LSA), stochastic Galerkin, and interval-based approaches.

1.3.1 Monte Carlo simulation

MC simulation is the earliest formal attempt to quantify uncertainty inherent in physical models, where pseudo random numbers are generated by computers and used in

evaluating models, although the technique was originally devised to numerically calculate deterministic integrals in quantum mechanics (with its inherent uncertainty). The effectiveness of MC relies on how truly “random” the numbers generated by the pseudo random number generators (PRNGs) are. Common implementations of PRNGs as the core of MC to generate uniformly distributed numbers include linear congruential method [10,11] and its various extensions [12–16] for longer periods and better uniformity, feedback shift register generators [17,18], and Mersenne twister [19]. Based on the uniformly distributed numbers, random variates that follow other distributions can be generated via computational methods such as inverse transform, composition, convolution, and acceptance–rejection. When MC is applied to assess the uncertainty associated with the inputs of a model, inputs with predetermined distributions are randomly generated. They are used to evaluate the model or run the simulation many times. The distribution of the resulting outputs is then used to assess the effect of uncertainty, which is quantified with statistical moments of different orders.

The major issue with MC for UQ in ICME is its computational cost. The quality of uncertainty assessment depends on how many runs of simulation can be conducted in order to generate statistical distributions of outputs and draw meaningful conclusions from the results. Worse yet, for a high-dimensional sampling space where many input variables are involved, the number of samples to densely cover the sampling space grows exponentially as the dimension increases. If each simulation run is expensive, as is the case with DFT and MD and with higher scale models that explicitly address 3D microstructure, the cost of UQ will be high in the pure sampling–based approach. In addition, MC also requires predetermined input distributions from which the samples are drawn.

If there is a lack of prior knowledge regarding the types of distribution types or lack of experimental data, the effect of model form uncertainty needs to be assessed. Second-order Monte Carlo (SOMC) [20,21] is a natural extension of MC to study the uncertainty associated with the input distributions. In the outer loop, the parameters or types of statistical distributions are randomly sampled. In the inner loop, classical MC is applied with each of the sampled distributions to study the variability. The SOMC results can provide an overall picture of the combined effects from both epistemic and aleatory uncertainties.

1.3.2 Global sensitivity analysis

Sensitivity analysis is a general concept of studying how uncertainty in the output of a model is attributed to uncertainty associated with model inputs. GSA [22] quantifies the effect of each individual input as well as their joint effects by conducting the analysis of variance.

For a given model or simulation input–output relation $Y = f(X_1, \dots, X_n)$ where input X_i ’s are random variables, by fixing input variable X_i to be x_i^* one at a time, the conditional variance of the output $\text{Var}(Y|X_i = x_i^*)$ is typically less than the original total variance $\text{Var}(Y)$. The difference between the two is an indicator of the contribution of variance from input variable X_i , i.e., the sensitivity of output uncertainty with

respect to input X_i . Given all possible values of x_i^* , $\text{Var}(Y|X_i = x_i^*)$ itself is a random variable. Thus, its expected value $\mathbb{E}[\text{Var}(Y|X_i)]$ can be calculated. The deterministic value $\text{Var}(Y) - \mathbb{E}[\text{Var}(Y|X_i)]$ therefore is a metric to quantify the importance of input X_i . Similarly, the conditional expectation $\mathbb{E}[Y|X_i = x_i^*]$ with all possible values of x_i^* is a random variable. Equivalently, the value $\text{Var}(Y) - \text{Var}(\mathbb{E}[Y|X_i])$ is an indicator of the contribution of variance from input variable X_i , because $\text{Var}(Y) = \mathbb{E}[\text{Var}(Y|X_i)] + \text{Var}(\mathbb{E}[Y|X_i])$. The first-order Sobol' sensitivity index [23,24] $S_i = \text{Var}(\mathbb{E}[Y|X_i])/\text{Var}(Y)$ is commonly used to quantify the sensitivity of output with respect to the uncertainty associated with the i th input variable, which is referred to as the main effect. The interactions among input variables are estimated by second- or higher-order sensitivity indices. By fixing two variables X_i and X_j simultaneously at a time, $\text{Var}(\mathbb{E}[Y|X_i, X_j])$ measures the joint effect of the two variables. The second-order index $S_{ij} = \text{Var}(\mathbb{E}[Y|X_i, X_j])/\text{Var}(Y) - S_i - S_j$ shows the interaction effect of the two input variables.

Higher-order indices can be defined in a similar way. In general, the total variance can be decomposed as $\text{Var}(Y) = \sum_i V_i + \sum_{i,j>i} V_{ij} + \sum_{i,j>i,k>j} V_{ijk} + \dots + V_{1,2,\dots,n}$ where $V_i = \text{Var}(\mathbb{E}[Y|X_i])$, $V_{ij} = \text{Var}(\mathbb{E}[Y|X_i, X_j]) - V_i - V_j$, $V_{ijk} = \text{Var}(\mathbb{E}[Y|X_i, X_j, X_k])$

$- V_{ij} - V_{jk} - V_{ik} - V_i - V_j - V_k$, etc. Therefore, $\sum_i S_i + \sum_{i,j>i} S_{ij} + \sum_{i,j>i,k>j} S_{ijk} + \dots + S_{1,2,\dots,n} = 1$. The total effect of X_i , including all orders that have X_i involved, is measured by the total effect index [25] $S_{Ti} = 1 - \sum_{j \neq i} S_j - \sum_{j,k>j,j \neq i} S_{jk} - \dots = 1 -$

$\text{Var}(\mathbb{E}[Y|X_1, \dots, X_{i-1}, X_{i+1}, \dots, X_n])/\text{Var}(Y)$. Using the latter approach to calculate the total effect index is computationally more tractable.

It should be noted that variance-based GSA does not require a known or closed-form mathematical function $Y = f(X_1, \dots, X_n)$ for the input–output relation. For black-box simulations, if enough runs of simulations are conducted with proper design of experiments to generate statistically meaningful pairs of input and output, GSA can be performed by the analysis of variance. Instead of variance, other moment-independent sensitivity indices [26,27] have also been proposed to directly quantify the importance of input uncertainty based on cumulative distributions or density functions.

The limitation of GSA for ICME applications is similar to the one in MC, since MC sampling is typically needed to estimate the variances. Notice that traditional MC only provides information regarding overall output distributions, whereas GSA can provide fine-grained information of individual and compounded effects of input variables. Instead of variance, other measures of uncertainty can also be applied for GSA, such as the Hartley-like measure [28] which quantifies the level of uncertainty by the width of an interval range. This approach can avoid the high computational cost of sampling in variance-based GSA.

1.3.3 *Surrogate modeling*

When the input–output relations in simulation models are too complex, expensive, or unknown, surrogate models can be constructed to approximate the response between inputs and outputs. The simplified surrogate models, typically in the form of polynomials or exponentials, can improve the efficiency of model evaluations and predictions. For UQ, surrogate models can be used for sensitivity analysis and prediction of response variation. The input–output responses can be generated by experimental designs such as factorial, fractional factorial, central composite, and orthogonal designs [29–31]. The resulting models are generally called response surfaces. They are constructed by interpolation or regression analysis of the results from simulations with combinations of input variable values. With the constructed response surfaces, performance of new input values and the sensitivity can be predicted without running the actual simulation itself.

To construct response surfaces, sampling the input parameter space thoroughly is important because predictions from interpolation are generally more reliable than those from extrapolation. For high-dimensional input parameter space, exhaustive sampling with all possible combinations can be very costly. The computational complexity grows exponentially as the dimension increases. Latin hypercube sampling (LHS) [32–34] is an efficient sampling approach to choose samples in high-dimensional space. It is a stratified sampling strategy for variance reduction where samples are taken from the predefined input subspaces. For each subspace, there is an equal probability that the input samples are drawn from. The sampling is then performed within each of these subspaces so that all subspaces can be covered by much fewer samples than classical MC sampling. Thus, the number of samples can be significantly reduced while results are still statistically representative. LHS is also extended to dividing subspaces with unequal probabilities, and the estimates are weighted by the corresponding probability values [35]. LHS is a versatile tool and can be applied to study statistical properties of responses directly without constructing response surfaces. The limitation of LHS is that the efficiency of the sampling strategy depends on the prior knowledge of probability distributions associated with input variables. When there is a lack of knowledge about the types and parameters, the variance reduction technique may introduce bias.

1.3.4 *Gaussian process regression*

Kriging or Gaussian process regression [36,37] is a regularized regression approach to find approximated response models between inputs and outputs. It predicts new functional value from some existing ones by modeling the underlying but unknown true function as a Gaussian process. Different from simple regression with the point estimation of model parameters, the probability distributions of model parameters are estimated. Gaussian process can be regarded a special type of stochastic process

which is only specified by the mean vector and covariance matrix. The modeling and prediction are based on Bayesian inference. That is, given the prior probability $P(M_\alpha)$ for different models M_α ($\alpha = 1, 2, \dots$), as well as the likelihood $P(D|M_\alpha)$ associated with observation D , the posterior probability of M_α is obtained as $P(M_\alpha|D) \propto P(D|M_\alpha)P(M_\alpha)$. The prediction of a new value y is the Bayesian model average, calculated as

$$P(y) = \sum_{\alpha} P(y|M_\alpha)P(M_\alpha|D) \quad (1.1)$$

The major assumption in Gaussian process regression is that the functional values for existing inputs follow a joint Gaussian distribution. As a result, the prediction of the new value is simplified to be the weighted average of the existing values plus an additive noise as a stationary covariance process with zero mean. This is illustrated with the following example of generalized linear regression. A Gaussian process is specified by a mean function $\mu(\mathbf{x}) = \mathbb{E}[Y(\mathbf{x})]$ and a covariance function $\mathbb{C}(Y(\mathbf{x}), Y(\mathbf{x}')) = k(\mathbf{x}, \mathbf{x}')$. Based on a finite set of basis functions $\{\phi_j(\mathbf{x}), j = 1, \dots, m\}$, the output function is expressed as

$$Y(\mathbf{x}) = \sum_{j=1}^m w_j \phi_j(\mathbf{x}) + \varepsilon = \boldsymbol{\phi}(\mathbf{x})^T \mathbf{w} + \varepsilon = y(\mathbf{x}; \mathbf{w}) + \varepsilon \quad (1.2)$$

where $\mathbf{w} = [w_1, \dots, w_m]^T$ is the weight vector, $\boldsymbol{\phi}(\mathbf{x}) = [\phi_1(\mathbf{x}), \dots, \phi_m(\mathbf{x})]^T$ is the vector of basis functions, and Gaussian noise $\varepsilon \sim N(0, \sigma_0^2)$ is assumed to be associated with observations. Let the prior probability distribution of the weight vector $\mathbf{w}$ be Gaussian $N(0, \boldsymbol{\Sigma}_w)$, as

$$P(\mathbf{w}) = \frac{1}{(2\pi)^{n/2} |\boldsymbol{\Sigma}_w|^{1/2}} \exp\left(-\frac{1}{2} \mathbf{w}^T \boldsymbol{\Sigma}_w^{-1} \mathbf{w}\right) \quad (1.3)$$

With the observed dataset $D = \{(\mathbf{x}_i, y_i), i = 1, \dots, n\}$ with n input–output tuples and independent observation assumption, the likelihood is

$$P(y_1, \dots, y_n | \mathbf{w}) = \frac{1}{(2\pi\sigma_0^2)^{n/2}} \prod_{i=1}^n \exp\left(-\frac{1}{2\sigma_0^2} (y_i - y(\mathbf{x}_i; \mathbf{w}))^2\right) \quad (1.4)$$

based on the Gaussian kernel $k(\mathbf{x}, \mathbf{x}') = \exp(-\frac{1}{2\sigma_0^2} |\mathbf{x} - \mathbf{x}'|^2)$. The posterior mean value of weights $\hat{\mathbf{w}}$ is obtained by minimizing the negative logarithmic of the posterior probability, as

$$\min_{\mathbf{w}} E(\mathbf{w}) = \min_{\mathbf{w}} \frac{1}{2\sigma_0^2} \sum_{i=1}^n (y_i - \mathbf{w}^T \boldsymbol{\phi}(\mathbf{x}_i))^2 + \frac{1}{2} \mathbf{w}^T \boldsymbol{\Sigma}_w^{-1} \mathbf{w} \quad (1.5)$$

By solving the linear equations $\partial E / \partial \mathbf{w} = 0$, we obtain

$$\hat{\mathbf{w}} = \sigma_0^{-2} \mathbf{A}^{-1} \mathbf{\Phi}^T \mathbf{y} \quad (1.6)$$

where $\mathbf{y} = [y_1, \dots, y_n]^T$ is the vector of observations, matrix $\mathbf{A} = \Sigma_w^{-1} + \sigma_0^{-2} \mathbf{\Phi}^T \mathbf{\Phi}$, and $\mathbf{\Phi}$ is the $n \times m$ design matrix with elements $\phi_j(\mathbf{x}_i)$'s. For a new input $\mathbf{x}_*$, the predicted mean function value is

$$\begin{aligned} \mathbb{E}[Y(\mathbf{x}_*)] &= \phi(\mathbf{x}_*)^T \hat{\mathbf{w}} = \sigma_0^{-2} \phi(\mathbf{x}_*)^T \mathbf{A}^{-1} \mathbf{\Phi}^T \mathbf{y} \\ &= \phi(\mathbf{x}_*)^T \Sigma_w \mathbf{\Phi}^T (\mathbf{\Phi} \Sigma_w \mathbf{\Phi}^T + \sigma_0^{-2} \mathbf{I}_n)^{-1} \mathbf{y} \end{aligned} \quad (1.7)$$

which shows that the new prediction is a weighted average of existing ones in $\mathbf{y}$. Here, $\mathbf{I}_n$ is the $n \times n$ identity matrix. The variance of the prediction is

$$\begin{aligned} \mathbb{V}[Y(\mathbf{x}_*)] &= \phi(\mathbf{x}_*)^T \mathbf{A}^{-1} \phi(\mathbf{x}_*) + \sigma_0^2 \\ &= \phi(\mathbf{x}_*)^T \left(\Sigma_w - \Sigma_w \mathbf{\Phi}^T (\mathbf{\Phi} \Sigma_w \mathbf{\Phi}^T + \sigma_0^2 \mathbf{I}_n)^{-1} \mathbf{\Phi} \Sigma_w \right) \phi(\mathbf{x}_*) + \sigma_0^2 \end{aligned} \quad (1.8)$$

It is important to note the difference in computational complexity of the two above equivalent ways presented in the foregoing to calculate the mean and variance of prediction. The computational bottleneck involves the inversion of covariance matrices. The size of matrix $\mathbf{A}$ is $m \times m$, whereas the size of $(\mathbf{\Phi} \Sigma_w \mathbf{\Phi}^T + \sigma_0^2 \mathbf{I}_n)$ is $n \times n$. Therefore, the complexities of computation increase in the orders of $O(m^3)$ and $O(n^3)$, respectively.

Gaussian process regression can be applied to construct the surrogates for simulations where the closed-form input–output functional relationships are not available. That is, Eq. (1.2) serves as the surrogate with input $\mathbf{x}$ and output Y . Based on the simulation data, hyperparameters $\mathbf{w}$ can be trained and obtained from Eq. (1.6). The predictions of means and variances for a new input are calculated based on Eqs. (1.7) and (1.8), respectively. More complex kernel functions with more hyperparameters can also be introduced. The training of hyperparameters can be done by maximizing the likelihood, similar to Eq. (1.5).

The major challenge of using Gaussian process regression is the computational complexity for high-dimensional problems. As the dimension of input $\mathbf{x}$ increases, the required number of training samples n grows exponentially in order to have a good coverage of the high-dimensional input space. Major research efforts have been given to improve the computational efficiency with large datasets. Besides traditional data processing techniques for dimension reduction (e.g., principal component analysis, factor analysis, and manifold learning), integrated statistical and computational methods have been developed. The first approach is to reduce the rank of the covariance matrix. For instance, a selected subset of samples can be taken to construct

a sub-Gaussian process to predict the original process [38,39]. In fixed ranking kriging, the covariance matrix is projected into a fixed dimensional space so that the inversion relies on the fixed-rank matrix in the projected space [40]. Based on the Karhunen–Lo  ve expansion to approximate the covariance function, the inverse of the covariance matrix can be obtained with reduced-rank approximation [41,42]. Gaussian Markov random field on sparse grid has also been used to approximate covariance [42]. The second approach is to reduce the computational complexity with the sparse approximation of covariance matrices. For instance, the spatial localization of covariance functions leads to sparse (or tapered) covariance matrices, and the inverse of sparse matrices can be computed more efficiently [43,44]. The bias introduced by the tapering also needs to be compensated [45]. Sequential sampling or active learning can also be applied to update the subset of data in approximation of the global model [46]. The third approach is using sparse spectral approximation of covariance functions, where a finite set of basis functions are chosen in the construction. For instance, sinusoidal functions [47,48] have been applied in the spectral approximation. The fourth approach to deal with the large dataset is distributed or clustered kriging, where the data are subdivided into subsets and multiple surrogate models are constructed. The new value is predicted as the weighted average of predictions from multiple models. The weights can be determined by an optimization procedure to minimize the predicted variance [49], the distances between the input to predict and the centers of clusters [50], or the Wasserstein distances between the Gaussian posteriors of the main cluster and the neighboring ones [51].

One issue with universal kriging for UQ is that the mean response is usually assumed to follow the polynomial form. Therefore, model form uncertainty is introduced in terms of particular orders of polynomial basis functions. To improve the accuracy of prediction, a Bayesian model update approach with multiple models has been proposed [52]. Similarly, blind kriging modifies polynomials with Bayesian update by incorporating experimental data [53]. As the alternative, sinusoidal functions instead of polynomials have also been used in predicting the mean response [54]. The assumption of covariance functions is another source of model form uncertainty. Stochastic kriging or composite Gaussian process [55,56] methods were introduced to decompose the covariance into two components. One covariance process is from the underlying true function, whereas the other is from experimental data. This approach allows for the decomposition of model form uncertainty. Nevertheless, the assumption of the unknown covariance of the two Gaussian processes still has to be made. One more issue of constructing Gaussian process regression models is the lack of data when extensive simulation runs and/or experiments are costly. Multifidelity cokriging [57,58] is a cost-effective approach for surrogate modeling with the consideration of experimental cost, where low- and high-cost data are combined to construct the surrogate. New sequential sampling strategies can be taken to decide the optimal combination of low- and high-fidelity data [59]. The low- and high-fidelity cokriging model can also be extended to multiple fidelity levels as a recursive model with nested design sites [60].

1.3.5 Bayesian model calibration and validation

One important procedure in modeling and simulation is model calibration, where parameters of physical models need to be tuned to match experimental measurements. Gaussian process regression has been applied in simulation model calibration [61,62]. As an extension of Eq. (1.2), the surrogate for simulations is modeled as a composite Gaussian process in

$$Y(\mathbf{x}) = \rho \eta(\mathbf{x}, \boldsymbol{\theta}; \mathbf{w}) + \delta(\mathbf{x}) + \varepsilon \quad (1.9)$$

where $\boldsymbol{\theta}$ are the model parameters to be calibrated, $\eta(\cdot)$ approximates the physical model, and $\delta(\cdot)$ is the model discrepancy. Both $\eta(\cdot)$ and $\delta(\cdot)$ are Gaussian process models. The additional hyperparameter ρ can be introduced as the scaling factor. Combining the simulated dataset $D = \{(\mathbf{x}_i, \boldsymbol{\theta}_i, \mathbf{y}_i)\}$, where simulations are run with different parameter values $\boldsymbol{\theta}_i$'s and inputs $\mathbf{x}_i$'s, with experimental measurements $D' = \{(\mathbf{x}_i', \mathbf{y}_i')\}$, Eq. (1.9) can be treated as a multivariate Gaussian process regression model with inputs $(\mathbf{x}_i, \boldsymbol{\theta}_i)$'s. The model parameters $\boldsymbol{\theta}$ can be similarly trained by maximizing the likelihood, along with all hyperparameters, in the calibration process if the covariance associated with the model parameters is also assumed to be Gaussian. Further extensions of capturing the model discrepancy in the Gaussian processes [63,64] and categorical parameters [65] were also studied.

In a more general setting without the assumption of Gaussian processes, model calibration can be performed by finding parameter values that minimizes the difference between the observation and simulation prediction as the posterior [66,67]. Calibration thus is an optimization process to minimize the difference. Choosing the prior however can affect the accuracy of calibration, especially when there are limited data. Besides parameter calibration, model forms can be calibrated with Bayesian model averaging to incorporate model form errors [68]. Fractional-order derivatives can also be treated as hyperparameters of model forms and similarly calibrated as continuous variables [69].

Model validation is to compare the model predictions with experimental experiments and evaluate the level of agreement [70]. A straightforward comparison is to check the confidence level associated with the difference between the predicted and measured quantities subject to statistical errors [71]. The Bayesian approach for model validation is comparing the prior and posterior probability distributions of the quantities of interests. The prior distribution is from the original model prediction, whereas the posterior is from the prediction after the model parameters are updated with experimental observations. The general criterion is the distance or difference between two probability distributions [72]. The composite Gaussian process model in Eq. (1.9) can also be applied in validation. When the posterior estimation of model bias $\delta(\cdot)$ with consideration of both simulation and experimental data is within an error threshold interval, the model is regarded as valid [73]. Bayesian hypothesis testing can also be applied for validation, where the null and alternative hypotheses are compared after they are updated with experimental observations [74].

1.3.6 Polynomial chaos expansion

Polynomial chaos expansion (PCE) [75–77] approximates random variables in functional or reciprocal space with orthogonal polynomials as bases. In PCE, a stochastic process or random variable is expressed as a spectral expansion in terms of orthogonal eigenfunctions with weights associated with a particular probability density. More specifically, a stochastic process $u(\mathbf{x}; \xi)$ can be approximated as

$$u(\mathbf{x}; \xi) \approx \sum_{m=1}^M \hat{u}_m(\mathbf{x}) \Psi_m(\xi) \quad M = \binom{N+P}{N} \quad (1.10)$$

where $\xi = [\xi_1, \dots, \xi_N]$ is an N -dimensional vector of random variables as parameters of $u(\mathbf{x}; \xi)$ which follows a particular distribution with probability density function $p(\xi)$, N -variant P -th order polynomials $\Psi_m(\xi)$'s form the orthogonal basis, and $\hat{u}_m$'s are the PCE coefficients. An example of the expansion is that the Wiener process (also known as Brownian motion) can be written as a spectral expansion in terms of the Hermite polynomials and normal distribution. Different polynomials are available for different probability distributions. For example, Legendre polynomials are for uniform distribution, Jacobi polynomials for beta distribution, Laguerre polynomials for gamma distribution, Charlier polynomials for Poisson, Krawtchouk polynomials for binomial, and Hahn polynomials for hypergeometric. Orthogonality ensures the efficiency of computation and ease of quantifying the truncation error.

The PCE coefficients in Eq. (1.10) can be calculated by projection as

$$\hat{u}_m(\mathbf{x}) = \int u(\mathbf{x}; \xi) \Psi_m(\xi) p(\xi) d\xi \quad (1.11)$$

The integral in Eq. (1.11) can be estimated with MC sampling. Yet a much more efficient approach is the quadrature as weighted summation. That is, discrete nodes $\xi^{(k)}$'s and associated weights are predefined, and the integral is calculated as the sum of the weighted values of $u(\mathbf{x}; \xi^{(k)}) \Psi_m(\xi^{(k)})$. In the nonintrusive PCE, the solution $u(\mathbf{x}; \xi^{(k)})$ with respect to each sample of random variable $\xi^{(k)}$ can be obtained by solving existing the deterministic model or simulation. Because of the orthogonality of polynomial basis, the statistical moments of the random process u can be easily obtained. The mean solution is estimated as

$$\mathbb{E}[u(\mathbf{x})] = \int \left(\sum_{m=1}^M \hat{u}_m(\mathbf{x}) \Psi_m(\xi) \right) p(\xi) d\xi = \hat{u}_1(\mathbf{x}) \quad (1.12)$$

The covariance function is

$$\mathbb{C}[u(\mathbf{x}_1), u(\mathbf{x}_2)] = \sum_{m=2}^M \hat{u}_m(\mathbf{x}_1) \hat{u}_m(\mathbf{x}_2) \quad (1.13)$$

The variance function is

$$V[u(\mathbf{x})] = \sum_{m=2}^M \hat{u}_m^2(\mathbf{x}) \quad (1.14)$$

The nonintrusive PCE approach has been applied to assess the sensitivity of input parameters in reaction–diffusion simulations [78] and perform variance estimation for GSA [79].

Computational efficiency is a challenge for nonintrusive PCE. A large number of samples are required, even though LHS and sparse grid can be applied. Each sample can correspond to a simulation run. Solving a stochastic differential equation is reduced to solving many deterministic differential equations. The efficiency of computation is directly related to the truncation, which also depends on types of distributions and the corresponding polynomials. Some distributions such as those with long and heavy tails cannot be efficiently modeled using PCE approximation.

1.3.7 Stochastic collocation and sparse grid

When the number of input parameters for simulation models is very high, i.e., in the hundreds, the direct construction of the high-dimensional response surface will become inefficient. Stochastic collocation [80,81] is an approach to alleviate the curse of dimensionality. The main idea is to choose the sampling positions of input wisely for functional evaluations in conjunction with the orthogonal polynomials in the problem solving process (i.e., partial differential equation with random inputs) so that a sparse grid [82] can be used. The samples can be selected as the zeros or roots of samples at the sparse grid can be used in either the construction of Lagrange interpolating polynomials or in the pseudospectral with quadrature interpolation.

In the Lagrange interpolation scheme, a set of nodes $\{\xi^{(k)}\}_{k=1}^K$ in the probabilistic parameter space of $u(\mathbf{x}; \xi)$ are predetermined. The solution $u(\mathbf{x}; \xi)$ of a stochastic differential equation can be approximated as

$$u(\mathbf{x}; \xi) \approx \sum_{k=1}^K u(\mathbf{x}; \xi^{(k)}) L_k(\xi) \quad (1.15)$$

where $L_k(\cdot)$'s are the Lagrange polynomials, and $u(\mathbf{x}; \xi^{(k)})$ is the solution of the deterministic differential equation when random variable ξ takes the sample value of $\xi^{(k)}$. To obtain $u(\mathbf{x}; \xi^{(k)})$, the existing deterministic solver can be readily applied.

In the pseudospectral interpolation, PCE style expansion is applied instead of the Lagrange interpretation. Similar to Eq. (1.10), the solution is approximated by

$$u(\mathbf{x}; \xi) \approx \sum_{m=1}^M \hat{c}_m(\mathbf{x}) \Psi_m(\xi) \quad M = \binom{N+P}{N} \quad (1.16)$$

where the expansion coefficients however are calculated as

$$\hat{c}_m(\mathbf{x}) = \sum_{j=1}^Q u(\mathbf{x}; \xi^{(j)}) \Psi_m(\xi^{(j)}) w^{(j)} \quad (1.17)$$

which are the weighted discrete sums realized at the sampled grid locations $\xi^{(j)}$'s. The grid locations $\xi^{(j)}$'s and weights $w^{(j)}$'s are carefully chosen so that the weighted sum can approximate the integral in Eq. (1.11) well.

The grid location selection in stochastic collocation is important for accuracy and efficiency. For a one-dimensional problem, Gauss quadrature is usually the optimal choice. The challenge is high-dimensional cases, where full tensor products will grow the number of grid points exponentially as the dimension increases. Sparse grid method is an approach to cope with the efficiency issue. It was proposed to reduce the number of grid points and improve the efficiency in multidimensional quadrature and interpolation [83] and has been widely applied in stochastic collocation. Instead of full tensor products to generate grids in a high-dimensional sampling space, a much coarser tensorization can be taken in Smolyak's quadrature. The subset of grid points is chosen with recursive hierarchical subspace splitting so that the interpolation can have small approximation errors.

1.3.8 Local sensitivity analysis with perturbation

In contrast to GSA, LSA studies the effect of input uncertainty locally. A straightforward way is to estimate derivatives of models with the finite-difference approach where the difference between two responses is divided by the perturbation of inputs. The finite-difference approach is a nonintrusive approach to assess sensitivity. In addition to these direct (forward) methods, adjoint (backward) SA approaches were also developed for deterministic simulation based on differential equations [84,85]. A more efficient LSA method that is specific for stochastic simulation is to estimate the derivatives of the expected values of output performance, i.e., the expected values of stochastic derivatives or gradients, from simulation directly. This can be achieved by either varying output performance w.r.t. input parameters as the infinitesimal perturbation analysis [86,87] or by varying the probability measures w.r.t. inputs as in the likelihood ratio method [88–90]. These approaches are intrusive in order to promote efficiency of computation.

1.3.9 Polynomial chaos for stochastic Galerkin

Similar to nonintrusive PCE, stochastic Galerkin method relies on polynomial expansion to estimate probability density and propagate parameter uncertainty. The difference is that stochastic Galerkin is an intrusive UQ approach to solve stochastic ordinary or partial differential equations. In the intrusive PCE approach, the target stochastic process $u(\mathbf{x}; \xi)$ is not readily available, and the approach in Eq. (1.11) to calculate PCE coefficients is of no use. Instead, it is assumed that $u(\mathbf{x}; \xi)$ can be

computed based on some physical models (i.e., ordinary and partial differential equations), and the mathematical forms of the models are available. The expansions are substituted for the variables into the differential equations, and the operations on the original variables are applied to the expansions.

1.3.10 Nonprobabilistic approaches

Differing from traditional probabilistic approaches, nonprobabilistic approaches for UQ have been developed. Perhaps the best known is the Dempster–Shafer evidence theory [91,92]. In this theory, evidence is associated with a power set of discrete random events, in contrast to random events in probability theory. Uncertainty is quantified with the so-called basic probability assignment (PBA). As an illustration, if the event space is $\Omega = \{A, B, C\}$, the probability assignments in traditional probability theory are $P(A)$, $P(B)$, and $P(C)$, subject to constraint $P(A) + P(B) + P(C) = 1$. In the Dempster–Shafer theory, imprecision of assignments is allowed. Therefore, probabilistic measures are assigned to the power set of events, $2^\Omega = \{\emptyset, \{A\}, \{B\}, \{C\}, \{A, B\}, \{A, C\}, \{B, C\}, \{A, B, C\}\}$. The assignments are BPAs, as $m(\emptyset)$, $m(\{A\})$, ..., $m(\{A, B, C\})$, subject to $\sum_{x \in 2^\Omega} m(x) = 1$. That is, uncer-

tainty is directly measured with a set of events. As a result, when we try to estimate the uncertainty associated with individual events, the probability becomes not precisely known. Two quantities are associated with each event. One is the lower limit of probability, also known as *belief*, calculated as $\underline{P}(y) = \sum_{x \subseteq y} m(x)$. The other is the up-

per limit of probability, also known as *plausibility*, calculated as $\bar{P}(y) = \sum_{x \cap y \neq \emptyset} m(x)$.

The belief–plausibility pair provides a convenient way to capture epistemic and aleatory uncertainty. The difference between the lower and upper probability limits is epistemic in nature, whereas the probability itself is aleatory.

There are several mathematical formalisms and theories that are very similar to the Dempster–Shafer theory, such as the theory of coherent lower previsions [93], probability box [94], interval probability [95], generalized interval probability [96], etc. These imprecise probability modeling approaches were developed from slightly different perspectives with different interpretations. Another mathematical formalism, random set [97,98], which quantifies uncertainty associated with random sets of events, is also equivalent to the Dempster–Shafer theory and other imprecise probability theories.

In engineering, interval analysis [99–101] has been widely applied to perform sensitivity analysis and model uncertainty propagation. It was originally developed to address the issue of numerical errors in digital computation due to the floating-point representation of numbers. It is based on a generalization in which interval numbers replace real numbers, interval arithmetic replaces real arithmetic, and interval analysis replaces real analysis. In other words, calculation is based on interval numbers with lower and upper limits. Interval provides a distribution-neutral form to represent uncertainty and error in measurement or computation. Similar to confidence interval in

statistics, the bounds provide an estimate of uncertainty, but without the need to keep track of the associated statistical distribution (which typically is computationally expensive to be tracked). Therefore, it is an efficient scheme to quantify uncertainty when statistical information does not need to be kept or is not available due to lack of data.

1.4 UQ in materials modeling

Chernatynskiy et al. [102] and Wang [103] previously provided reviews on UQ in multiscale materials simulation. This section focuses on an overview of research efforts in the most recent years of rapid growth of interest in UQ for ICME.

1.4.1 UQ for *ab initio* and DFT calculations

Model form error in first principles simulation has been recently explored. Formal UQ methods have been applied to quantify uncertainty in DFT calculations. Particularly, Bayesian approach to estimate the errors associated with DFT exchange-correlation functionals by incorporating experimental data has been extensively studied, including GGA [104], van der Waals interactions [105], meta-GGA [106,107], and Bayesian model calibration [108]. Regression analysis has also been used to predict the systematic errors associated with the exchange-correlation functionals for different crystal structures [109,110]. Gaussian process regression has been applied to construct surrogates of potential energy surface and quantify errors from DFT calculations [50,111–113]. Generalized polynomial chaos was also applied to construct surrogate of energy surface [114]. Other UQ methods such as LSA [115] and resampling [116] are used to estimate the error distribution of DFT calculations.

In addition to UQ methods, comprehensive comparisons of accuracy among *ab initio* methods have been studied. Irikura et al. [117] studied the bias in vibration frequency predictions of Hartree-Fock with 40 different basis sets. Lejaeghere et al. [118,119] provided a comprehensive quantitative error analysis for DFT energy predictions from over 40 different methods including all-electron, projector-augmented wave (PAW), ultrasoft (USPP), and norm-conserving pseudopotential (NCPP). It is seen that model form errors increase because of simplification and approximation in order to gain computational time. Tran et al. [120] compared the error of Rungs 1 to 4 in DFT Jacob's ladder based on lattice constant, bulk modulus, and cohesive energy of solids.

1.4.2 UQ for MD simulation

Uncertainty in materials simulation was first recognized with sensitivity of interatomic potential selection in MD simulation of solid materials [121,122], water molecule [123,124], irradiation damage [125], and others, as well as the effect of cut-off radius. Only recently, formal UQ methods have been applied.

To construct better interatomic potentials in MD, Bayesian calibration has been extensively applied to different potentials such as MEAM [126], Lennard-Jones [127–129], TIP4P [130,131], and coarse-grained MD models [132,133]. Based on experimental observations, the parameters of potentials are adjusted to maximize the likelihood. The major challenge of Bayesian approach is the computational load of Markov chain Monte Carlo involved in estimating the posterior. Numerical approximations can be applied to improve the efficiency [134,135].

Surrogate modeling can also be applied to construct response surfaces from MD simulations as the structure–property relationships to predict material properties. The uncertainty associated with property predictions with respect to interatomic potential parameters can also be evaluated based on surrogate modeling. The modeling methods such as PCE [136,137], Kriging [138], and Lagrange interpolation [139] have been used to assess the uncertainty effect or sensitivity of interatomic potentials on MD simulations.

Instead of constructing response surfaces, the straightforward sensitivity analysis can be done by varying the values of input parameter values based on factorial experimental design [140,141] or MC sampling [142–144]. The above UQ and sensitivity analysis approaches are categorized as nonintrusive, where MD simulation is treated as a black box. Data are collected as input–output pairs for response analysis. Therefore, multiple runs of simulations are needed. Different from the above, Tran and Wang [145,146] developed an interval-based MD mechanism via Kaucher interval arithmetic to assess sensitivities on-the-fly. This is an intrusive approach where the detailed knowledge of MD simulation is needed and simulation packages need to be modified. The new MD simulation tool is an extension [147] of original LAMMPS [148]. Only one run of MD simulation is enough to predict the propagation of uncertainty. Also as gray-box approaches, Tsourtis et al. [149] measured the state distribution variation with respect to the model parameter perturbation in the Langevin dynamics of MD, where only two simulation runs are needed for sensitivity analysis. Reeve and Strachan [150] developed a functional local perturbation approach based on the knowledge of interatomic potential forms to estimate computational prediction errors associated with the Lennard-Jones potential.

Sensitivity analyses exploring uncertainty of MD simulations have gone beyond consideration of interatomic potentials. For instance, Patrone et al. [151] evaluated the variabilities of model size and simulation time on the glass transition temperature of polymers. Kim et al. [152] studied the effects of model size and simulation time on the shear viscosity prediction by the Green–Kubo formulation. Alzate-Vargas et al. [153] assessed the sensitivities of molecular weight, force field, and data analysis scheme in predicting glass transition of polymers.

1.4.3 UQ for meso- and macroscale materials modeling

UQ methods have been widely applied at macroscale or continuum level modeling and simulation. Particularly related to structural materials, methods of Karhunen–Loève expansion [154], PCE [155], and Kriging [156] for Gaussian and non-Gaussian processes or random fields have been well studied in stochastic mechanics given the

variability of material distributions [157,158]. Multiphase material morphology and corresponding properties have been modeled by non-Gaussian random fields such as level-cut filtered Poisson field [159], Markov random field [160], and nonparametric random field [161]. Porosity in solid structures can also be modeled by Gaussian random fields and integrated in FEA [162]. In addition to Karhunen–Loève and polynomial expansions, random fields can also be approximated by Fourier series [163], autoregressive moving average [164], and wavelets [165].

Because of missing physics in traditional ordinary and partial differential equations, stochastic versions of ordinary and partial differential equations have been introduced, where loads or coefficients are random variables, to capture the randomness of material properties and behaviors. Stochastic partial differential equations can be solved by MC sampling, or more efficiently by second-order moment approximation [166], Neumann expansion [167], interval convex method [168,169], Karhunen–Loève expansion [170], stochastic collocation [80,171–173], and PCE [64,77,174]. For stochastic differential equations, Fokker–Planck equation [175] that is equivalent to the Itô process can be formulated to simulate evaluation of probability distributions in dynamics simulation such as Langevin dynamics. Real physical processes, however, are not perfectly Markovian although they may be Gaussian. Generalization of the Fokker–Planck equation thus is needed. For example, generalized Fokker–Planck equation with time-dependent friction coefficients can model the velocity field of Brownian particles subjected to arbitrary stochastic forces [176]. A generalization with a memory kernel introduced in the diffusion coefficient simulates the Brownian motion of particles in viscoelastic fluid more accurately [177]. Non-Gaussian Brownian and Lévy processes can be modeled through transformations or mappings to Gaussian–Markovian process [178].

Traditional models of random fields as well as statics and dynamics behaviors cannot efficiently capture the physical complexity of material properties such as memory effects and energy dissipation in viscoelastic materials, fractal porous media, liquid–solid mixture, sub- and superdiffusive transport, etc. Fractional calculus has been introduced to reduce the model form error caused by traditional integer-order integrals and derivatives [69]. For instance, the viscoelastic behavior of materials is modeled more efficiently with fractional derivatives [179]. The sub- and superdiffusion can be captured by the fractional Langevin equation [180]. The effective reaction–diffusion process in porous media can be modeled as Lévy process [181]. Fractional-order continuum mechanics for fractal solid materials was also introduced [182].

UQ for mesoscale simulations is relatively unexplored. For instance, in PF simulation of solidification, the majority of existing work remained on sensitivity analysis on the model parameters, such as solute expansion factor [183], convection [184], grain orientation [185], and latent heat [186]. Recently, the nonintrusive PCE was applied to quantify the effects of microstructural parameters and material properties on the macrosegregation and solidification time [187] and microstructure [188] in PF simulations. To alleviate the numerical instability in simulation because of model approximation, empirical antitrapping current term can be introduced [189]. Stochastic Cahn–Hilliard equation [190] and stochastic Allen–Cahn equation [191] have been studied.

Fractional Cahn–Hilliard and Allen–Cahn equations [192] were also introduced to mitigate model form uncertainty.

1.4.4 UQ for multiscale modeling

One unique need of UQ for materials modeling is the multiscale nature of simulation predictions. Model calibration and validation may have to be based on experimental observations of QoIs that are different from the predicted QoIs at a different length or time scale. To enable cross-scale or cross-domain information fusion, Bayesian approaches based on different information sources in sensing and modeling can be done, where the hidden or latent variables can be introduced as in hidden Markov models [193], and cross-scale model calibration and validation with epistemic and aleatory uncertainties can be accomplished [194,195]. The hidden Markov model can also be used to establish the connection between coarse-grain and fine-grain model parameters [196]. Even at the same scale, different models may exist to describe the same QoIs. Bayesian approaches can also be taken to reconcile model inconsistency. For example, to calibrate crystal plasticity models and combine models derived from bottom-up atomistic simulations and top-down experimental measurements, the maximum likelihood criterion can be extended to include the constraints of model parameter inconsistency [197] or model form discrepancy [198] so that the regularized likelihood incorporates different sources of information. The Bayesian model average approach can also be taken to reconcile the discrepancy between predictions of QoIs from different scales, e.g., between quantum and molecular level simulations [199].

Another unique need of UQ for materials modeling is to support cross-scale uncertainty propagation. QoIs predicted by simulations at different scales are usually coupled, as the outputs of a smaller-scale simulation can be the required inputs for a larger-scale simulation. To model cross-scale uncertainty propagation, Bostanabad et al. [200] developed a nested random field approach where the hyperparameters of an ensemble of random fields at the lower scale is characterized by yet another random field at the upper scale. Variations and perturbations can be applied in the input–output relationships between different simulation models, such as from MD to PF, DD, and crystal elasticity, to assess the sensitivities [201].

1.4.5 UQ in materials design

Design is an iterative process of searching feasible solutions and identifying in some sense the optimal subset during which decisions are made based on available information. Uncertainty needs to be incorporated in engineering and materials design for robustness consideration. UQ methods have been applied for robust design of structural materials given the uncontrollable factors in complex fabrication processes. For instance, polynomial regressions have been used as surrogates for simulations in simulation-based robust design of materials [202]. The constructed response surface models as the structure–property relationships can be applied to identify feasible design space and search for the optimum [203]. In junction with atomistic simulations, nanoscale materials can also be designed with the optimum macroscopic properties,

for instance, the maximum yield strength of nanowires under the uncertainty associated with environment variables (e.g., strain rate, temperature, and size) [204]. When multiple design objectives are considered, the Pareto frontier can also be identified efficiently aided by the response surfaces [205]. Most recently, Bayesian optimization is recognized as a useful tool for robust global optimization. Instead of the original design objective, an acquisition function is used as the utility function to guide the sequential sampling process to construct Gaussian process surrogates [51,206]. The uncertainty associated with simulation predictions thus can be considered, and a balance between exploration and exploitation is achieved. Acquisition functions such as the expected improvement function can be used in designing NiTi-based alloys with the minimum thermal dissipation based on Bayesian optimization [205,207].

To quantify the uncertainty in materials, random fields have a unique advantage of modeling spatial distributions of phases or properties. Random fields have been used to predict the stochasticity of material properties as well as uncertainty propagation between design parameters so that the response surfaces at multiple scales can be constructed applied for multilevel robust optimization [208]. For topological optimization of materials and metamaterials, the robustness of optimal topology can be improved by incorporating random fields of loads [209,210]. The random material distributions can also be modeled with polynomial chaos [211]. For robust topological optimization, local sensitivities of geometry and topology variations [212,213], manufacturing errors [214], and external loads [215,216] with respect to the optimal solutions need to be assessed. The simultaneous considerations of mean and variance in design objectives with confidence bounds are typically needed to ensure robustness [217].

1.5 Concluding remarks

Uncertainty is an inherent factor in various aspects of modeling, design, and development of materials. Aleatory uncertainty or randomness has been a core focus in physics, e.g., quantum mechanics and statistical mechanics. Nevertheless, the importance of epistemic uncertainty was only recognized more recently in the research community of materials science and engineering. Given the limitations of both experimental observation and physics-based modeling, the lack of knowledge is the most common cause of uncertainty in materials. This is manifested primarily as approximation and simplification. Compared to most science and engineering disciplines, materials research faces specific challenges in bridging the knowledge gap from the scale of electrons and atoms in physics to the scale of homogenized material properties that support traditional engineering design. Uncertainty naturally arises from the lack of good physical models to address phenomena at different length and time scales, as well as the lack of data for calibration and validation of complex empirical or semiempirical models. Obviously elevating the level of knowledge is the ultimate solution to reduce epistemic uncertainty. This will lead to higher quality and more powerful physical models in the future. Along the way, acknowledging the uncertainty and imperfection associated

with existing models is essential to advance scientific discovery and exploit the control of structure to enable materials design and development.

Developing practical UQ tools for the materials domain that are scalable for high-dimensional complex problems is also essential. Most of existing tools can be mathematically sound for small and academic problems. However, they are often not applicable to ICME because of its special needs, including high-dimensionality of the design space, operation of phenomena at multiple length and time scales, both short- and long-range phenomena of interest, and parallel and high-performance computing environments. Development of domain-oriented UQ methods for these particular needs is relevant to this community.

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The uncertainty pyramid for electronic-structure methods

2

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2.1 Introduction

Materials modeling is a booming discipline. Over the last decades, its use has gradually shifted from a purely explanatory activity to a cutting-edge tool in the search and design of advanced new materials. This shift has been triggered by strongly improved predictive capabilities, enabled by a rise in computational power and the appearance of increasingly intricate modeling techniques. Although model parameters are sometimes calibrated based on experimental observations, a more powerful approach is to construct predictions from first principles, relying on nothing more than fundamental laws of nature. This is the case when considering quantum mechanical methods for the electronic structure, which only build upon the nonrelativistic Schrödinger or relativistic Dirac equation to predict materials properties from scratch. The sheer intensity of such computations restricts quantum mechanical simulations to a few hundreds of atoms and a few hundreds of picoseconds, but the resulting data have proven instrumental for the construction of nonempirical multiscale models [1,2] and the discovery of new materials [3,4].

A wide variety of quantum mechanical modeling techniques exist. However, one method currently dominates the field: density-functional theory or DFT for short [5–7]. It has been applied to materials ranging from industrial steels [8] to pharmaceuticals [9] and specialized functional materials [10–12]. DFT owes its popularity to its often good accuracy at an acceptable cost. Due to its first-principles character, it is sometimes even—mistakenly—thought to provide an absolute standard. This is obviously not true. Like all models, DFT simulations require some assumptions and approximations to make them feasible, at the cost of a less-than-perfect predictive quality. Reliable use of DFT for material design therefore calls for a firm grasp of the associated uncertainties, and of the possible techniques to decrease those uncertainties when needed. Such insights become ever more important in view of the increasing role of high-throughput computational research, which generates huge amounts of data to screen for trends and novel materials solutions [13–16].

Uncertainty quantification (UQ) is a relatively new field of study in the DFT community. Although systematic efforts to investigate the agreement between DFT predictions and high-quality reference values have been going on since the late 1990s, both in quantum chemistry [17–22] and quantum physics [18,23–25], these studies mainly served to rank different DFT approaches with respect to each other, and therefore only provided a rough estimate of the DFT uncertainty. The search for a statistically

significant error bar only started halfway the previous decade [26,27] and took another 10 years to take off completely [28–31]. This chapter aims to give a broad overview of the insights that have grown over these last years. The overview does not intend to be exhaustive, but rather highlights some important rules of thumb for DFT UQ by means of two case studies. Before considering these uncertainties, first a brief summary of DFT in the Kohn–Sham formalism is given.

2.2 Density-functional theory

2.2.1 The Kohn–Sham formalism

The key quantity in quantum mechanics is the wave function Ψ . It represents the state of (a subsystem of) the universe, from which in principle every observable property may be derived. For a typical material, the system of interest consists of a collection of M positively charged nuclei and N negatively charged electrons. Its wave function corresponds to a complex-valued scalar field depending on $3(M+N)$ continuous variables (the particle coordinates) and N discrete ones (the electronic spins). However, because of the large difference in mass, the electrons generally move much faster than the nuclei. Any nuclear rearrangement then leads to an almost instantaneous repositioning of the electrons. In the so-called Born–Oppenheimer approximation, only the electronic degrees of freedom are therefore considered, and the positions of the atomic nuclei are treated as environmental parameters. For a nonrelativistic problem, the electronic wave function can be extracted from the Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{\alpha=1}^M \sum_{i=1}^N \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\bar{\mathbf{r}}_i - \bar{\mathbf{R}}_{\alpha}|} + \sum_{i=1}^N \times \sum_{\substack{j=1 \\ j \neq i}}^N \frac{e^2}{4\pi\epsilon_0 |\bar{\mathbf{r}}_i - \bar{\mathbf{r}}_j|} \right] \Psi(\bar{\mathbf{x}}_1, \dots, \bar{\mathbf{x}}_N) = E \Psi(\bar{\mathbf{x}}_1, \dots, \bar{\mathbf{x}}_N) \quad (2.1)$$

where $\bar{\mathbf{r}}$ and $\bar{\mathbf{R}}$ are electronic and nuclear coordinates, respectively, $\bar{\mathbf{x}} = (\bar{\mathbf{r}}, s)$ with s the electron spin, Z is the nuclear atomic number, m_e is the electronic mass, ϵ_0 is the vacuum permittivity, and E is the system's total electronic energy. Although many wave functions can be found from this eigenvalue equation, the ground-state wave function is usually sought after, i.e., $\Psi_0(\bar{\mathbf{x}}_1, \dots, \bar{\mathbf{x}}_N)$ for which $E_0 \leq E \forall \Psi$.

There are many methods to solve Eq. (2.1) based on wave functions [32], but they tend to be limited to small systems. Indeed, solving such a high-dimensional differential eigenvalue equation even in an approximate fashion quickly becomes computationally very intensive. DFT resolves that problem by introducing a bijective

mapping between the $(3N + N)$ dimensional wave function and the three-dimensional ground-state electron density $\rho_0(\bar{r})$:

$$\rho_0(\bar{r}) = N \sum_{s_1, \dots, s_N} \int d\bar{r}_2 \dots d\bar{r}_N |\Psi_0(\bar{r}, s_1, \bar{r}_2, s_2, \dots, \bar{r}_N, s_N)|^2 \quad (2.2)$$

It can be shown that this mapping is unique and exact [33]. Moreover, Kohn and Sham proved the existence of an independent-particle model $\{\phi_1(\bar{x}_1), \dots, \phi_N(\bar{x}_N)\}$ that gives rise to the same overall ground-state density [34].

$$\rho_0(\bar{r}) = \sum_{i=1}^N \sum_{s_i} |\phi_i(\bar{r}, s_i)|^2 \quad (2.3)$$

The single-particle wave functions (or orbitals) can be solved from the Kohn–Sham equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{\alpha=1}^M \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\bar{r} - \bar{R}_{\alpha}|} + \int d\bar{r}' \frac{e^2 \rho(\bar{r}')}{4\pi\epsilon_0 |\bar{r} - \bar{r}'|} + v_{xc}(\bar{x}) \right] \phi_i(\bar{x}) = \epsilon_i \phi_i(\bar{x}) \quad (2.4)$$

where ϵ_i represent the Kohn–Sham single-particle energies. A crucial element in the theory of Kohn and Sham is the occurrence of an additional one-electron potential v_{xc} , which is required to obtain the correct overall ground-state density. Although this so-called exchange-correlation (xc) potential should in principle exist, its exact shape is not known. As a result, practical DFT equations have to rely on educated guesses for v_{xc} , which have nevertheless proven quite effective. These potentials are usually derived from energy densities E_{xc} , referred to as exchange-correlation functionals, by means of a functional derivative to the density: $v_{xc}(\bar{r}) = \frac{\delta E_{xc}}{\delta \rho(\bar{r})}$. Local-density approximation (LDA) functionals are solely based on the local electron density, while generalized-gradient approximation (GGA) and meta-GGA functionals also include the gradient and second-order derivative, respectively. Hybrid functionals mix back in some (occupied single-particle) orbital character.

2.2.2 Computational recipes

Eq. (2.4) can be solved numerically for a given spin polarization by introducing a basis set $\{\xi_n(\bar{r}); n = 1, \dots, N_b\}$ for the single-particle orbitals ϕ_i . Each orbital can then be uniquely expanded as $\phi_i(\bar{r}) = \sum_{n=1}^{N_b} c_n^i \xi_n(\bar{r})$. If we rewrite Eq. (2.4) as $\hat{H}\phi_i(\bar{r}) = \epsilon_i \phi_i(\bar{r})$, multiplication by $\xi_m^*(\bar{r})$ and integration over $\bar{r}$ yields

$$\sum_{n=1}^{N_b} \left[\int d\bar{r} \xi_m^*(\bar{r}) \hat{H} \xi_n(\bar{r}) \right] c_n^i = \sum_{n=1}^{N_b} \left[\int d\bar{r} \xi_m^*(\bar{r}) \xi_n(\bar{r}) \right] c_n^i \epsilon_i \quad (2.5)$$

Considering all values of i yields the matrix equation,

$$HC = SCE \quad (2.6)$$

with $H_{mn} = \int d\vec{r} \xi_m^*(\vec{r}) \hat{H} \xi_n(\vec{r})$, $C_{ni} = c_n^i$, $S_{mn} = \int d\vec{r} \xi_m^*(\vec{r}) \xi_n(\vec{r})$, and $E_{ij} = \varepsilon_i \delta_{ij}$. The generalized eigenvalue problem expressed by the matrix Eq. (2.6) can be solved numerically with a complexity of $\mathcal{O}(N_b^3)$ [35]. Note moreover that due to the dependence of the Hamiltonian $\hat{H}$ on the density in Eq. (2.4), which itself results from the required single-particle orbitals through Eq. (2.3), the problem needs to be solved in an iterative fashion.

Eq. (2.6) yields an exact solution to Eq. (2.4) if the basis set is complete. In principle, this means that an infinite number of basis functions should be considered. In practice, a finite-sized basis set works well if there are enough basis functions to capture the most important features of the wave function. A better resemblance between the basis functions and the shape of the wave function therefore decreases the required basis set size. However, it is then more difficult to find generally transferable basis functions, which are efficient across a wide range of materials.

Because the complexity of the matrix Eq. (2.6) scales with the cube of the basis set size, it is important to limit N_b as much as possible. N_b especially blows up due to wave function features near the atomic nuclei. The Coulomb attraction between electrons and nuclei displays singularities at these positions. This gives rise to sharply oscillating electron orbitals for both core and valence electrons, which typically require large basis set sizes to describe. Different approximations have therefore been introduced to reduce the computational cost. The issue may be circumvented for deep electron states by applying the frozen-core approximation. The wave functions of core electrons are then frozen in their free-atom shapes because they do not contribute to the chemical bonding and change the total energy only up to second order [36]. Another solution is to apply a different (more suitable) type of basis function for the description of the core orbitals and relax them in the crystal field of the surrounding nuclei and electrons [37,38].

Valence electrons are more problematic. Their wave functions are much more delocalized, requiring basis functions that describe both sharp features near the nuclei and more slowly varying behavior in bonds or vacuum. All-electron methods tackle this problem by tuning the basis functions to this ambiguity, often by using a different functional form in different regions of space [37–43]. In contrast, pseudization approaches remove the singularity of the potential at the nuclei to obtain an overall smoother wave function. This smoother or pseudized wave function can then be represented by much fewer basis functions. There are many different options to construct such a nonsingular pseudopotential [44,45]. In addition, the so-called projector-augmented wave (PAW) method establishes a transformation back from the pseudized to the all-electron wave functions using an additional (yet nontrivial) partial-wave basis set [46]. Hence, there is a large variety in methods to solve the Kohn–Sham equations, all of them associated with their own precision.

2.3 The DFT uncertainty pyramid

Although DFT calculations are rooted in the fundamental theory of quantum mechanics, the previous section shows that they rely on both theoretical and technical approximations. DFT predictions should therefore be considered as inherently uncertain, and for practical purposes, each value should be reported with some notion of the associated error.

However, typical DFT-predicted properties result from complex sequences of calculations and suffer from various sources of uncertainty [47]. Casting all levels of uncertainty into only a single set of parameters is often a bit too simplistic. There are only few examples where a DFT calculation directly yields a macroscopically relevant property that can be compared to an experimental standard. In most cases, reporting one DFT error covers up a wide range of deviations from the exact description, ranging from the Born–Oppenheimer approximation over the treatment of core electrons to the shape of the exchange-correlation functional. Each of these approximations adds another layer of uncertainty onto the computed result. We propose to distinguish three methodological levels, forming a DFT uncertainty pyramid. They are represented in Fig. 2.1.

2.3.1 Numerical errors

Numerical errors constitute the bottom of the pyramid (Fig. 2.1). They originate in the technical parts of a DFT calculation and vary from purely hardware- or algorithm-related effects, such as floating-point precision, to more physical approximations to reduce the computational load, such as series truncations or the use of a particular

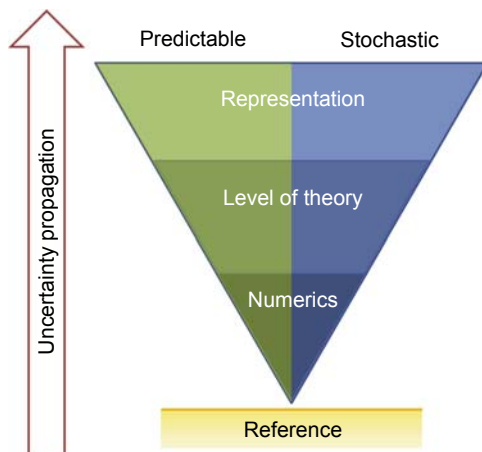


Figure 2.1 The uncertainty on DFT predictions represented as an inverse pyramid. Compared to a reference, three levels of errors can be distinguished. They increase in size as the uncertainties propagate to increasingly drastic approximations. We differentiate between predictable error contributions and errors of a stochastic nature (see Section 2.4.1).

pseudopotential (see [Section 2.2.2](#)). As a result, they are the only contributions to the uncertainty for which it does not make sense to compare to a reference from experiment or a higher level of theory. Instead, one would like to compare to some idealized values that result from exactly the same theoretical formalism yet without incurring any numerical deviations. To emphasize this change of reference compared to more usual UQ, we will refer to numerical uncertainty as *precision*, while *accuracy* relates to the comparison to experiment or more advanced theories.

A common uncertainty factor in all types of DFT calculations is due to the used numerical settings [7]. The selected basis set size plays an important role in this respect, as complete basis sets are in principle required to reproduce the exact solution to the Kohn–Sham problem. Because only finite basis set sizes are practically possible, convergence tests need to be performed to find the right balance between numerical error and computational load. For crystalline solids, k -point sampling is a second important aspect. Bloch’s theorem shows that an independent wave function exists for every point in (the irreducible part of) the first Brillouin zone of reciprocal space. Each of them is required to reconstruct the Kohn–Sham Hamiltonian (through the electron density, for example). In practice, this continuous k -space needs to be sampled on a discrete grid. Convergence tests may identify a suitable grid density that compromises between precision and computing power. Finally, there are also other settings that should be systematically converged, such as the FFT grid density (which can lead to eggbox and aliasing effects if improperly set), electronic smearing, and all kinds of iteration thresholds intrinsic to the used methodology (e.g., for the electronic self-consistency cycle). It was recently proven that both basis set size and number of k -points are machine learnable [48]. A similar approach may therefore be possible for other settings as well. In contrast, the influence of some settings may be more difficult to assess. The use of less robust iterative solvers for the Kohn–Sham equations may lead to incorrect electronic states, for example. Although such aspects are more difficult to quantify, in general, every DFT study should mention the precision to which its combined numerical settings amount. This is an aspect of the simulation uncertainty that is highly dependent on the study at hand, and therefore hard to assess by outsiders.

Errors due to improper numerical settings can sometimes distort simulation results [49], but they can in principle be reduced to a negligible level. Other numerical errors are intrinsic to the used Kohn–Sham DFT implementation, however, and are therefore harder to avoid. All-electron implementations of the Kohn–Sham equations are generally accepted to be most precise, since they do not pseudize the potential. However, even all-electron codes sometimes use radically different solution approaches to the Kohn–Sham problem, varying in their type of basis functions or the way they deal with core electrons, for example. There is therefore no such thing as an unequivocal standard for DFT algorithms. Some strategies may be considered more precise than others, but there is no single code that can be deemed the most precise across the board. Note moreover that precision is not the only objective, as computational stability and load are generally of interest too.

How to quantify precision? As a single standard cannot be identified, the error needs to be evaluated through a pairwise comparison of different DFT codes. In these comparisons, a privileged status can be attributed to all-electron implementations, as is

done in some of the pseudopotential tests proposed by the PseudoDojo project, for example [50]. However, the all-electron uncertainty itself can only be determined by mutually comparing a large set of independent all-electron calculations. Besides a direct comparison of predicted materials properties, errors have been analyzed in terms of a Δ criterion for the energy versus volume behavior (see Fig. 2.2) [29].

$$\Delta = \frac{1}{n} \sum_{i=1}^n \Delta_i = \frac{1}{n} \sum_{i=1}^n \left[\frac{1}{\Delta V} \int_{\langle V_0 \rangle - \Delta V/2}^{\langle V_0 \rangle + \Delta V/2} (E_{i,2}(V) - E_{i,1}(V))^2 dV \right]^{1/2} \quad (2.7)$$

where the energy minima of $E_{i,1}(V)$ and $E_{i,2}(V)$ are aligned, the underlying crystal geometries are kept fixed, and the volume integration is performed in a range of $\pm 6\%$ of the average equilibrium volume $\langle V_0 \rangle$ [51,52]. The Δ measure expresses the uncertainty per material i as a root mean square energy difference, which is averaged over the entire benchmark set. Because Δ is intrinsically larger for materials with a steeper $E(V)$ curve, the Δ package also reports a relative value Δ_{rel} [51].

$$\Delta_{rel} = \frac{1}{n} \sum_{i=1}^n \Delta_{i,rel} = \frac{1}{n} \sum_{i=1}^n \frac{\Delta_i}{\langle E_i \rangle} \quad (2.8)$$

$$= \frac{1}{n} \sum_{i=1}^n \left[\frac{\int_{\langle V_0 \rangle - \Delta V/2}^{\langle V_0 \rangle + \Delta V/2} (E_{i,2}(V) - E_{i,1}(V))^2 dV}{\int_{\langle V_0 \rangle - \Delta V/2}^{\langle V_0 \rangle + \Delta V/2} \left(\frac{E_{i,2}(V) + E_{i,1}(V)}{2} \right)^2 dV} \right]^{1/2} \quad (2.9)$$

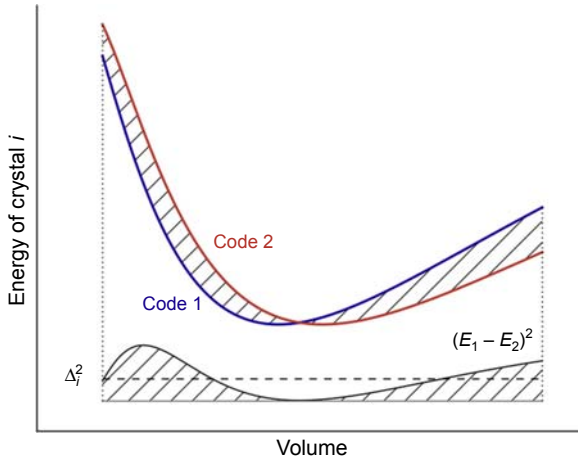


Figure 2.2 Δ Gauge as a tool to compare two equations of state. Δ_i corresponds to the root mean square energy difference between two energy—volume profiles for crystal i .

Other possibilities are rescaling every equation of state $E_i(V)$ in Δ to the height of an average material [53] or defining a reference integration range to transform Δ into a distance metric [52]. Whatever the used gauge, we recommend to report both an absolute and a relative/rescaled error measure, as they contain different information.

The comparison of codes is not a straightforward undertaking, as it requires expertise in various software packages or the availability of various methods in a single implementation. In solid-state DFT, for example, even the few existing comparisons between DFT codes are therefore quite limited [29,50,52–59]. Only one large-scale intercode comparison was published recently and relied on the combined efforts of a collaboration of 69 code developers and expert users [60]. These results have moreover been further extended on the DeltaCodesDFT website [51]. The project is based on equation-of-state predictions for up to 71 elemental ground-state crystals [29]. Results for these materials show that numerical errors between recent Kohn–Sham DFT implementations are generally very limited. Δ values vary from 0.1 to 1 meV/atom between all-electron codes up to 2 meV/atom between pseudization methods. This corresponds to average variations in the volume V_0 of 0.1–0.3 Å³/atom, the bulk modulus B_0 of 0.5–2.5 GPa, and the pressure derivative of the bulk modulus B_1 of 0.5–1. The main influence on the precision is the treatment of the valence electrons. PAW implementations typically differ less among each other than ultrasoft pseudopotentials (USPPs), which in turn tend to outperform norm-conserving pseudopotentials (NCPPs). The best agreement is obtained between all-electron codes. However, although all-electron approaches confirm their status as reference methods, there are potential libraries in each class of pseudization methods that yield equation-of-state predictions of the same quality. The remaining differences of 0.1–1 meV/atom are not due to the potential but can mainly be attributed to the used basis set or numerical settings. Other effects, due to, e.g., differences in the used theory of scalar relativity, do not change Δ more than 0.02–0.2 meV/atom [60].

The above discussion shows that individual static DFT calculations can be run at great precision. Similarly, the contribution of high-level theories to the numerical uncertainty, such as the GW or RPA formalism, can generally be reduced to a low level [61–65]. In contrast, methodologies combining multiple single-point steps may increase the numerical uncertainty considerably. The quality of fitting an equation of state $E(V)$ or $P(V)$, for example, depends on the fitting range and spacing between fitting points. The use of a geometry optimizer may also introduce additional uncertainties. Indeed, a varying efficiency in scanning the potential energy surface may yield different atomic geometries. This level of precision is intimately linked with the step size with which the structure is deformed in response to the calculated forces. Finally, when moving on to molecular dynamics (MD), the number of settings to tune becomes even larger. Parameters such as time step, simulation length, equilibration time, and time constants of thermostat and barostat may all affect the simulation results. Their contribution to the numerical uncertainty is mostly related to correlations between MD steps and has been quantified using various resampling and subsampling methods [66–70].

2.3.2 Level-of-theory errors

Literature on molecular modeling methods primarily associates UQ with accuracy, i.e., the agreement with experiment. Especially, the used level of theory has been considered in quite a few studies and is often even the only examined source of error. Some work is available to quantify the accuracy of force fields in molecular mechanics simulations, for example [69,71–73]. For DFT, besides fundamental assumptions such as the Born–Oppenheimer approximation or wave function single-reference character, the level-of-theory uncertainty is essentially linked with the performance of the chosen exchange–correlation functional. Although such an error contributes only part of the overall uncertainty, it is certainly the most striking one. The development and subsequent assessment of *xc* functionals is therefore the focus of much research and has given rise to a wide range of different benchmarks (see, e.g., Refs. [17–25,74]). The main goal of these studies is to identify or construct an *xc* functional that yields the best correspondence to reference data for a set of benchmark materials. Based on these benchmark results, two conclusions can be drawn. On the one hand, they allow us to decide whether the used level of theory yields a satisfactory accuracy or not. If the accuracy is insufficient, higher levels of theory can be considered. On the other hand, even a satisfactorily accurate result can benefit from an estimate of the residual uncertainty. Such a more instructive approach is the focus of this work.

DFT error measures that are quantifiable and statistically sound are challenging to obtain. Civalieri et al. showed that many measures are available, but that conclusions on functional performance are often affected by them [28]. Most available benchmarks of *xc* functionals focus on simple criteria, such as the mean absolute or relative error. These statistics do not distinguish stochastic effects from more predictable deviations, such as the known overbinding by the LDA functional [18]. A regression-based approach to UQ is more suitable in that respect (see Section 2.4.1). In addition, for some properties specialized error measures were proposed. They include the previously mentioned Δ gauge for equations of state and fitted elemental-phase reference energies [75] or ground-state structure prediction success rates [76] for formation energies. LDA and GGA results were moreover found to often reliably bracket the experimental value [77]. Finally, there are some exchange–correlation functionals available with intrinsic UQ capabilities [27,78], although they tend to describe the sensitivity of the used functional shape rather than the actual agreement with experiment. Overall, it is important to realize that most common types of error bars solely provide a magnitude of the uncertainty, and it is dangerous to blindly apply them to rank different methods.

Despite the difficulty in establishing reliable error measures, most benchmark studies broadly agree on the overall performance of different classes of *xc* functionals. Their errors are generally an order of magnitude larger than numerical errors, displaying Δ values of a few tens of meV/atom, for example [29]. Not unexpectedly, it is found that additional layers of complexity increase the accuracy of a functional, with the error decreasing from LDA over GGA to meta-GGA and eventually hybrid functionals. This systematic increase in complexity and accuracy (at the cost of

computational load) is referred to as Jacob's ladder [79]. Meta-GGA functionals capture midrange dispersion to some extent, for example [80], and hybrid functionals are necessary to improve band gap predictions [81]. Nevertheless, even LDA and GGA (especially the popular PBE functional [82]) have proven to provide good all-round quality predictions for a wide range of materials classes and properties, such as molecular geometries and cohesive energies. This accuracy is sometimes due to fortuitous error cancellation, as demonstrated by the good LDA predictions for graphite despite its intrinsic inability to describe dispersion interactions [83]. Treating dispersion requires using dedicated *xc* functionals or a posteriori correction schemes. Such schemes improve the accuracy for dispersion-governed systems but introduce their own uncertainties [84].

Finally, an important note about the reference data is in order. Quantifying accuracy requires comparing DFT predictions to experimental values, but high-precision measurements are not always available. One option is to resort to more advanced levels of theory, such as RPA [85] or quantum Monte Carlo [86]. This approach was taken by Zhang et al., who established a database of high-quality electronic-structure reference data for light-weight elements [87]. The most important advantage of such an approach is the comparability: when comparing theoretical data, all structures and conditions can be matched exactly (see also [Section 2.3.3](#)). In addition, numerical errors can generally be decreased to a controllable level. In contrast, when comparing to experimental reference data, one needs to consider the influence of varying experimental error bars. An exhaustive evaluation of experimental error bars for surface property predictions was performed by De Waele et al., for example [88]. These error bars affect both predictable uncertainty estimates and stochastic contributions (e.g., through [Eq. \(2.15\)](#), see further). In extreme cases, experimental outliers may even be present. If not dealt with, they can strongly distort any conclusion on the agreement between DFT calculations and experiment. On the other hand, this also presents a great opportunity. Many experimental data on materials properties are unique, i.e., there is only one measurement available for a property of a given material. In those cases, the comparison with DFT within a large-scale benchmark allows the identification of unreliable experimental numbers relatively easily [88–90].

2.3.3 Representation errors

All remaining contributions to the disagreement between DFT and experiment are gathered in the top tier of the uncertainty pyramid ([Fig. 2.1](#)). This broadest class of errors represents all deviations between theory and reality because of deliberate approximations or inadvertent assumptions that are not directly linked to the level of theory. They correspond to a mismatch between what is calculated and what is experimentally measured, i.e., an incomplete atomistic representation of the conditions of the macroscopic material under study. Note that this mismatch is not necessarily unfavorable. Some experimental conditions are hard to control, while simulations allow singling out particular effects or fixing parameters that are otherwise difficult to access.

The possibilities for misrepresentation are numerous. It is therefore not the intention to provide an exhaustive list of all possible representation errors, but rather an overview of how such uncertainties are introduced. We broadly distinguish three types of representation errors: (1) the simulated material may differ from the experimental one, (2) deviating boundary conditions may have been used, or (3) the connection between atomistic and macroscopic properties may be ill-defined. These errors are omnipresent in atomic-scale simulations and are sometimes difficult to deconvolute from level-of-theory errors. Even a simple volume prediction may suffer from an overly simplified unit cell, for example. Nevertheless, misrepresentation effects are important to identify and take into account as much as possible, as their effect can vary from a slight uncertainty to a total lack of agreement between the calculated and intended result.

Assumptions on the material of interest can be introduced in several ways. On the one hand, the structure of a material is typically much more complex than what can be considered in simulations. Atomic disorder, microstructure, and long-range surface reconstructions are typical experimental phenomena that take great effort to tackle computationally. Sometimes residual solvents or precursors are present in the experimental sample, which may need to be taken into account as well. In addition, solvation effects can often not be neglected, and implicit solvation models such as a polarizable continuum model [91] are not always sufficient. Finally, the sheer dimensions of a macroscopic material are also difficult to take into account, such as the number of monolayers in a thin film or the dilution of a given impurity.

On the other hand, even high-purity monocrystalline bulk phases may be misrepresented. Most simulations start from an experimental input structure, i.e., a given crystal symmetry and set of Wyckoff positions. These parameters are not always easy to resolve, as X-ray or neutron diffraction patterns are sensitive to conditions such as sample purity or fitting procedures such as Rietveld refinement [92]. A first-principles optimization of the experimental structure solves most issues and can even be used to remove uncertainties in the experimental structure characterization [93]. Only if the starting point is too unrealistic or if the energy landscape as a function of the geometrical degrees of freedom is too rugged, may it be hard to obtain a realistic optimized structure. This is because metastable geometries or artificially high symmetries are sometimes very persistent. In those cases, fully *ab initio* crystal structure prediction provides a useful alternative [94].

A second source of representation errors arises from the boundary conditions under which a certain material or reaction is simulated. Thermodynamic conditions, such as temperature and pressure, are often important to achieve a decent accuracy. Neglecting or approximating them therefore adds to the overall uncertainty. Thermodynamic parameters can be taken into account quasistatically, using the quasiharmonic approximation, for example [95,96], or via dynamic calculations [97]. The performance of the former method strongly depends on the presence of anharmonic contributions [98], while in the latter case, a reliable thermostat and/or barostat is essential. Phase transitions or reactions are more difficult to model and often require resorting to advanced dynamical sampling schemes [99].

While the inclusion of thermodynamic parameters improves the agreement with experiment, restrictive conditions are applied to simplify the calculations and mostly have a negative effect on the accuracy. Rather than considering all structural freedom during a dynamical simulation, one may choose to scan only a few relevant collective variables, for example [99]. The use of an equation of state for determining elastic constants is another example. While fitting energies versus deformations allows the removal of numerical noise, high-order derivatives of the energy are strongly affected by the proposed fit shape [100] (see also [Section 2.5.1](#)).

A third and final contribution to the uncertainty originates in the use of atomic-scale quantities as descriptors of macroscopically observable properties. While multiscale modeling techniques offer a hierarchical way to establish this link, several semiempirical methods were proposed to directly relate microscopic to macroscopic features through structure–property relationships [101]. Elastic constants or cohesive energies are strongly correlated to melting temperature and inversely proportional to thermal expansion, for example [102]. The currently booming field of high-throughput DFT takes this approach even a step further [13]. Databases can be mined for relevant first-principles descriptors, and quantitative relations can be established using a wide range of machine learning methods. To establish the best possible descriptors, representation learning techniques can be applied, such as principal component analysis [103]. Nevertheless, even the best performing semiempirical relation is prone to some uncertainty, which needs to be taken into account.

2.4 DFT uncertainty quantification

Although understanding of the different factors that give rise to DFT uncertainty constitutes an essential first step, a quantified view on computational error bars is important for practical applications. Different measures of the error can be obtained by comparing theoretical results to reference data. Here, we focus on a regression-based approach, which allows detailed and statistically rigorous error measures.

2.4.1 Regression analysis

When predicting a property of a given material i from first principles, the DFT result x_i does not agree perfectly with reality. Compared to a reference value y_i from experiment or a more advanced level of theory, a deviation $d_i = y_i - x_i$ is observed. This deviation may be due to errors on both the theoretical and the reference data. Because the comparison can be made for a wide range of materials, i , x_i , y_i , and d_i can be considered as samples of stochastic variables X , Y , and D :

$$Y = X + D \quad (2.10)$$

In general, the probability distribution function (pdf) of the deviation D depends on the system in a nonstraightforward way. Although it is difficult to identify all dependencies, some simple relations between the theoretical and reference data may be established. The LDA to DFT, for example, is known to overbind materials, resulting

in overestimated binding energies and too small bond lengths [18]. Such a systematic deviation may be separated from the total uncertainty. In that case,

$$Y = f(X; \{\beta\}) + \varepsilon \quad (2.11)$$

where $\{\beta\}$ is a set of p parameters describing the expected relation between Y and X , and ε is a zero-mean stochastic variable representing the remaining error. It has been stressed at several occasions that removing the systematic part from the error is indispensable to obtain reliable error statistics [26,29,30]. This is necessary to transfer uncertainties on DFT predictions from one material to another. Characterizing the uncertainty with a sole mean signed or unsigned error, as is commonly done in the ranking of exchange-correlation functionals, can therefore only be considered as a first estimate. Instead, a linear relation $Y = \beta_1 X + \beta_0 + \varepsilon$ has been found to perform well in most cases [30,88]. This is demonstrated in Fig. 2.3.

In the following, we will refer to the parameters $\{\beta\}$ as predictable errors and to ε as a stochastic contribution. Note that DFT predictions are in principle deterministic, so none of the errors are truly stochastic in nature. Indeed, contrary to typical experimental measurements, starting from the same crystal structure and numerical settings consistently results in the same DFT value. However, when considering a large sample of different materials, Eq. (2.11) shows that the model inadequacy can be separated into a predictable (and hence correctable) part, as well as a zero-mean uncertainty that can be treated as a fully stochastic quantity. Depending on the source, these

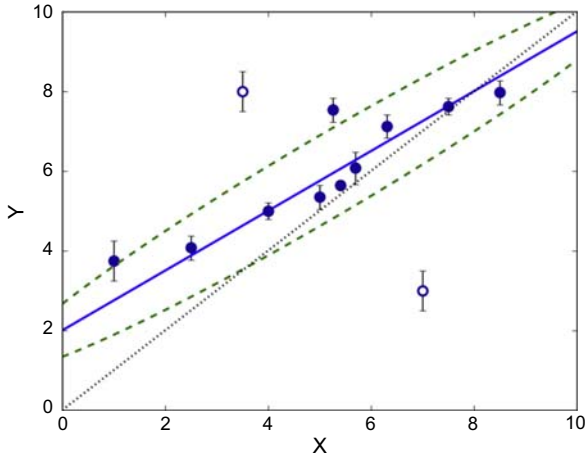


Figure 2.3 Use of a weighted least-squares linear regression to identify different uncertainty contributions. *Blue dots* represent different materials for which reference data Y are compared to theoretical predictions X . The regression line is depicted by a full *blue line* and deviates from the first-quadrant bisector $Y = X$ (*dotted black line*). The intercept β_0 and slope β_1 therefore represent predictable effects. The stochastic uncertainty σ^2 consists of the sum of $\sigma_{approx}^2 + \sigma_f^2(x)$ (*green dashed lines*, see Eqs. 2.13 and 2.16) and the reference data error σ_y^2 (*error bars*). Finally, outliers (*empty symbols*) are removed from the fit.

two parts of the error are sometimes also called systematic or explainable and unpredictable, random, or unexplainable, respectively.

In general, the pdfs of the predictable and stochastic errors are not known a priori. However, they can be extracted empirically from a sufficiently representative sample of (X, Y) . By comparing x_i to y_i for a large number of relevant benchmark materials ($i = 1, \dots, n$), the characteristics of their underlying distributions may be estimated.

A popular way of estimating the predictable errors consists in a (weighted) least-squares linear regression, yielding estimates $\{\hat{\beta}\}$ for the regression parameters [104]. In this case, the goodness of fit for a given data point i is expressed by comparing the squared residual $\left(y_i - f\left(x_i, \{\hat{\beta}\}\right)\right)^2$ to a weight factor that scales with the error on the residual, $w_i = 1/\sigma_{\varepsilon,i}^2$. Note that this approach minimizes only the difference between y_i and $f\left(x_i, \{\hat{\beta}\}\right)$. When there is an additional error on the DFT predictions x_i , more sophisticated regression models are necessary [105,106]. However, in general, we will assume that X is not a stochastic variable but can be considered as a perfectly reproducible parameter (see also the Section 2.3.1).

Stochastic errors are usually addressed through their variance $\sigma_{\varepsilon,i}^2$. It represents the remaining spread on the deviation between DFT predictions and reality after correcting for systematic deviations $\{\beta\}$. $\sigma_{\varepsilon,i}^2$ is a compound uncertainty and contains contributions from all levels of DFT approximations σ_{approx}^2 (see Fig. 2.1), as well as a baseline uncertainty $\sigma_{y,i}^2$ attached to the reference data. Indeed, it is generally not possible to know the reference data exactly, and some sort of measurement error $\sigma_{y,i}$ needs to be taken into account for y_i . One can then write

$$\sigma_{\varepsilon,i}^2 = \sigma_{y,i}^2 + \sigma_{approx}^2 \quad (2.12)$$

where some notion of $\sigma_{y,i}^2$ is available a priori. If σ_{approx}^2 is considered independent of i , it can be estimated from the expected values of $\sigma_{\varepsilon,i}^2$ and $\sigma_{y,i}^2$ [30].

$$\hat{\sigma}_{approx}^2 = \frac{1}{n-p} \sum_{i=1}^n \left(y_i - f\left(x_i, \{\hat{\beta}\}\right)\right)^2 - \frac{1}{n} \sum_{i=1}^n \sigma_{y,i}^2 \quad (2.13)$$

Note that in this formula, the regression parameters $\{\hat{\beta}\}$ are estimated by minimizing the weighted sum of squares of the differences between the DFT and the reference values. $\{\hat{\beta}\}$, and by extension $f\left(x_i, \{\hat{\beta}\}\right)$ and $\hat{\sigma}_{approx}$, therefore depends on the weights, while the weights $w_i = 1/\sigma_{\varepsilon,i}^2$ in turn depend on $\hat{\sigma}_{approx}$ through Eq. (2.12). $\hat{\sigma}_{approx}$ therefore needs to be solved self-consistently, similarly to the iteratively reweighted least-squares method [107].

A crucial deliverable of DFT UQ is the ability to estimate the true property $\hat{y}$ of a system, including the total prediction uncertainty $\hat{\sigma}$, when a simulation yields x . This requires taking into account both predictable and stochastic errors (see Fig. 2.3):

$$\hat{y} = f\left(x, \left\{\hat{\beta}\right\}\right) \quad (2.14)$$

$$\hat{\sigma}^2 = \hat{\sigma}_\varepsilon^2 + \hat{\sigma}_f^2(x) = \sigma_y^2 + \hat{\sigma}_{approx}^2 + \hat{\sigma}_f^2(x) \quad (2.15)$$

where $\hat{\sigma}_f(x)$ expresses the estimated uncertainty introduced by the regression parameters through linear uncertainty propagation

$$\hat{\sigma}_f^2(x) = \sum_{ij=1}^p \frac{\partial f\left(x, \left\{\hat{\beta}\right\}\right)}{\partial \hat{\beta}_i} \hat{\sigma}_{\hat{\beta}_i \hat{\beta}_j} \frac{\partial f\left(x, \left\{\hat{\beta}\right\}\right)}{\partial \hat{\beta}_j} \quad (2.16)$$

and $\hat{\sigma}_{\hat{\beta}_i \hat{\beta}_j}$ represents the covariance between the estimated fit parameters $\hat{\beta}_i$ and $\hat{\beta}_j$. $\hat{\sigma}_{\hat{\beta}_i \hat{\beta}_j}$ may be obtained through analytical formulas [104] or through means such as bootstrapping [31]. To translate $\hat{\sigma}$ into a confidence interval, it is commonly assumed that the residual error ε_i follows a zero-mean normal distribution with variance $\sigma_{\varepsilon,i}^2$. In that case, confidence intervals may be constructed for $\left\{\hat{\beta}\right\}$ and the estimated material property $\hat{y}$ using a Student's t -distribution. However, while ε is often acceptably described by a normal distribution [29,88], this is not always the case. The error on the residuals sometimes needs to be expressed in terms of other materials properties (see the scaling of $\hat{\sigma}_{approx}$ in the subsequent case studies, for example [108]). In addition, the empirical cumulative distribution function can be used, which does not require any assumptions on the error distribution, but expresses confidence intervals via percentiles extracted from the benchmark data [109].

2.4.2 Representative error measures

The procedure described above allows the quantification of the uncertainty on DFT predictions. However, suitable error estimates entail more than a purely quantitative analysis. A representative set of benchmark materials is required, which adequately cover a given chemical space and for which reliable reference data are available. If this is not the case, outliers and transferability issues may severely compromise any conclusions.

Outliers are data points that lie far from the expected regression behavior, and which have the potential to bias fitted parameters (see Fig. 2.3). They occur due to DFT or reference data that are significantly worse (or better) than for most materials. Because DFT theories typically do not take into account all physical interactions to

the same extent, outliers are quite common. For example, when using the GGA to DFT, dispersion is not taken into account. Materials that are not greatly affected by dispersion effects will therefore perform quite well using GGA, while all predictions for dispersion-governed materials will fail and can be considered as outliers. It does not make sense to try and look for a systematic dependence between properties that are intrinsically dominated by dispersion and predictions that do not whatsoever. Moreover, a GGA error bar that is based on both dispersion-governed and dispersion-less benchmark materials will be overly large and will not be useful for any practical purposes. Before performing any uncertainty analysis, it is therefore prudent to first investigate whether outliers can be identified and, if a valid reason is found, be removed from the benchmark. In this sense, outliers may be considered as a predictable effect to the uncertainty, as one can in principle know beforehand which materials need to be excluded. Outlier identification can be done by inspection of the residuals, by means of jackknife resampling [110] or using more advanced approaches [111].

A second challenge is the transferability of the obtained error characteristics. The uncertainty on a DFT prediction of a given materials property is highly dependent on both the considered material and property. The functional performing best for property A and B simultaneously might even differ from the best choices for A and B separately [112]. It is therefore not straightforward to transfer error bars from one system to another or propagate errors toward increasingly more complex quantities. The main cause is the distribution underlying the errors, which is mostly unknown and tends to display important correlations. The problem persists even when removing known biases from DFT predictions. Indeed, correcting for systematic deviations requires a model (see [Section 2.4.1](#)), and remaining uncertainties are then typically associated with sensitivities of the model parameters. However, this practice of so-called parameter uncertainty inflation is only valid if the parameter sensitivities follow the same distribution as the model error. Because the typical assumption of normally distributed residuals is not always valid, conclusions on the errors are generally not transferable to derived properties [113].

There are several ways to deal with the unknown dependencies of level-of-theory errors. A popular practice in literature is to only quantify errors for subsets of compounds that share a given feature. This approach restricts the number of possible correlations and yields smoother error distributions. As the error bar tends to depend on the fraction of bond type present [114], specialized benchmark sets have mostly been defined to cover subsets of materials that are dominated by a given bond type or electronic-structure trait, such as van der Waals bonding or multireference character [21,22]. This strategy stands in contrast to the definition of a test set that is as representative as possible, in order to provide a single all-encompassing uncertainty estimate [29]. However, establishing such test sets is not simple, and corresponding error bars are overestimated. A second approach is to inherently take into account some correlations between material predictions and their errors based on physical considerations. Such a strategy is followed in the case studies below for errors on the volume, bulk modulus, and bulk modulus derivative, as these quantities have been shown to be correlated through a common link to the energy profile [108].

Alternatively, correlations to the volume can be eliminated by performing calculations at the experimental lattice parameters. This removes part of the first-principles character of the DFT simulations, however. Finally, Pernot and Savin proposed to use empirical cumulative distribution functions to define error ranges [109]. This is an excellent technique to deal with the unknown analytical form of the level-of-theory error distribution but should best be applied after similar materials are grouped and physically inspired correlations have been extracted.

2.5 Two case studies

In the subsequent sections, the role and magnitude of DFT uncertainties will be highlighted for two distinct cases. First, the aspect of precision is further elaborated on, expanding upon previous results in a statistically more rigorous way. A second case study examines both precision and accuracy in more detail by considering the ductility of a W–Re alloy.

2.5.1 Case 1: DFT precision for elemental equations of state

We recently published a large-scale comparison of all-electron and pseudization codes using the Δ gauge (Eq. 2.7). The energy versus volume behavior was calculated for the elemental ground-state crystals and was compared between different codes. These results were generally converged to extraordinarily tight settings, so the observed precision could be nearly fully attributed to the DFT implementation. An excellent mutual agreement of recent DFT methods was demonstrated [60].

However, the uncertainty was only estimated energetically from the equation of state. More detailed information on numerical errors can be obtained by considering the volume, bulk modulus, and bulk modulus derivative separately. Predictable and stochastic contributions to their uncertainty can be distinguished by fitting the agreement between predictions of two codes to a linear trend $\hat{y} = f\left(x_i, \left\{\hat{\beta}\right\}\right) = \hat{\beta}_0 + \hat{\beta}_1 x$ (see Section 2.4.1). Because purely theoretical data are compared, it is not necessary to take into account an additional error bar σ_y on the reference data. However, it was shown that in equations of state, the error σ_{approx} on V_0 scales with $1/B_0$, the one on B_0 with $1/V_0$, and the one on B_1 with $1/B_0 V_0$ [108]. This behavior can be taken into account using a weighted least-squares regression. The error σ on a given materials property x can then be written as $\sqrt{\sigma_{approx}^2(x) + \sigma_f^2(x)}$, with

$$\hat{\sigma}_{approx}^2(x) = \frac{1}{w} \frac{\sum_{i=1}^n w_i \left(y_i - \hat{\beta}_0 - \hat{\beta}_1 x_i \right)^2}{n - 2} \quad (2.17)$$

and the weight w equal to B_0^2 when comparing volumes, for example. This corresponds to a rescaling of the used weighting factors to the observed weighted sum of squared

residuals. The resulting uncertainty measures $\hat{\beta}_0$, $\hat{\beta}_1$, and $\langle \hat{\sigma}_{approx} \rangle$ are reported in [Table 2.1](#) for a wide range of codes and potential libraries compared to all-electron methods (with $\langle \hat{\sigma}_{approx} \rangle$ calculated via $\langle w_i \rangle$). Results represent averages over 10,000 bootstrapped data sets. Outliers were identified through a jackknife procedure as materials for which the distance to the regression line exceeds 5 times $\sigma(x)$ (for either V_0 , B_0 , or B_1). If the errors were to be considered normally distributed, this would correspond to a probability of 4×10^{-6} that comparing to 70 test materials yields a more extreme deviation from the regression line (two-sided p-value). Finally, Δ values are listed using the same bootstrap sampled data.

As before, both the Δ gauges and the regression parameters are found to demonstrate the same order of precision, i.e., improving from NCPP over USPP and PAW to all-electron methods. However, more detailed information can now be extracted. An important conclusion is related to the intrinsic difficulty in characterizing an equation of state $E(V)$. The fundamental property resulting from an electronic-structure calculation is the electronic energy. If DFT implementations of the same quality and equally stringent numerical settings are used, differences in this energy are quite limited. This is demonstrated by Δ . However, derived properties are more sensitive to the exact shape of the equation of state. Δ_{rel} , for example, expresses the energy difference with respect to the average height of the $E(V)$ curve in the considered interval. Such a criterion inherently assumes that a higher precision is required for shallower equations of state, such as for the noble gases. This high precision is typically much more difficult to achieve, as indicated by the relatively high values of Δ_{rel} . Similarly, observable materials properties, such as V_0 , B_0 , and B_1 , are derivate quantities. They are typically obtained after fitting an analytical form to the $E(V)$ behavior and are related to the derivative of the energy with respect to volume (or, equivalently, pressure). As such, higher-order properties such as B_0 and B_1 are increasingly more affected by numerical noise, while the overall change in Δ is very limited. This problem again deteriorates for shallow equations of state. The effect is especially critical in determining B_1 . [Table 2.1](#) indicates that even codes with the most reliable Δ values suffer from an appreciable error bar $\langle \hat{\sigma}_{approx} \rangle$ of 0.2–0.3. For some codes, the noise distorts the fit so badly that no correspondence between codes can be obtained anymore, even though the deviation of the energy Δ remains quite limited. In these cases, a 7-point equation of state between $V_0 \pm 6\%$ does not suffice to obtain reliable B_1 data, which are too sensitive to the quality of the fit. This does not mean that the code performs worse than others in general, but it rather suggests that the noise on the equation of state is not fully under control. A wider fit range, an increased number of fitting points, or stricter numerical settings can remediate this.

A second important observation is related to predictable effects. While systematic deviations are crucial to adequately describe the uncertainty of DFT with respect to experiment (see [Section 2.5.2](#)), they appear to be mostly negligible when considering precision. Indeed, most values of the intercept $\hat{\beta}_0$ or the regression slope $\hat{\beta}_1$ are within one or two standard deviations of the expected values (0, 1). The only predictable uncertainty worth mentioning consists in the outliers. Because every element is treated

Table 2.1 Predictable and stochastic uncertainties associated with numerical errors of all-electron, projector-augmented wave (PAW), ultrasoft pseudopotential (USPP), and norm-conserving pseudopotential (NCP) methods.

			V_0 ($\text{\AA}^3/\text{at}$)			B_0 (GPa)			B_1 (—)			Outliers
	Δ (meV/ at)	Δ_{rel} (%)	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	
Elk	0.5(1)	11(2)	1.000(1)	0.01(1)	0.016(2)	1.000(1)	0.02(6)	0.6(1)	1.00(6)	−0.1(3)	0.30(4)	Cd, O
Exciting	0.4(1)	9(2)	1.001(1)	0.00(1)	0.015(2)	1.000(1)	−0.01(4)	0.5(1)	0.99(5)	0.1(3)	0.23(4)	—
FHI-aims/tier2	0.4(1)	9(2)	1.001(1)	0.00(1)	0.014(2)	1.000(1)	−0.02(4)	0.4(1)	0.93(5)	0.3(2)	0.22(4)	—
FLEUR	0.5(1)	11(2)	1.001(1)	−0.01(1)	0.018(3)	0.997(2)	0.06(6)	0.7(1)	0.83(7)	0.7(3)	0.28(4)	Fe, P
FPLO/T+F+s	0.8(1)	15(2)	1.001(1)	−0.04(2)	0.031(4)	0.998(2)	−0.17(8)	0.7(1)	1.02(6)	0.0(3)	0.23(4)	B, Mn
RSPt	0.7(1)	19(4)	0.996(1)	0.04(1)	0.021(3)	1.004(1)	0.09(7)	0.5(1)	0.89(5)	0.5(2)	0.25(5)	Bi, Cl, Cr, Sr, Tc
WIEN2k/acc	0.4(1)	10(2)	1.001(1)	0.00(1)	0.014(2)	1.000(1)	0.04(5)	0.5(1)	0.94(5)	0.3(2)	0.22(4)	Fe
<i>All-electron average</i>	0.6	12	1.000	0.00	0.018	1.000	0.00	0.5	0.94	0.3	0.25	
GBRV12/ABINIT	0.9(1)	13(2)	0.999(1)	0.02(2)	0.037(5)	0.997(1)	0.06(7)	0.6(1)	0.96(5)	0.2(2)	0.18(3)	Mn
GPAW09/ABINIT	1.4(2)	19(2)	1.003(2)	−0.03(4)	0.065(9)	1.000(2)	−0.04(6)	0.7(1)	0.90(5)	0.4(2)	0.19(3)	Cr, Mn
GPAW09(g)/ GPAW	1.5(2)	25(3)	1.004(2)	−0.06(4)	0.071(10)	1.000(2)	−0.08(6)	0.7(1)	0.99(5)	0.1(2)	0.24(4)	Cr
GPAW09/GPAW	1.6(2)	25(3)	1.005(2)	−0.06(4)	0.070(9)	0.998(2)	−0.06(7)	0.7(1)	0.95(4)	0.2(2)	0.19(3)	Cr
JTH03/ABINIT	0.6(1)	11(2)	1.000(1)	0.00(1)	0.023(3)	0.997(2)	0.03(6)	0.9(2)	0.86(9)	0.7(4)	0.35(7)	—
PSlib100/QE	0.7(1)	13(2)	1.002(1)	−0.02(2)	0.030(4)	0.998(1)	−0.01(5)	0.4(1)	1.01(6)	0.0(3)	0.19(4)	Fe, Hf, Mn, N, O
VASPGW2015/ VASP	0.6(1)	10(2)	1.001(1)	−0.01(1)	0.018(3)	0.997(1)	0.06(5)	0.5(1)	0.93(6)	0.3(3)	0.22(4)	Y

Continued

Table 2.1 Continued

			V_0 (Å ³ /at)			B_0 (GPa)			B_1 (–)			Outliers
	Δ (meV/ at)	Δ_{rel} (%)	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	$\hat{\beta}_1$	$\hat{\beta}_0$	$\langle \hat{\sigma}_{approx} \rangle$	
<i>PAW average</i>	1.0	16	1.002	−0.02	0.045	0.998	−0.01	0.65	0.94	0.3	0.22	
GBRV15/CASTEP	0.9(1)	14(3)	1.000(1)	0.00(2)	0.033(5)	0.999(2)	0.07(8)	0.7(1)	1.02(7)	−0.1(3)	0.22(4)	Cr, Fe, I, N
GBRV14/QE	0.8(1)	13(3)	1.000(1)	0.01(2)	0.034(6)	0.996(1)	0.05(6)	0.5(1)	0.93(5)	0.3(2)	0.18(3)	Cr, Fe, Mn, N
OTFG9/CASTEP	0.6(1)	16(3)	1.001(1)	0.01(1)	0.021(3)	0.997(2)	0.05(5)	0.6(1)	0.95(6)	0.3(3)	0.22(4)	Au, Cr, Mn, Pd
SSSPacc/QE	0.4(1)	9(2)	1.000(1)	0.00(1)	0.017(3)	0.998(1)	0.01(4)	0.4(1)	0.96(5)	0.2(2)	0.18(3)	Cr, Fe, Hf, Hg, Mn
Vdb2/DACAPO	5.2(11)	52(8)	0.980(14)	0.31(21)	0.254(45)	0.987(4)	0.24(20)	1.4(3)	0.89(7)	0.5(3)	0.28(5)	Fe, Mn, Ru
<i>USPP average</i>	1.6	21	0.996	0.06	0.072	0.995	0.08	0.71	0.95	0.2	0.21	
FHI98pp/ABINIT	8.2(12)	79(7)	1.010(14)	−0.43(23)	0.308(57)	0.992(6)	−0.09(21)	2.2(5)	0.93(5)	0.3(2)	0.22(4)	Fe, W
HGHsc/ABINIT	1.8(4)	21(3)	1.000(3)	0.05(5)	0.089(7)	0.994(3)	0.14(7)	0.8(1)	0.87(6)	0.6(2)	0.22(4)	Cr, Fe, Mg, Mn
HGH-NLCC2015/ BigDFT	1.0(1)	17(2)	1.000(2)	0.01(3)	0.054(8)	0.991(5)	0.14(10)	1.1(2)	0.93(7)	0.4(3)	0.24(5)	Fe, Zn
MBK2013/ OpenMX	2.0(2)	33(4)	1.000(3)	−0.05(4)	0.070(10)	0.985(4)	0.03(11)	1.6(3)	0.62(10)	1.7(5)	0.48(6)	—

ONCVPSP(PD0.1)/ ABINIT	0.7(1)	13(2)	1.000(1)	0.00(2)	0.027(3)	1.004(2)	0.02(5)	0.5(1)	0.97(5)	0.1(2)	0.20(3)	Cr, F, Fe, Mn
ONCVPSP(SG15) 1/Octopus	0.8(1)	16(3)	0.997(1)	0.07(2)	0.029(4)	0.999(2)	−0.07(10)	0.9(2)	0.91(6)	0.4(3)	0.25(4)	Cr, Fe, Hf, Mn, Na, Ni
ONCVPSP(SG15) 1/QE	0.8(1)	13(2)	0.997(2)	0.04(3)	0.036(5)	1.000(2)	0.03(5)	0.6(1)	0.94(5)	0.3(2)	0.18(3)	Cr, Fe, Mn
ONCVPSP(SG15) 2/ATK	1.9(2)	36(5)	0.999(3)	0.00(5)	0.077(12)	0.972(14)	−0.55(42)	5.4(11)	0.02(2)	4.4(1)	0.61(7)	—
ONCVPSP(SG15) 2/CASTEP	0.9(1)	15(2)	0.997(2)	0.04(3)	0.037(5)	1.003(2)	0.00(7)	0.7(1)	0.94(5)	0.3(2)	0.20(3)	Cr, Fe, Mn
<i>NCPP average</i>	2.0	27	1.000	−0.03	0.081	0.993	−0.04	1.5	0.79	0.9	0.29	

Results reflect an average uncertainty compared to the seven considered all-electron codes and are extracted from a weighted least-squares linear regression after removal of outliers and bootstrapping the data sets (see text). The underlying data are available online [\[51\]](#).

differently, either by atomic potential or basis functions, distinct elements can easily perform worse than others. They are therefore the most important points of improvement for a given code or potential library. This is evident when comparing Δ values with and without exclusion of outliers. Compared to the all-electron codes, $\Delta(\text{FHI98pp/ABINIT})$ decreases by 5.2 meV/atom when excluding Fe and W and $\Delta(\text{GBRV14/QE})$ changes by 0.3 meV/atom due to its four outliers, for example. Note, however, that an outlier does not necessarily mean that predictions for this material cannot be trusted at all. Outliers merely correspond to crystals for which the predictive quality is considerably worse than the overall test set. This predictive quality can still be quite good. The volume of Cd with Elk, for instance, differs by only 0.3 Å³/atom or 1% with respect to the other all-electron codes.

2.5.2 Case 2: DFT precision and accuracy for the ductility of a W–Re alloy

In a second case study, we discuss all tiers of the uncertainty pyramid for the prediction of the ductility of a tungsten–rhenium alloy. Tungsten is a refractory metal with the highest known melting temperature of all pure elements. It moreover possesses other interesting high-temperature properties, such as a low thermal expansion and high thermal conductivity, as well as a reasonably low level of neutron activation [115]. These qualities make tungsten one of the prime candidates for plasma-facing components of future nuclear fusion machines [116]. However, tungsten suffers from a few disadvantages, most notably its high brittleness at room temperature. It limits operating conditions to temperatures above the ductile-to-brittle transition temperature (DBTT) and compromises the long-term integrity of tungsten components.

One possible approach to the ductilization of tungsten is alloying. Unfortunately, it is not a priori clear which combinations of alloying elements affect the DBTT in a beneficial way. Rhenium was experimentally found to reduce the brittleness of tungsten [117], but the price of rhenium is prohibitive for large-scale use. First-principle design offers a cheap approach to screen many alternative alloys [118]. As an example, we investigate W–Re in more detail from first principles below to get some feeling for the uncertainties involved in DFT-based ductility predictions, necessary for such further searches.

To estimate the ductility of W–Re, we consider a W₁₅Re supercell, i.e., tungsten with a 6.25 at% rhenium concentration. This alloying level is well below the solubility and mechanical instability limit of Re in W [119] and was shown to significantly decrease the DBTT [117]. We compare it to a pure tungsten W₁₆ supercell. For both materials, first the cell geometry is optimized, after which the elasticity tensor is determined and several ductility descriptors are constructed (see Fig. 2.4). These ductility descriptors are all qualitative, as quantitative ductility descriptors at the atomic scale are currently not available yet.

A first step consists in determining the equilibrium geometry of W₁₆ and W₁₅Re. Performing fixed-volume geometry relaxations at 13 volumes between $\pm 6\%$ of the estimated volume reveals an energy versus volume relation that can be fitted to an

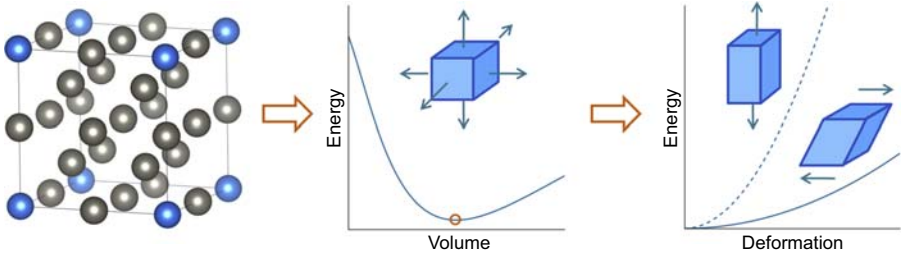


Figure 2.4 Procedure used to calculate the elastic constants of $W_{15}Re$: (i) unit cell construction from a 16-atom body-centered cubic supercell (gray: W, blue: Re), (ii) determination of the equilibrium volume and bulk modulus under hydrostatic loading, and (iii) extraction of the $C_{11} - C_{12}$ and C_{44} elastic constants from the energetic response to tensile (*dashed line*) and shearing deformation (*full line*), respectively.

empirical equation of state (Fig. 2.4, middle panel). We use the PBE functional [82], state of the art PAW potentials (VASPGW2015/VASP with a Δ below 1 meV/atom [51,60]) and high numerical settings (500 eV cutoff energy, $17 \times 17 \times 17$ k -grid). We thus find fitted equilibrium volumes of 257.8924 and 256.7800 $\text{\AA}^3$ (Birch–Murnaghan equation of state [120]) or 257.8929 and 256.7804 $\text{\AA}^3$ (Rose–Vinet equation of state [121]) for W_{16} and $W_{15}Re$, respectively. The uncertainty due to the used equation of state is therefore very minor and even significantly lower than typical differences between codes (see Table 2.1). Also the effect of a slightly changed volume range for the fit does not change the volume estimates appreciably. Uncertainties due to the chosen numerical settings are checked by increasing the cutoff energy to 600 eV and the k -space sampling to $21 \times 21 \times 21$ and remain below 0.02 $\text{\AA}^3$. The main contribution to the error arises from the use of the PBE functional. Level-of-theory errors were previously found to contain a significant predictable component in addition to a slight stochastic error bar. Using a zero intercept and an ordinary least-squares fitting procedure, PBE volumes were found to be overestimated by 3.8%, besides a supplementary error bar of 1.1 $\text{\AA}^3/\text{atom}$ [29]. A good estimate for the actual low-temperature volume of W is therefore $15.5 \pm 1.1 \text{\AA}^3/\text{atom}$. When taking into account the $1/B_0$ scaling of the error bar through a weighted least-square fit (see Section 2.5.1) and allowing for a nonzero intercept, this becomes $15.7 \pm 0.2 \text{\AA}^3/\text{atom}$ (see Fig. 2.5). This confirms that error estimates may strongly depend on the underlying error assumptions, with the second approach being the more reliable one. Nevertheless, both estimates display an excellent agreement between theory and experiment (15.8 $\text{\AA}^3/\text{atom}$ after correction for zero-point effects [122]). This agreement is especially good given the typically small experimental errors (e.g., 0.05 $\text{\AA}^3/\text{atom}$ for W at room temperature [123]). This suggests that representation errors might be small when the volume is concerned. Such uncertainties are for example due to the simulation of a perfectly ordered crystal without microstructural features.

In a second step, we determine the elastic constants C_{ij} (in Voigt notation). The bulk modulus B_0 of W_{16} and $W_{15}Re$ is extracted from the analytical equation of state. We obtain 304.6 and 308.1 GPa with a Birch–Murnaghan fit and 304.8 and 308.3 GPa

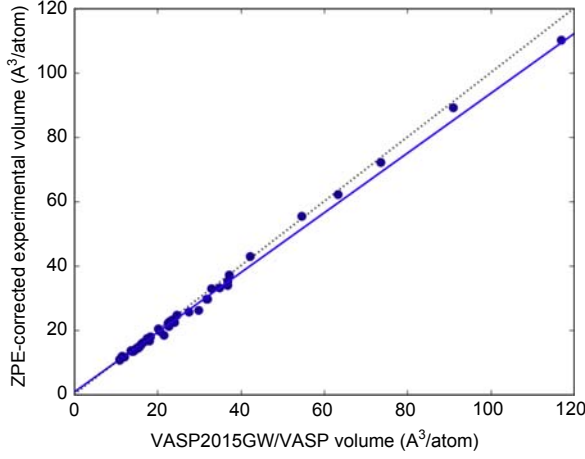


Figure 2.5 Weighted least-squares fit of experiment to VASP2015GW/VASP for the volume per atom of the ground-state elemental crystals (*circles*) [29]. Systematic outliers were excluded from the analysis, and zero-point effects (ZPE) were corrected for. The regression line (*full line*) corresponds to $\beta_0 = 0.7$ and $\beta_1 = 0.928$ and is compared to the $y = x$ line (*dotted line*).

using a Rose–Vinet equation of state. For the other elastic constants, we start from the systematically overestimated PBE volume, which guarantees a positive semidefinite elastic tensor in DFT. The C_{ij} parameters can then be obtained using either a stress-based [124] or an energy-based approach [125]. However, because stresses represent derivatives of the energy and are typically more affected by both noise and systematic deviations (e.g., Pulay effect [49,126]), we choose to directly work with energies. The tetragonal strain modulus $C_{11} - C_{12}$ and shear modulus C_{44} are extracted from the energy behavior as a function of two volume-conserving strains (Fig. 2.4, right panel) [127,128].

$$\epsilon_1 = \left(\frac{1}{\sqrt[3]{1 + \delta_1}} - 1, \frac{1}{\sqrt[3]{1 + \delta_1}} - 1, \left(\sqrt[3]{1 + \delta_1} \right)^2 - 1, 0, 0, 0 \right) \quad (2.18)$$

$$\epsilon_2 = \left(0, 0, \frac{\delta_2^2}{4 - \delta_2^2}, 0, 0, \delta_2 \right) \quad (2.19)$$

so

$$\begin{cases} E_1/V = 3(C_{11} - C_{12})\epsilon_{1,1}^2 + \mathcal{O}(\epsilon_{1,1}^3) \\ E_2/V = \frac{1}{2}C_{44}\epsilon_{2,6}^2 + \mathcal{O}(\epsilon_{2,6}^4) \end{cases} \quad (2.20)$$

These values can be combined with the bulk modulus $B_0 = (C_{11} + 2C_{12})/3$ to obtain C_{11} , C_{12} , and C_{44} .

$C_{11} - C_{12}$ and C_{44} are determined by fitting the energy per volume to a polynomial of order n ($n \geq 2$). However, such a procedure is quite sensitive to numerical uncertainties since a second-order derivative of the energy is targeted. We demonstrate this in Fig. 2.6 for the case of a single conventional unit cell of tungsten at 600 eV cutoff, $35 \times 35 \times 35$ k -points, and using the VASP2012/VASP potential. There is a tradeoff between the order of the polynomial to which the energy is fit, which should not be too high to avoid overfitting, and the width of the fitting range, as the energy curve becomes increasingly less polynomial in nature when the cell is deformed out of equilibrium. We find a suitable compromise when a polynomial of fourth order is used and when the deformation parameter δ is 0.04. These conclusions are similar to the ones obtained by Golesorkhtabar et al. [129] The remaining error on the elastic constants is of the order of 2–4 GPa. If we use these settings to determine the elastic constants of W_{16} and $W_{15}Re$, we find C_{11} , C_{12} , and C_{44} to equal 519, 197, and 142 GPa for W_{16} and 514, 205, and 144 GPa for $W_{15}Re$. After incorporating level-of-theory errors [29], this becomes 529 , 201 , and 145 ± 23 GPa for W_{16} and 524 , 209 , and 147 ± 23 GPa for $W_{15}Re$. The level-of-theory error bar therefore dominates strongly over the numerical error bars. A comparison to the available measurements for tungsten (533, 205, and 163 GPa) [130] shows a good agreement, with experimental error bars below 0.5%.

Note that despite the overall correspondence with experiment, the difference in elasticity between W_{16} and $W_{15}Re$ is smaller than the error bar. Using the current error model, the predicted change in elastic constants is therefore not significant. On the other hand, the above confidence intervals are based on a benchmark across a wide range of different crystals. When comparing similar materials such as W_{16} and $W_{15}Re$, a large degree of error cancellation may occur. A similar observation

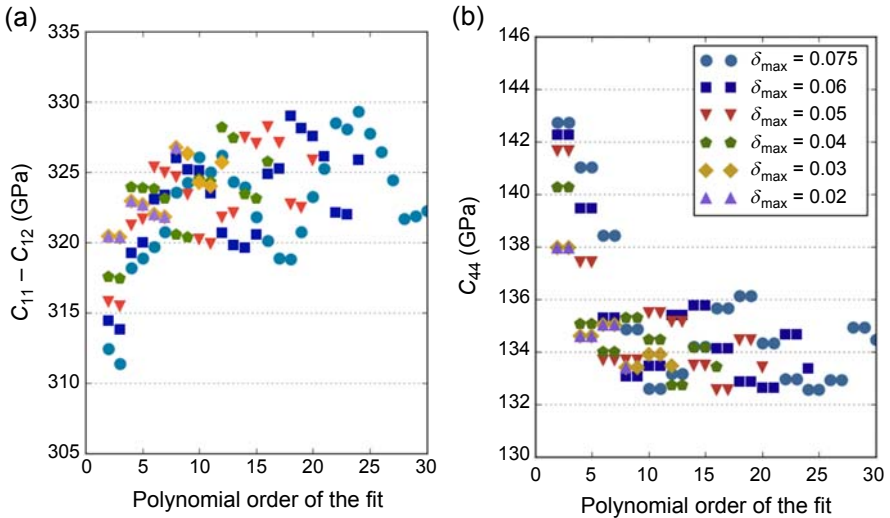


Figure 2.6 Fitted $C_{11} - C_{12}$ and C_{44} of tungsten as a function of the order of the polynomial to which $E/V(\epsilon)$ is fit (Eq. 2.20). δ is varied in steps of 0.005 between $\pm\delta_{\max}$.

was made for formation energies, which were found to be more accurate when looking at polymorphs of the same chemical makeup [76]. This correlation is not taken into account in the present approach, which is an important limitation. It can be addressed by considering a specialized benchmark of tungsten alloys only. The decrease in C_{11} and increase in C_{12} and C_{44} is indeed confirmed both experimentally [131] and in other DFT studies [132].

To predict the DBTT evolution from W to W–Re, a final step consists in linking the DFT descriptors to ductility via a structure–property relationship. One possible approach is to link ductility to the covalent character of bonding in the alloy. Brittle materials can be well described by purely pairwise atomic interactions, while ductile materials possess softer bending modes. Ductility is therefore associated with high Poisson’s ratios $\nu = E/2G - 1$ [133], Cauchy pressures $P_C = C_{12} - C_{44}$ [134], or Pugh ratios B_0/G [135] (with E the Young’s modulus and G the shear modulus). A different way to look at ductility is from the viewpoint of dislocation mobility. A lower Peierls stress allows easy displacement of a dislocation and facilitates plastic deformation. Thus, one option would be to actually model the dislocation movement [136]. Alternatively, it was found that the Peierls stress correlates well with the C_{44} elastic constant or the prelogarithmic energy $\mathcal{E}$ ($Gb^2/2$ in the polycrystalline approximation [137], with b the Burgers vector) [138]. A similar criterion is the one by Rice and Thomson, bG/γ with γ the surface energy, which expresses the ease of emission of dislocations at a crack tip [139].

It is not our intention to critically assess all ductility descriptors. Instead, we focus on the Cauchy pressure to demonstrate the propagation of level-of-theory errors. Correcting for predictable effects results in $P_C = 56$ GPa for W₁₆ and 62 GPa for W₁₅Re. Linear uncertainty propagation, similar to Eq. (2.16), yields a residual error bar of 15 GPa, since C_{12} and C_{44} are strongly correlated (Pearson correlation coefficient of 0.8). This is in good agreement with a direct regression analysis, which yields an error bar of 18 GPa. These error estimates indicate that the increase in Cauchy pressure due to Re alloying is statistically not significant, although the uncertainty may again be overestimated due to important correlations between the two similar crystals. In that case, our DFT calculations suggest rhenium to ductilize tungsten, in agreement with experimental observations. On the other hand, other theoretical studies suggest representation errors to be substantial here. The Cauchy pressure of W–Ta also increases compared to pure tungsten, for example [118], while it is experimentally found to embrittle the material [140]. A similar mismatch between theory and experiment is found for the Poisson’s ratio and Rice–Thomson criterion [141]. This is because such simple descriptors are not able to capture complex phenomena, such as the dislocation core structure and slip plane [142], or the important influence of microstructure on the DBTT [143].

The case of the ductility of tungsten alloys nicely shows how uncertainties are crucial to take into account and how they increase in magnitude when climbing the uncertainty pyramid (Fig. 2.1). Numerical errors are usually limited, although derived properties like the elastic constants are much more prone to noise than directly accessible ones. Level-of-theory errors generally have a more important effect. Especially correcting for predictable effects, which are seldom taken into account, enhances

the agreement with experiment substantially. Finally, representation errors affect results most drastically. The used descriptors for ductility introduce too large an uncertainty to capture the complex microstructural evolutions that underly plastic deformation. Other criteria may prove more suitable. Alternatively, if sufficient quantitative reference data are available, a machine learning approach may provide further improvements.

2.6 Discussion and conclusion

Electronic-structure theory, and particularly DFT, has evolved drastically over the past few decades. Originally limited to theoretical support for experimental studies, the method is now fully capable of quantitative predictions. Computational material design is therefore becoming a perfectly valid equivalent for experiments, which is further facilitated by the availability of several high-precision software packages. This is demonstrated by the boom in high-throughput first-principle screenings, for example, or the willingness with which experimentalists have embraced DFT as a quick tool for validation of measurement results. Unavoidably, the wide-spread use of electronic-structure methods also implies that electronic-structure codes are increasingly considered as a black box. While this is not necessarily a bad thing, it is vital that users are aware of and report any uncertainties their approach introduces. As such, this chapter aimed to provide a broad overview of which types of errors might be present, illustrated by means of two case studies.

We separated the uncertainty in three levels with both predictable and stochastic contributions. They are schematically depicted in an uncertainty pyramid (Fig. 2.1). Numerical errors are the most technical ones and require thoroughly converging all numerical settings and parameters, as well as carefully evaluating any fitting or sampling procedure. When taking sufficient care, these errors can be kept to an almost negligible minimum. However, it is important to realize that some simulations are intrinsically more prone to numerical noise than others, e.g., when considering large systems or high-order derivatives of the energy.

Level-of-theory errors constitute a second layer of the uncertainty pyramid and can be substantially larger. This is because no electronic-structure theory is perfect. In the popular DFT, the crucial element is the exchange–correlation functional, possibly combined with an a posteriori dispersion correction scheme. Different choices yield varying predictions, which moreover depend on the studied property and material. It is therefore necessary to possess a good grasp of the shortcomings of the used level of theory. This can be done in terms of systematic deviations and residual error bars. In addition, one must take into account that some materials or properties are intrinsically impossible to describe well with a particular electronic-structure method. Before selecting a level of theory for a given materials problem, one should therefore examine benchmarks from literature to see which methods are suitable. A brief validation for the system of interest compared to experimental or high-level theoretical data is moreover always recommended. Afterward, predictable errors may be corrected for to improve the agreement with experiment. Such a correction may make more

advanced methods unnecessary and offers additional insight into the performance of the chosen approach.

Finally, representation errors can have the most drastic effect and are unfortunately the hardest to avoid. To minimize this uncertainty contribution, one must make sure that the atomic-scale simulation actually corresponds to the physical process that is to be modeled. Some approximations have a larger effect than others, so it is important to carefully reflect which assumptions are expected to hold. On the other hand, there are several known cases where a first-principles quantity offers an acceptable descriptor for a macroscopic observable. This idea is the core concept behind data mining and machine learning, which offer a promising new route to inexpensive yet accurate materials properties predictions. They therefore constitute a powerful alternative for multiscale modeling techniques.

It is evident that UQ is a necessity for reliable materials modeling. Nevertheless, UQ for electronic-structure methods is still in its infancy, especially when solid-state calculations are concerned. While the quantum chemistry community has developed extensive benchmarks using high-quality experimental or theoretical reference data, to which different levels of theory can be compared, such information is only available to a very limited extent for periodic systems. The recent work of Zhang et al. is a notable exception [87]. In addition, current benchmark sets are mostly biased toward a limited number of materials classes, while all types of bonding character should be considered (either in one exhaustive set or in separate dedicated ones). Establishing better tests for electronic-structure methods will allow a better quantification and transferability of level-of-theory uncertainties.

From a more technical point of view, the theory behind first-principle errors also requires further elaboration. Standard distributions are not always suitable to describe error statistics. In that respect, the empirical cumulative distribution function concept of Pernot and Savin is promising [109], although it does not solve the problem of error correlations and trends. Especially error correlations require further investigation, as, for example, the case study on tungsten alloys suggested that comparing similar materials might be possible with much smaller errors than apparent from broad benchmarks. Also uncertainty propagation, necessary to treat complex multistep procedures such as MD or thermodynamic integration, remains challenging for the same reasons. Evolutions in these fields may benefit from further insight into the behavior of and correlations between first-principle simulations.

We presented a brief demonstration of the different levels of uncertainty by means of two case studies. However, in complex electronic-structure studies, uncertainties tend to coalesce. As the field of electronic-structure UQ keeps evolving [16], it is expected that increasingly performant methods will be developed to tackle these problems. These methods may vary from levels of theory with intrinsic UQ capabilities to automated approaches to make appropriate choices within a given confidence interval. Nevertheless, they share one common purpose: underpinning the reliability of first-principle results.

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Bayesian error estimation in density functional theory

3

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3.1 Introduction

Density functional theory (DFT) [1,2] has provided researchers within many different areas with a useful computational tool to describe atomic-scale properties. Applications range from chemistry and biochemistry over condensed matter physics to materials science. However, DFT comes in many flavors depending on the choice for the exchange-correlation (xc) energy functional, as we in practice have to resort to approximations to the exact functional theoretically proven to exist. For a given functional, it is hard to know the reliability or accuracy of calculated properties. In the following, we focus on errors related directly to the choice of functional approximation neglecting other fundamental but generally much smaller errors (e.g., lack of relativistic effects) as well as errors related to computational practice (e.g., the basis set), which can be systematically reduced [3]. The functionals can be grouped or ranked [4] according to how much information is used to determine the xc-energy: the local density, gradients of the local density, the kinetic energy density, the exchange energy etc., and it is usually expected that the degree of reliability of the calculations increases as the xc-functional gets more advanced and includes more physical contributions. Furthermore, many systematic investigations and tests of different functionals for properties such as molecular binding energies or cohesive energies of solids have been carried out and a large knowledge therefore exists about their performance. However, for the individual user with a particular problem at hand, it is difficult to obtain a reliable estimate of the “error bar” on the result of a given calculation.

The main output of a DFT calculation is the electron density and the total energy, and one could naively hope that error estimates of these quantities for a given functional would directly provide insight into the performance of the functional. However, as is well known, this is typically not the case because of error cancellation. The total energy of, e.g., a molecule typically has a much larger error than the binding energy of the molecule, *i.e.* the energy difference between the molecule and its constituent atoms. In general, energy differences between systems which resemble each other are better determined than absolute energies. One example, which we shall return to later, is the cohesive energy of a metal versus the energy difference between the metal

in two different crystal structures like fcc and bcc. For a typical generalized gradient approximation (GGA) functional, the error on the former is typically several tenths of an eV, while the error in the latter is one or two orders of magnitude smaller. Any useful error estimate will have to take this situation into account. In the following, we shall give an overview of the approach behind the Bayesian error estimation functionals (BEEFs), which do exactly this.

3.2 Construction of the functional ensemble

The main idea behind the BEEF functionals is to consider a probability distribution or, equivalently, an ensemble of functionals. In Bayesian probability theory, the use of probability distributions over models is quite common and forms the basis for Bayesian model selection. With the BEEF functionals, instead of using a single functional to make predictions of physical quantities, a whole ensemble is used and the spread of the calculated values provides an error estimate.

The functional ensemble is determined based on a model space and a database. In the first studies [5], only GGA functionals were considered together with a small database of experimental values for atomization energies of molecules and cohesive energies of solids. Later developments have included van der Waals interactions (BEEF-vdW) [6], meta-GGA (mBEEF) [7], and the combination (mBEEF-vdW) [8]. The databases have been greatly expanded both with respect to the number of systems considered and with the inclusion of more properties such as chemisorption energies and bulk moduli. The Bayesian error ensemble approach has been used by other groups in the development of another meta-GGA functional [9] and a hybrid xc-functional (LC*-PBE0) [10].

Before moving to the construction of the ensemble, we shall briefly review the standard Bayesian probabilistic approach. This is based on Bayes' theorem, which states that the probability $P(M(a)|D)$ (the posterior distribution) for a model $M(a)$ with parameters a and given some data D can be expressed as $P(M(a)|D) \propto P(D|M(a))P_0(M(a))$. The first term, $P(D|M(a))$, is the so-called likelihood, while the last term, $P_0(M(a))$, is the prior probability distribution and accounts for knowledge about the model based on previous data or other considerations. A simple example would be the prediction of function values y_i based on some input variables x_i ($i = 1, 2, \dots$). The model with parameters a predicts the values $y_i(a)$, and if we assume a Gaussian distribution with noise parameter σ for the likelihood $P(D|M(a))$, we get the distribution

$$P(a|D) \propto \exp\left(-\sum_i (y_i - y_i(a))^2 / 2\sigma^2\right) P_0(a), \quad (3.1)$$

where we have suppressed the explicit reference to the model M . We can find the most probable values for the parameters a by maximizing the posterior distribution $P(a|D)$. If we neglect the prior, this is equivalent to minimizing the cost function $C(a) = \sum_i (y_i - y_i(a))^2 / 2\sigma^2$ known from the usual least-squares regression. If the

prior is expressed in exponential form $P_0(a) = \exp(-R(a))$, a new cost function, $\tilde{C}(a) = C(a) + R(a)$, appears, now with an additional regularization term $R(a)$. If the regularization term is quadratic in the model parameters, we obtain the so-called ridge regression.

Eq. (3.1) provides a probability distribution over the model parameters, which in principle could be used to estimate errors on predicted properties. However, there is the implicit assumption behind this expression that the true model is in the model space that we investigate, or at least that the model space contains models which are able to describe the data within the noise on the data points. One can see this by considering the limit where the noise parameter σ becomes very small. In that case, the Gaussians approach delta functions so that only models which reproduce the data very accurately will have any appreciable probabilistic weight. In our case, where we consider highly accurate data (either from experiment or high-quality quantum chemistry calculations) the noise parameter will be small compared to the errors we must expect due to limitations in the functional (for example, if the functional is of the GGA type). Another feature of Eq. (3.1) is that as we add more data the probability distribution for the parameters will become increasingly well defined. As an example of this, in a simple linear regression with a normal distribution, the uncertainty on the mean goes as $1/\sqrt{N}$, where N is the number of data points. Usually as more data are added, it is possible to generalize the model by introducing more parameters, reduce the regularization, and thereby obtain a better model. In the case with the xc-functionals, this approach is not straightforward. For example, within the class of GGA functionals, one could introduce more parameters in the description of the enhancement factor. This would lead to more flexibility in the model, but it would not be able to reproduce the data because the exact xc-functional is much more complicated. The set of GGA functionals is *insufficient*. This is illustrated in Fig. 3.1 where the exact functional is outside the region covered by GGA functionals. One way forward is then of course to consider higher-level modes (meta-GGA, hybrids, etc.), but that does not provide

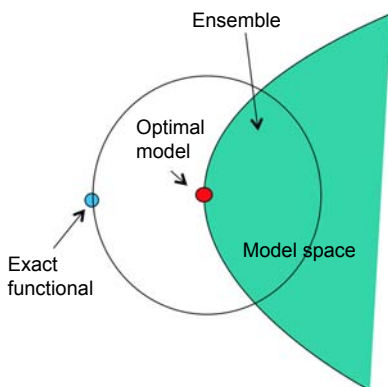


Figure 3.1 A particular class of models (for example, GGAs) does not include the exact functional. The ensemble is defined to cover a region of model space with the extent of the minimum cost around the optimal model.

error estimates for GGA functionals as such. We therefore need a slightly different approach to deal with insufficient models.

The aim is to construct a probability distribution $\mathcal{P}(a)$, where a are the model parameters, so that the width of predicted probability distributions provides an estimate of the actual errors. Note that this is different from the distributions in (1). Let us denote the parameters of the optimal model, i.e., the model that maximizes $\mathcal{P}(a)$, by a_0 . For a given data point, we can thus define the error as $\Delta y_i = y_i - y_i(a_0)$, where as above y_i denotes the actual target value. For a given value of the parameters a we can similarly define the deviation from the optimal value at the data point as $\delta y_i(a) = y_i(a) - y_i(a_0)$, and let δy_i denote the root mean square deviation $(\delta y_i)^2 = \int (\delta y_i(a))^2 \mathcal{P}(a) da$.

Now, ideally at each data point, the average deviation would equal the error $(\delta y_i)^2 = (\Delta y_i)^2$. However, this is a too strong requirement the fulfillment of which essentially corresponds to making an improved functional. What we can require is that this relation is present for the average for all data points:

$$\sum_i (\delta y_i)^2 = \sum_i (\Delta y_i)^2. \quad (3.2)$$

This does not by itself determine the probability distribution $\mathcal{P}(a)$; however, one can apply maximum entropy principles to show that in the case of linear models this requirement leads to a probability distribution of the form [11]

$$\mathcal{P}(a) \propto \exp(-\mathcal{E}(a) / T), \quad (3.3)$$

where the cost function is $\mathcal{E}(a) = \sum_i (y_i - y_i(a))^2$, and T is a parameter to be determined by the constraint Eq. (3.2). To determine the parameter T , we use an analogy with statistical physics, where the temperature enters the Boltzmann factor in a similar way. A linear model results in a quadratic cost function, which in this analogy would correspond to a harmonic energy expression. According to the equipartition theorem, each degree of freedom contributes an average energy of $T/2$, which means that the average value of the cost function becomes

$$\left\langle \mathcal{E}(a) \right\rangle = \left\langle \sum_i \Delta y_i^2 \right\rangle + \left\langle \sum_i \delta y_i^2 \right\rangle = \mathcal{E}_{\min} + N_p T / 2. \quad (3.4)$$

N_p is here the number of parameters in the model, i.e., the length of the vector a . Applying the constraint Eq. (3.2) we find the parameter T to be given by $\mathcal{E}_{\min}$ as

$$T = 2 \sum_i \Delta y_i^2 / N_p = 2 \mathcal{E}_{\min} / N_p. \quad (3.5)$$

The probability distribution $\mathcal{P}(a)$ thus samples models with a typical value of the cost function twice the value of the minimum cost. This is illustrated in Fig. 3.1 where

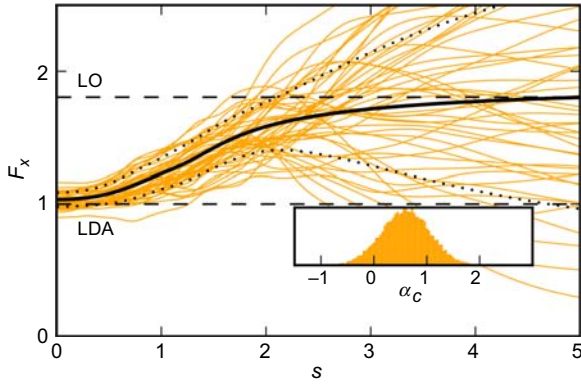


Figure 3.2 The ensemble of enhancement factors in the BEEF-vdW functional and the distribution of the LDA correlation parameter α_c . LO denotes the Lieb-Oxford bound. The figure is from J. Wellendorff, K.T. Lundgaard, A. Møgelhøj, V. Petzold, D.D. Landis, J.K. Nørskov, T. Bligaard, K.W. Jacobsen, Density functionals for surface science: exchange-correlation model development with bayesian error estimation. *Phys. Rev. B*, 85(June 2012): 235149.

the ensemble spans a region of the model space out to about the same distance from the optimal model as the distance from the optimal model to the exact functional.

Comparing with the standard Bayesian probability expression Eq. (3.1), we see that both the cost function $\mathcal{C}$ and the parameter T scale with the number of data points, because T is proportional to the minimal cost. The uncertainty of the model parameters does therefore not necessarily decrease with increasing number of data points.

The ensemble constructed in the BEEF-vdW functional is illustrated in Fig. 3.2, which shows the ensemble of exchange enhancement factors as a function of the dimensionless reduced density gradient s . The figure also shows the distribution of the parameter α_c , which describes the contribution of the LDA correlation, which must sum to 1 with a contribution to correlation from the PBE functional. The width of the ensemble is seen to increase for high values of the gradient, because these values are not appearing much in the database and are less important for the calculation of the energy.

The actual construction of the functional ensembles requires consideration of a number of aspects, which we shall only briefly mention here. These have been described in detail in the papers about the functional construction [5–8].

The BEEF functionals are constructed as linear models so that the total energy, E , is a linear function of the model parameters: $E = E_0 + \sum_i a_i E_i$, where a_i are the individual model parameters. The number of energy terms E_i is typically less than 50.

The linearity has two advantages. Firstly, the optimization process necessary to construct the optimal functional can benefit from the usual tools with a quadratic cost function. However, one complication here is that even though the functional is explicitly linear in the parameters, there is an implicit dependence through the change in density: a change in the parameters gives rise to a new ground state density which affects the change of the energy. This implicit dependence is weak because of the variational principle: the first-order change in the energy when the functional parameters

are changed can be obtained without changing the density. But still this effect has to be taken into account when constructing the optimal best-fit functional.

The second advantage of a linear model is that the ensemble predictions become computationally very fast. The different energy contributions E_i are obtained from a single self-consistent calculation with the optimal functional. When the parameters a_i subsequently are varied to create the ensemble, non-self-consistent calculations are used in the sense that the energy contributions E_i are kept at the values for the optimal potential and only the parameters a_i are varied. The ensemble predictions can thus be calculated at essentially no computational cost by simply evaluating the sum $\sum_i a_i E_i$. This allows the ensemble to contain several thousand models.

Within a given class of functionals, the flexibility of the model has to be controlled to avoid overfitting. This requires introduction of regularization terms in the cost function enforcing, for example, that functions are sufficiently smooth. The strength of the regularization can be determined using cross validation.

The databases used in the construction of the functionals consist of different types of systems covering molecular fragmentation energies, bulk material properties, surface properties, and chemisorption strengths of small adsorbates. These databases vary significantly in size and can be correlated. It is a delicate issue to balance the weight of the different databases.

The issue of balancing the prediction of different physical properties can be illustrated by plotting, for example, the errors on calculated chemisorption energies versus the errors on surface energies as shown in Fig. 3.3. The GGA functionals are seen to have a difficulty in getting both the surface energies and the chemisorption energies right at the same time. Details in their construction lead to different compromises between the two quantities. The meta-GGAs do somewhat better with mBEEF-vdW to some extent breaking the correlation.

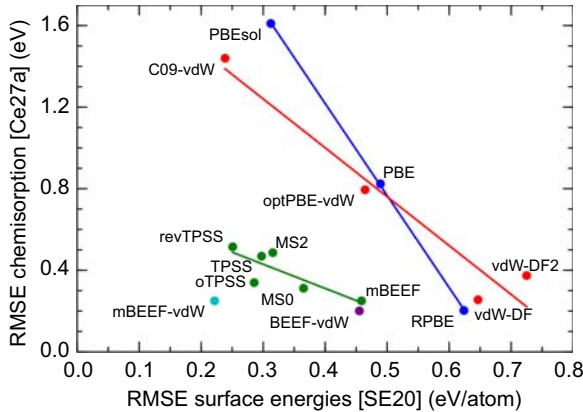


Figure 3.3 Bivariate analysis of chemisorption energies versus surface energies. The lines are linear fits to functionals of the same type: GGAs (blue), GGAs with vdW (red), and meta-GGAs (green).

The Figure is from K.T. Lundgaard, J. Wellendorff, J. Voss, K.W. Jacobsen, T. Bligaard, mBEEF-vdW: Robust fitting of error estimation density functionals, *Phys. Rev. B* 93(2) (June 2016) 235162, where the datasets are also described.

Going beyond surface energies and chemisorption energies, the overall compromise for different properties, expressed through the weights given to each database, will ultimately define the performance of the xc-functional. The ambition for the BEEF functionals has been to develop multipurpose functionals, which perform well for a range of different properties. This is also true for the ensembles. However, the ensembles will tend to overestimate or underestimate on average the error for some properties [6,8]. Better error estimates can be obtained for specific properties by renormalizing the ensemble to, on average, predict the observed errors for a specific database [12].

The BEEF approach does have its limitations. As mentioned above, the resulting probability distribution does not only depend on the model space but also on the databases employed. Another important limitation comes from the fact that not only the optimal functional but also the full ensemble belongs to the preselected model space. To illustrate this issue, consider two atomic systems which are separated in space so they have no density overlap. The two systems do, however, still interact through van der Waals forces. This interaction cannot be captured by semilocal functionals like the GGAs, so if our model space is limited to this class, all functionals in the ensemble will predict zero interaction energy between the two systems. This means that not only the prediction by the optimal functional will be wrong but also, since all functionals in the ensemble predict the same, the estimated error will be zero. The only way to remedy this issue is to move to a class of more advanced functionals, which can properly describe the van der Waals interactions.

3.3 Selected applications

The BEEF functionals have been used in several studies [13–29]. In particular, BEEF-vdW has been applied in numerous investigations of surface reactions and catalysis. We shall not go through these applications here but only show a couple of examples, which illustrate how the uncertainty estimation works within the BEEF framework. Firstly, we discuss the basic use of the ensemble approach to studies of the cohesive energy and structural energy differences of solids. Secondly, we illustrate how error propagation works for the prediction of rates of catalytic ammonia synthesis. Correlations between the different functionals in the ensemble are seen to reduce the uncertainty significantly. Finally, it is demonstrated how these correlations can be used to identify systematic errors within a given xc-functional model space.

The first example is the calculation of equilibrium volumes and cohesive energies of some simple solids using the BEEF GGA functional [5]. Fig. 3.4 shows the calculated values with the optimal functional together with the ones obtained with PBE. The experimentally measured values are also indicated. The “clouds” show the results obtained by applying the ensemble. It is seen that the correlations between predictions for the volumes and the cohesive energies vary significantly with system. For a weakly bound system with a large volume like sodium, the uncertainty is dominantly in the volume, while the opposite is the case for the tightly bound diamond crystal. The strongly ionic solids LiF and NaCl show a strong correlation between cohesive energy and volume in agreement with the error relative to experiment.

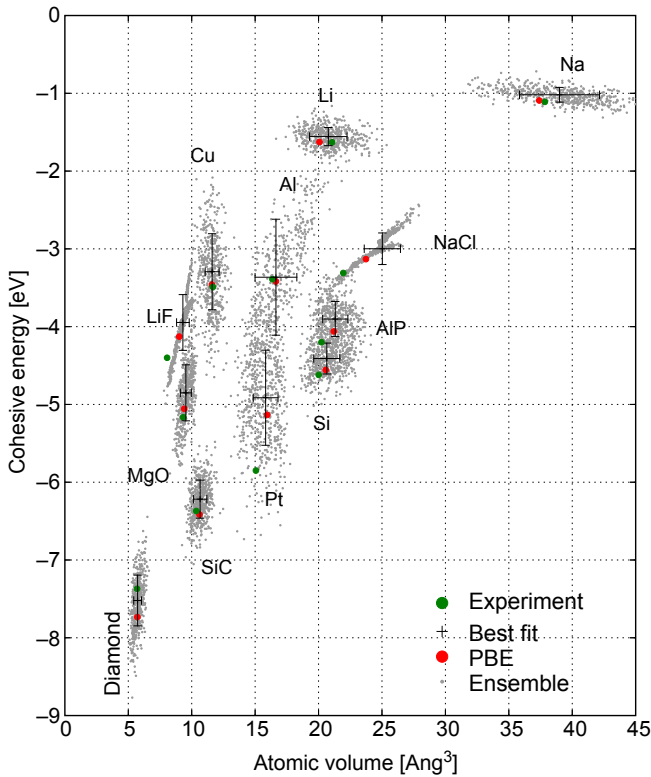


Figure 3.4 Calculated cohesive energies and atomic volumes for a selection of solids. Error bars are the ensemble standard deviations.

Figure by courtesy of Kristen Kaasbjerg.

Error cancellation plays an important role in the application of DFT. Energy differences between two similar systems are usually more reliably calculated than separate total energies, and the more similar the systems are, the more accurate the calculation. Energy differences may depend more or less strongly on the xc-functional. The energy difference between a metal in two different close-packed structures depends only weakly on the xc-functional at least as long as the functional is semilocal. This feature can be understood based on the force theorem [30–32], which shows that if the structural energy difference is calculated based on non-self-consistent potentials within the so-called atomic-sphere approximation, the semilocal xc-energy completely drops out. This insensitivity to the xc-functional is reproduced in the ensemble predictions. Fig. 3.5 shows the calculated ensemble predictions for the cohesive energy of copper and for the energy difference between copper in the bcc and fcc structures. The uncertainty on the cohesive energy is seen to be two orders of magnitude larger than the uncertainty on the structural energy difference confirming the insensitivity of the latter to the xc-functional even though bcc is not close packed. Calculations of the structural energy differences for the transition metals show that in all cases except gold, the correct crystal structure is predicted [31], confirming that despite the small energy differences the calculations are surprisingly accurate.

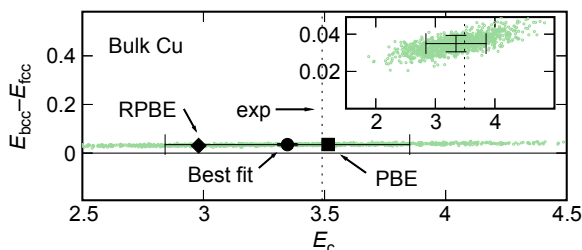


Figure 3.5 Functional ensemble predictions for the cohesive energy of copper and for the fcc–bcc energy difference. The uncertainty of the cohesive energy is much larger than the one of the structural energy difference. The inset shows the same results but with the axes rescaled. Figure from J. J. Mortensen, K. Kaasbjerg, S. L. Frederiksen, J. K. Nørskov, J. P. Sethna, K. W. Jacobsen, Bayesian error estimation in density-functional theory, *Phys. Rev. Lett.*, 95 (November 2005) 216401.

The ensemble approach makes it possible to consistently propagate errors in more complicated modeling. An example of this is the work by Medford et al. [12], where the catalytic ammonia synthesis rates are calculated for some selected metal catalysts. The synthesis rates are determined based on a microkinetic model, which involves the elementary steps in the synthesis process. The rates of the individual processes are obtained from DFT calculations of the intermediate reactant binding and transition energies. The transition rates depend exponentially on the energy barriers divided by the temperature and are therefore very sensitive to errors in the energy barriers. Since the uncertainty on a single energy barrier is often much larger than the temperature, one might think that only very little could be concluded about the overall synthesis rate. However, this is not the case. Due to the so-called scaling relations and the Brønsted–Evans–Polanyi relations, the binding and transition state energies are correlated [34,35] and this correlation is captured by the functional ensemble. The final synthesis rates obtained from the microkinetic model using the BEEF-vdW ensemble (including a small renormalization to improve the error prediction of chemisorption energies, please see Ref. [12]) are shown in Fig. 3.6 as a function of the nitrogen binding energy on the surface. The rate exhibits the common Sabatier “volcano” shape. For strong nitrogen binding, the hydrogenation process and the release of ammonia is slow leading to suppressed activity. If the nitrogen binding is weak, nitrogen molecules do not dissociate on the surface, and the activity is again low. The “clouds” in the figure show the ensemble predictions for the rate with different colors corresponding to different metal surfaces. The “clouds” are seen to stretch along the volcano showing that the ensembles obey the scaling relations. Furthermore, the figure illustrates that clear conclusions can be drawn about the relative activity of the different metals with ruthenium being the most active one. The uncertainty on the relative activity of two of the metals, say iron and ruthenium, can be further reduced by explicitly considering the ensemble predictions for the difference instead of the two metals separately [12].

As a final example we shall discuss how the ensemble approach can be used to identify systematic errors within a class of xc-functionals and to devise ad hoc corrections

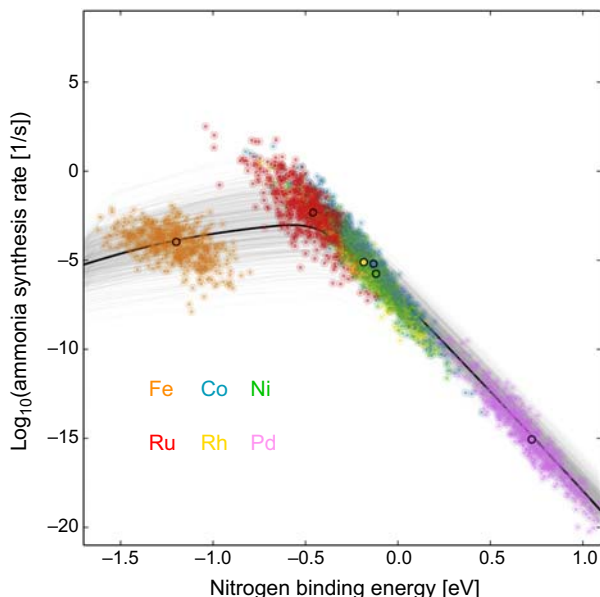


Figure 3.6 The rate of ammonia production for the metal catalysts Fe, Co, Ni, Ru, Rh, and Pd. The “clouds” show the calculated rates for the ensemble functionals.

Adapted with permission from A.J. Medford, M. Ross Kunz, S.M. Ewing, T. Borders, R. Fushimi. Extracting knowledge from data through catalysis informatics. *ACS Catal.* 8(8) (2018) 7403–7429. Copyright (2018) American Chemical Society.

to these errors. The method was introduced by Christensen et al. [37,38] to improve the accuracy of GGA-level DFT calculations for heterogeneous catalysis. Using the method, it was found that the formation energy of individual carbon–oxygen double bonds is highly functional dependent at the GGA level. This was found to cause significant systematic errors for a range of GGA functionals (with PBE being a notable exception). Part of the analysis can be seen in Fig. 3.7, which shows the calculated reaction enthalpies of several reactions plotted versus one another. Two observations can be made. Firstly, the calculated enthalpies are strongly correlated within the ensemble. Secondly, the experimentally available data lie on the correlation lines although in the outskirts of the ensemble distributions. An analysis of the ensemble predictions may therefore provide information about how to make ad hoc corrections to the calculated energies. A further analysis of the slopes of the correlation lines shown in the figure (together with correlation lines for several additional reactions [37]) indicates that the main source of the error is the description of individual carbon–oxygen double bonds. Two such double bonds are present in the CO₂ molecule. By introducing an ad hoc correction of the C=O double bonds in CO₂ and relevant product molecules, the predictions move along the correlation lines and by an appropriate choice for this one parameter, the predicted enthalpies of reaction greatly improve.

As seen in Fig. 3.7(d), correlations can also be established between gas-phase reactions with quantifiable errors and reactions involving adsorbates. We do not

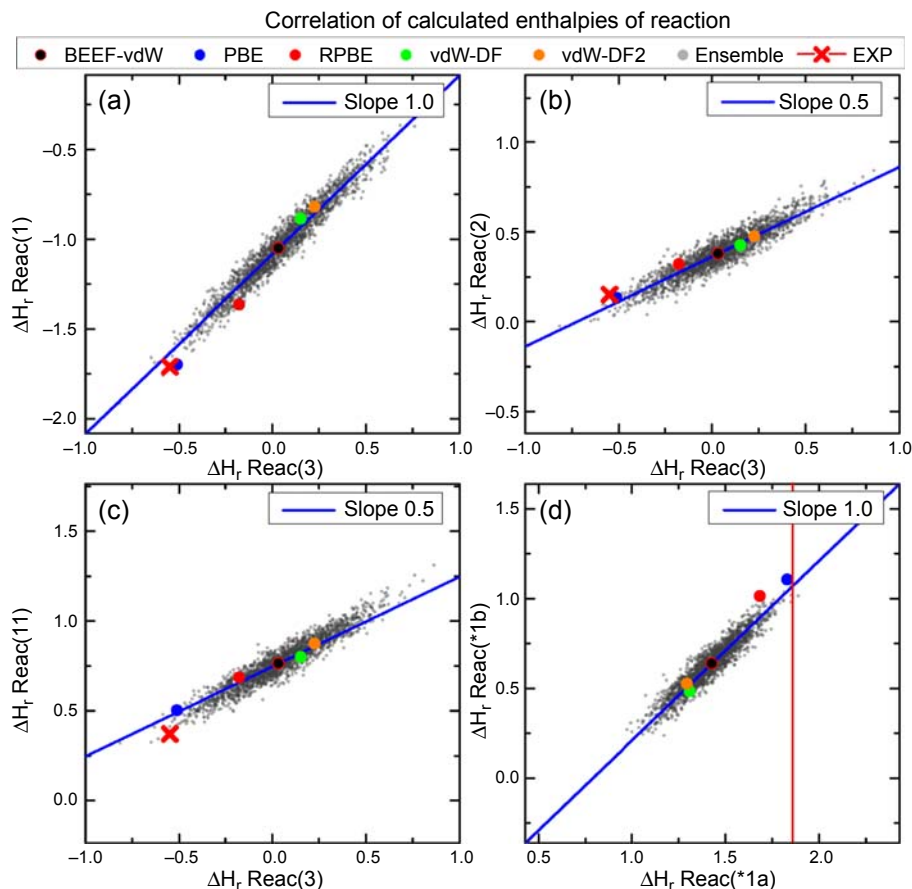


Figure 3.7 Correlations in the calculated enthalpies of reaction (eV) for some reactions (a–d). Reac(1) $4 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$; Reac(2) $\text{H}_2 + \text{CO}_2 \rightarrow \text{HCOOH}$; Reac(3) $3 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$; Reac(11) $2 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$; Reac(*1a) $2 \text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{HCOOH} + 3 \text{H}_2$; Reac(*1b) $2 \text{H}_2\text{O} + \text{CH}_3^* \rightarrow \text{COOH}^* + 3 \text{H}_2$. CH_3^* and COOH^* are adsorbed on Cu(111). Blue lines are drawn with predicted slopes equal to the ratio of broken/formed C=O bonds in the compared reactions. Larger points are self-consistent calculations using different functionals, crosses (red line in d) are the experimental reference values [36], and the smaller gray semitransparent points represent the values for 2000 BEEF-ensemble functionals [37].

Figure from R. Christensen, H.A. Hansen and T. Vegge, Identifying systematic DFT errors in catalytic reactions, *Catal. Sci. Technol.* 5, 2015, 4946–4949. Published by The Royal Society of Chemistry.

know the true calculational error of the reaction involving adsorbates as we do not have empirical data. We can, however, from the correlation deduce that an identical systematic error is carried by the C=O bond in the adsorbed carboxyl group (COOH^*) as in the C=O bond in gas-phase formic acid (HCOOH).

Use of correlations to deduce a dominant source of systematic errors does not depend on comparison with empirical data and is thus not limited by the quality and availability of such data. This stands in contrast to the more straightforward approach of identifying errors by comparing calculated and experimental values. Quantitative measures such as mean absolute error (MAE) are well suited for quantification of an already known error, but can often be deceptive when used to identify the error source.

Differences in residual MAE after fitting of various hypothesized systematic errors can be insignificant when compared against each other [39–41]. The differences are also sensitive to the chosen data set and the quality of the data. While the quality of empirical data does not impact the deduction of systematic errors through correlations in the BEEF ensembles, the established correlations will reveal outliers in the empirical data. Increased scrutiny of the reference data for outliers can even in some cases help identify low quality or faulty use of reference data [37].

3.4 Conclusion

The construction of fast and accurate exchange-correlation functionals remains a challenge which is constantly being addressed [42,43]. A crucial ingredient has been and still is the inclusion of more physical effects like van der Waals interactions and the explicit evaluation of exchange energies. Furthermore, within a particular class of models, the satisfaction of exact constraints is believed to play an important role [44,45]. The development of new higher-level BEEF functionals including the error estimation is mostly limited by the availability of sufficient databases. As the complexity of the models increases, it is necessary to use larger databases with a higher degree of variability, and the requirement to the quality of the databases also increases. For some types of systems, such as small molecules, high-level quantum chemistry calculations are available, but for more complicated systems, like physisorption and chemisorption energies on surfaces or defect formation in oxides, sufficiently high-quality data are still in need.

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Uncertainty quantification of solute transport coefficients

4

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4.1 Introduction

Diffusion in crystals is a fundamental defect-driven process leading to transport of solutes via interstitial- or vacancy-mediated mechanisms [1]. Diffusion controls a variety of phenomena in materials including ion transport, irradiation-induced degradation of materials, recrystallization, and the formation and growth of precipitates [2]. Transport coefficients are fundamental inputs for models at the length and time scales of microstructure evolution. Accurate knowledge of transport coefficients can aid in the design of novel alloys via an integrated computational materials engineering approach. Experimental determination of transport coefficients rely on measurements of solute concentration profiles of tracers using serial sectioning, residual activity, or secondary ion mass spectroscopy analysis. Generally, these experimental measurements are accessible only for limited temperatures and can require large investments in time and resources to generate a transport database. Diffusion modeling coupled with first-principles data is a promising alternate strategy to generate a database of transport coefficients over a broad temperature range [3–5], similar to the role that computational thermodynamics has played in the development of phase diagrams.

The accuracy of computed transport coefficients is affected from the approximations made in the diffusion model [6–8] as well as the uncertainties inherent to first-principles calculations [3,9,10]. Agarwal and Trinkle showed that an approximate treatment of vacancy correlations in the vacancy-mediated transport of solutes lead to an overestimation of 100 meV in the activation energy of diffusion [8]. The computationally efficient Green's function (GF) approach removes approximations associated with the correlation in defect trajectories to compute exact transport coefficients for interstitial and vacancy-mediated diffusion in the *dilute limit* of solute [11]. The GF approach can also enable uncertainty quantification of transport coefficients by propagating uncertainty from the density functional theory (DFT) data. In DFT, the treatment of electron's exchange and correlation (XC) can be approximated with different approaches. Medasani et al. [9] and Shang et al. [10] systematically computed the vacancy formation energy and vacancy migration barrier in bulk lattices for various XC functionals and showed that these energies vary significantly across different functionals. Shang et al. [10] also computed the self-diffusion

coefficients for 82 pure elements for four different XC functionals but a comprehensive methodology to quantify uncertainty in diffusion coefficients is missing. Currently, there are no published theoretical studies to quantify uncertainty for vacancy-mediated solute transport coefficients, and compare with experimental studies.

This chapter presents a methodology based on a Bayesian framework to quantify uncertainties in transport coefficients, applied to a transport database for 61 solutes in HCP Mg. The uncertainties in DFT energies due to XC functionals is computed empirically, while the GF approach computes transport coefficients, and we quantify the probability distributions of transport predictions. [Section 4.2](#) details the diffusion model of vacancy-mediated solute transport, and [Section 4.3](#) lays out the methodology of uncertainty quantification. [Section 4.4](#) explains the DFT parameters and XC functionals used to quantify the uncertainty in DFT parameters for input into the diffusion model. [Section 4.5](#) discusses the distribution of diffusion coefficients and drag ratios of 61 solutes in Mg. We show that the GF approach enables the development of computationally efficient Bayesian sampling scheme. We show that the drag ratios distributions are highly non-normal, while diffusion coefficients follow log-normal distributions; we quantify the uncertainties in activation energies, and find these to be between 90 and 120 meV. We show that the experimentally measured solute diffusion coefficients in Mg fall within our quantified uncertainties for most solutes; the remaining outliers may either suggest different diffusion mechanisms than considered here, or possible issues with the experimental measurements.

4.2 Diffusion model

The Onsager coefficients $\underline{L}^{AB}$ are second rank tensors that relate the flux of species A to chemical potential gradients in species B [1]. For vacancy-mediated transport in a binary alloy, the fluxes $\mathbf{J}^s$ of solutes (s) and $\mathbf{J}^v$ of vacancies (v) are linearly related to (small) chemical potential gradients $\nabla\mu$,

$$\begin{aligned}\mathbf{J}^s &= -\underline{L}^{ss}\nabla\mu^s - \underline{L}^{sv}\nabla\mu^v, \\ \mathbf{J}^v &= -\underline{L}^{vs}\nabla\mu^s - \underline{L}^{vv}\nabla\mu^v.\end{aligned}\tag{4.1}$$

The diagonal Onsager coefficients $\underline{L}^{ss}$ and $\underline{L}^{vv}$ quantify the solute and vacancy transport under their respective chemical potential gradients, which act as driving forces for diffusion. The off-diagonal Onsager coefficients $\underline{L}^{sv} = \underline{L}^{vs}$ quantify the “flux coupling” between solutes and vacancies: a driving force for vacancies also creates a flux of solutes, and vice versa. The solute diffusivity, from Fick’s first law ($\mathbf{J}^s = -\underline{D}\nabla C_s$), in the dilute limit of solute concentration C_s is proportional to $\underline{L}^{ss}$

$$\underline{D} = (k_B T / C_s) \underline{L}^{ss}\tag{4.2}$$

where k_B is the Boltzmann constant and T is temperature [1]. The drag ratio, defined as $\underline{L}^{sv}(\underline{L}^{ss})^{-1}$, quantifies the drag of solutes via vacancies. A positive drag ratio implies

the flux of vacancies drags solutes in the same direction and a negative drag ratio implies the motion of solutes opposite to the flux of vacancies. The flux coupling between vacancies and solutes can lead to solute segregation to vacancy sinks such as grain boundaries and causes the Kirkendall effect [12].

A variety of methods are possible for computing diffusivities from atomistic details. These include stochastic methods like kinetic Monte Carlo [13–17], master-equation methods like the self-consistent mean-field method [18,19] and kinetic mean-field approximations [20–22], path probability methods for irreversible thermodynamics [23–25], GF methods [11,26–28], and Ritz variational methods [29–31]. A recent paper showed that many of these methods are, in fact, examples of a variational principle [32], which allows for the comparison of accuracy in connecting atomistic scale information to the mesoscale transport coefficients. That connection between atomistic scale information and transport coefficients can be most easily seen from the (modified) Einstein relation, where the Onsager tensor coefficients are the thermodynamic averages of mean-squared displacements of infinite time trajectories,

$$\underline{L}^{AB} = \lim_{t \rightarrow \infty} \left\langle \frac{(\mathbf{R}^A(t) - \mathbf{R}^A(0)) \otimes (\mathbf{R}^B(t) - \mathbf{R}^B(0))}{2t\Omega k_B T} \right\rangle \quad (4.3)$$

where $\mathbf{R}^A(t) - \mathbf{R}^A(0)$ is the total displacement of all atoms of species A from time 0 up to time t , and Ω is the total volume of the sample. In the case of kinetic Monte Carlo, the trajectories are sampled directly from computed rates for a given atomic configuration under the assumption of a Markovian process. The need for a finite length trajectory introduces a controlled approximation as longer trajectories reduce the error in transport coefficients. Other approaches, such as matrix methods, which produce the different “multifrequency” methods (8- and 13-frequency, for the case of HCP [33–35]) make particular uncontrolled approximations in the form of the rates, and for the computation of the infinite time limit. The recent GF approach [11] is exact in the dilute limit and avoids both approximations in the form of the rates and in the infinite time limit. All of these methods require accurate atomic-scale information about the transitions that cause diffusion in the crystal, and all assume Markovian processes for each discrete step in the trajectory.

Modeling vacancy-mediated solute diffusion requires the geometry of solute–vacancy complexes as shown in Fig. 4.1 and all possible vacancy jumps through these complexes as shown in Fig. 4.2. In the HCP crystal, there are two unique first nearest-neighbor vacancy–solute complexes: 1b, where a vacancy and a solute lie in the same basal plane, and 1p, where a vacancy and a solute lie in neighboring basal planes. There are seven more complex configurations—2p, 3c, 4p, 4b, 5p, and 6b—that are one transition away from 1b or 1p. Generally, the solute–vacancy binding energy for these seven configurations are ignored because they are significantly less than the 1b and 1p complexes, but such approximations can affect the transport coefficients if any of the seven configurations have significant binding energy. There are 15 symmetry unique transition states for vacancy jumps out of 1p and 1b complexes: two solute–vacancy exchange jumps, 1b-sol and 1p-sol, where a solute exchanges

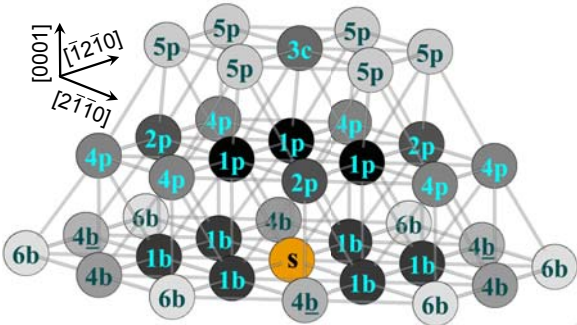


Figure 4.1 Possible vacancy–solute complexes out to sixth nearest neighbors in an HCP crystal. Complexes are identified by the position of the vacancy relative to the solute (orange “s”). Complexes are labeled by the shell distance between solute and vacancy (lighter colors correspond to larger separation), and with “b” (basal), “p” (prismatic), and “c” (c-axis). There are nine symmetrically unique complexes, with the vacancy in the 1b or 1p configurations closest to the solute.

From R. Agarwal, D.R. Trinkle, Exact model of vacancy-mediated solute transport in magnesium, *Phys. Rev. Lett.* 118 (2017) 105901.

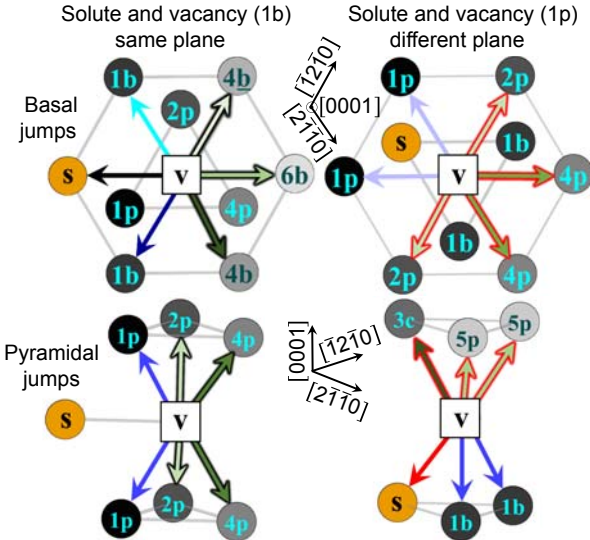


Figure 4.2 Vacancy (v) jumps in an HCP crystal from 1b and 1p complexes, divided into basal and pyramidal jumps. The 24 vacancy jumps consist of 15 symmetry unique transition states: two solute–vacancy exchanges (*black and red arrows*), four vacancy reorientations around the solute (*arrows in blue*), and nine solute–vacancy complex dissociations (*arrows in green with outline in black from 1b configuration and outline in red from 1p configuration*).

From R. Agarwal, D.R. Trinkle, Exact model of vacancy-mediated solute transport in magnesium, *Phys. Rev. Lett.* 118 (2017) 105901.

position with a vacancy; four reorientation jumps, 1b-1b, 1b-1b, 1b-1p (or 1p-1b), and 1p-1p, where a vacancy moves around the solute and remains in the 1b or 1p complex; and nine dissociation jumps, 1b-4b, 1b-4b, 1b-6b, 1b-2p, 1b-4p, 1p-2p, 1p-4p, 1p-3c, and 1p-5p, where a vacancy jumps away from the interaction range of a solute. Note that the reverse of a dissociation jump is an association jump. The vacancy jump energy barriers between non-first neighbor solute-vacancy complexes are approximated with pyramidal (“pyr”) or basal (“bas”) vacancy jump energy barriers from the pure Mg crystal. This approximation will lead to errors if non-first neighbor solute-vacancy complexes have significant binding energies, and changes to the jump network barriers would need to be accommodated. Note that the vacancy jump network can be different for other elements with the same crystal structure; for example, unlike in Mg, the basal migration of vacancy passes through a metastable state in HCP-Ti [36,37] and HCP-Zr [38], which also requires proper treatment in vacancy-mediated solute transport.

The binding energy of solute-vacancy complexes, the vacancy jump network and rates between those complexes, and the equilibrium vacancy concentration are the inputs to our diffusion model. The uncertainties in these inputs get translated to the error bars on transport coefficients. The binding energy of a complex E_{α}^{bind} quantifies the interaction between a solute and a vacancy and is computed as

$$E_{\alpha}^{\text{bind}} = E[X + \text{sv}_{\alpha}] - E[X + \text{sv}_{\infty}], \quad (4.4)$$

where $E[X + \text{sv}_{\alpha}]$ is the energy of a system having host lattice of X , and one solute and one vacancy in configuration α and $E[X + \text{sv}_{\infty}]$ is the energy of a system where the distance between the solute atom and the vacancy approaches infinity. A positive or a negative value of binding energy denotes repulsive or attractive interaction between a solute and a vacancy, respectively. From harmonic transition state theory, the rate $\omega_{\alpha-\beta}$ for a vacancy to jump from complex α to β through the transition state $\alpha-\beta$ is

$$\omega_{\alpha-\beta} = \nu_{\alpha-\beta}^* \cdot \exp\left(-E_{\alpha-\beta}^{\text{mig}} / k_{\text{B}}T\right), \quad (4.5)$$

where $\nu_{\alpha-\beta}^*$ and $E_{\alpha-\beta}^{\text{mig}}$ are the attempt frequency and migration barrier for the vacancy transition, respectively. The migration barrier is computed using

$$E_{\alpha-\beta}^{\text{mig}} = E[X + \text{sv}_{\alpha-\beta}] - E[X + \text{sv}_{\alpha}], \quad (4.6)$$

where $E[X + \text{sv}_{\alpha-\beta}]$ is the energy of a system containing one solute and one vacancy at the transition state $\alpha - \beta$ in the host lattice of X . The attempt frequency is computed using the Vineyard expression [39] under the moving atom approximation [3,8], which is the product of three vibrational frequencies $\nu_{\alpha,p}$ associated with the moving atom at the initial state α divided by the product of two real vibrational frequencies $\nu_{\alpha-\beta,q}$ associated with the moving atom at the transition state

$$\nu_{\alpha-\beta}^* = \frac{\prod_{p=1}^3 \nu_{\alpha,p}}{\prod_{q=1}^2 \nu_{\alpha-\beta,q}}. \quad (4.7)$$

The equilibrium vacancy concentration in the solute-free system is

$$C_v = \exp\left(-\frac{E_v^{\text{form}} - TS_v^{\text{form}}}{k_B T}\right), \quad (4.8)$$

where E_v^{form} and S_v^{form} are the vacancy formation energy and entropy, respectively. The concentration $C_{v,\alpha}$ of solute–vacancy complex α is

$$C_{v,\alpha} = C_v \exp\left(-\frac{E_{\alpha}^{\text{bind}}}{k_B T}\right) \exp\left(\frac{S_{\alpha}^{\text{bind}}}{k_B}\right) \quad (4.9)$$

where E_{α}^{bind} and S_{α}^{bind} are the solute–vacancy binding energy and binding entropy in complex α . The entropy S_{α}^{bind} quantifies the change in atomic vibrations due to the formation of solute–vacancy complex α compared to when the solute and vacancy are infinitely far apart. Uncertainties may get introduced in solute–vacancy binding energies and entropies, vacancy migration barriers and their attempt frequencies, and vacancy formation energy and entropy due to the atomistic method used to compute them. For example, the DFT-computed quantities have uncontrolled error (c.f. Ref. [40]) due to the exchange-correlation treatment of electrons; as this error cannot be reduced by systematic improvement of computational parameters, we require quantification of the possible error.

An additional source of uncertainty in the computation of transport coefficients is the computational model itself, in particular, the treatment of correlated motion inherent in vacancy-mediated diffusivity. The state and transition state energies for different configurations can be easily transformed into equilibrium probabilities and rates, but the transformation of that data into transport coefficients is nontrivial. For an HCP material, there are the traditional 8- and 13-frequency models [33–35] that force approximations on both the form of the rates—imposing equality for cases that are not enforced by symmetry—and make uncontrolled approximations on the correlation coefficients. The correlation can be thought of as a correction to the “bare” diffusivity; in a kinetic Monte Carlo calculation, this is converged by taking increasingly long trajectories to compute the transport coefficients [32]. A recent GF-based method [11] analytically computes the transport coefficients for an infinitely dilute model of one solute and one vacancy; in this case, it is possible to mathematically compute the infinitely long trajectory limit. Moreover, this is significantly computationally efficient compared with, say, a kinetic Monte Carlo calculation and has the advantage of not introducing additional sources of uncertainty that an 8- or 13-frequency model might.

The GF approach is computationally more efficient, but it is worth understanding the computational effort as it motivates particular choices that we make in our uncertainty quantification approach. In order to compute the infinite trajectory limit for diffusion in the presence of a solute, we use the Dyson equation to compute it from the infinite trajectory limit *without* a solute. As the solute–vacancy interaction has a finite range, we can compute g , the vacancy GF with a solute, on a subspace of states with a nonzero solute–vacancy interaction, from the vacancy GF without a solute $g^{(0)}$ and the change in rates $\delta\omega$, as

$$g = \left(\left(g^{(0)} \right)^{-1} + \delta\omega \right)^{-1} \quad (4.10)$$

In addition, the size of the subspace to evaluate this matrix inverse is reduced by taking advantage of crystal symmetry; for the case shown in Fig. 4.1, this amounts to inverting a 17×17 matrix. However, in order to compute $g^{(0)}$, the GF calculation without a solute is evaluated for 42 different separation vectors; in our calculations, this takes the longest time in a particular calculation, due to the three-dimensional inverse Fourier transform (see Ref. [11] for specific details of the computational methodology used). Due to the computational cost, the implementation [41] caches values of $g^{(0)}$ that have been computed for a given set of rates; this is *independent* of the solute, and all of the solute-dependent effects enter through the $\delta\omega$ rate matrix. Normally, this is used to make the computation of multiple solutes at a single temperature more efficient; here, we will consider the sampling of the “pure vacancy” degrees of freedom separate from the solute degrees of freedom in order to increase the computational efficiency of the method. This is strictly a practical consideration which is not driven by an inherent need to separately treat the different degrees of freedom. However, as we will note below, the diffusivity of some solutes are more strongly affected by uncertainty in the vacancy data, while others are more strongly affected by uncertainty in the solute data, depending on which terms dominate in Eq. (4.10).

4.3 Methodology for uncertainty quantification

Computing uncertainties in solute transport coefficients require the probability distributions describing uncertainties in the inputs of diffusion model. We consider the uncertainties in the vacancy formation energy, solute–vacancy binding energies, and vacancy migration barriers. We assume that these energies θ follow a multivariate normal distribution $P(\theta)$

$$P(\theta) = \det(2\pi\Sigma)^{-1/2} \exp \left[-\frac{1}{2} (\theta - \bar{\theta}) \Sigma^{-1} (\theta - \bar{\theta}) \right], \quad (4.11)$$

where $\bar{\theta}$ is the vector of the mean, and Σ is a covariance matrix describing variance and correlations between the different energies. In case of HCP Mg, the energy vector

θ is $\left[E_{\text{v}}^{\text{form}}, E_{\text{pyr}}^{\text{mig}}, E_{\text{bas}}^{\text{mig}}, E_{1\text{p}}^{\text{bind}}, E_{1\text{b}}^{\text{bind}}, E_{1\text{p-sol}}^{\text{mig}}, E_{1\text{b-sol}}^{\text{mig}}, E_{1\text{p-1p}}^{\text{mig}}, E_{1\text{p-1b}}^{\text{mig}}, E_{1\text{b-1b}}^{\text{mig}}, E_{1\text{b-1b}}^{\text{mig}}, E_{1\text{p-2p}}^{\text{mig}}, E_{1\text{p-3c}}^{\text{mig}}, E_{1\text{p-4p}}^{\text{mig}}, E_{1\text{p-5p}}^{\text{mig}}, E_{1\text{b-2p}}^{\text{mig}}, E_{1\text{b-4p}}^{\text{mig}}, E_{1\text{b-4b}}^{\text{mig}}, E_{1\text{b-4b}}^{\text{mig}}, E_{1\text{b-6b}}^{\text{mig}} \right]^T$, where the first three elements are solute-independent energies (vacancy formation, and vacancy migration barrier in pyramidal and basal direction of bulk Mg). The remaining 17 elements of θ are solute-dependent energies consisting of solute–vacancy binding at 1p and 1b complex, and 15 vacancy migration barriers near the solute. For simplicity, we assume no uncertainties in the vacancy formation entropy, solute–vacancy binding entropies, and the attempt frequency of vacancy migrations. For mass transport, the attempt frequencies for atomic jumps in materials typically are dominated by the mass of the chemical species involved (which we account for in our “jumping atom” approach). It would be extremely unusual for different exchange-correlation potentials to predict variations even as large as a factor of two for a given solute, as that would indicate changes in atomic force constants on the order of a factor of four.

We separate the distribution of energies into solute-independent (v) and solute-dependent (s) energies for computational efficiency. The energy vector θ in separated form is

$$\theta = \begin{pmatrix} \theta^{\text{v}} \\ \theta^{\text{s}} \end{pmatrix}, \quad (4.12)$$

and the covariance matrix in a block diagonal is

$$\Sigma = \begin{pmatrix} \Sigma^{\text{vv}} & \Sigma^{\text{vs}} \\ \Sigma^{\text{sv}} & \Sigma^{\text{ss}} \end{pmatrix}. \quad (4.13)$$

We rewrite the probability distribution of solute–vacancy energies as

$$P(\theta) = P^{\text{v}}(\theta^{\text{v}})P^{\text{s}}(\theta^{\text{s}}|\theta^{\text{v}}), \quad (4.14)$$

where $P^{\text{v}}(\theta^{\text{v}})$ is the multivariate normal distribution of solute-independent energies with covariance matrix Σ^{vv} and mean $\bar{\theta}^{\text{v}}$, and $P^{\text{s}}(\theta^{\text{s}}|\theta^{\text{v}})$ is the distribution of solute-dependent energies for a given θ^{v} of solute-independent energies. The distribution $P^{\text{s}}(\theta^{\text{s}}|\theta^{\text{v}})$ is a multivariate normal distribution with covariance matrix $\Sigma^{\text{ss}} - \Sigma^{\text{sv}}(\Sigma^{\text{vv}})^{-1}\Sigma^{\text{vs}}$ and mean $\bar{\theta}^{\text{s}} + \Sigma^{\text{sv}}(\Sigma^{\text{vv}})^{-1}(\theta^{\text{v}} - \bar{\theta}^{\text{v}})$. Note that the latter covariance matrix is independent of θ^{v} or $\bar{\theta}^{\text{v}}$, so it needs to be computed once unlike the mean which is different for every solute-independent energy vector. This separation of solute–vacancy energies has two advantages: (1) sampling of solute-independent energies remains the same for all the solutes, so only needs to be performed once. (2) The GF approach requires computation of the vacancy GF $g^{(0)}$ which is computationally expensive and depends only on the solute-independent energies; this quantity can be computed once and saved to use in later calculations.

A Bayesian framework is employed to determine the uncertainties in solute transport coefficients. The average of a function $f(\theta^v, \theta^s; T)$ at temperature T is

$$\langle f(\theta^v, \theta^s; T) \rangle = \int_{\theta^v} d\theta^v P^v(\theta^v) \left[\int_{\theta^s} d\theta^s P^s(\theta^s | \theta^v) f(\theta^v, \theta^s; T) \right]. \quad (4.15)$$

Generally, the θ^v vector has smaller dimension (three for HCP Mg) compared to the θ^s vector (17 for HCP Mg); this can make Gauss–Hermite (GH) quadrature a computationally efficient scheme for the integration over θ^v domain. Due to the large dimension of θ^s , the integration over the θ^s domain is performed stochastically using multivariate distribution sampling of $P^s(\theta^s | \theta^v)$. Then, the numeric approximation to the average of a function $f(\theta^v, \theta^s; T)$ at temperature T is

$$\langle f(\theta^v, \theta^s; T) \rangle \approx \sum_{i=1}^{N_{\text{GH}}} \frac{w_i}{N} \sum_{j=1}^N f(\theta^{v,i}, \theta^{s,j}, T), \quad (4.16)$$

where N_{GH} and N are the number of GH quadrature points and stochastic multivariate samples, respectively. The $\theta^{v,i}$ are the GH quadrature points with weights w_i and $\theta^{s,j}$ are the multivariate samples for a given $\theta^{v,i}$, obtained by sampling $P^s(\theta^s | \theta^v)$. The covariance matrices for the θ^v parameters are computed empirically from a set of different exchange-correlation potentials (c.f. [Section 4.4](#)). The covariance matrices for the θ^s parameters are computed empirically from a set of different exchange-correlation potentials *and* evaluated over a set of 13 selected solutes under the assumption that the covariance in the solute parameters is *independent* of the solute chemistry; this assumption was found to be valid for the 13 selected solutes but is applied to a total set of 61.

In what follows, we evaluate uncertainties for two mass transport predictions: the diffusivity, D , and the drag ratio $\underline{L}^{\text{sv}} / \underline{L}^{\text{ss}}$, which require different uses of averages and distributions from [Eq. \(4.16\)](#). In the case of diffusivity, we find that the diffusivities are log-normally distributed for our specific case of solute diffusion in Mg. While the uncertainty in the diffusivity is important, we are also interested in the propagation of uncertainties to the Arrhenius *parameters* that represent the temperature dependence; we explain our approach below. The drag ratios, on the other hand, are found to be highly non-normal. To describe the uncertainties in the drag ratios, we compute empirical probability distributions and compute medians and upper and lower quartiles as a function of temperature for all solutes, along with skewness for a set of solutes to highlight the non-normality of the distributions. This is expanded further in [Section 4.5.3](#).

A correlated error fit on diffusion coefficients with respect to temperature is essential to obtain uncertainties in Arrhenius parameters. For the diffusivities, $\underline{D} = k_B T \underline{L}^{\text{ss}} / C_s$ (c.f. [Eq. 4.2](#)), we find that they follow log-normal distributions; however, the values at each temperature T are highly correlated with each other. Typically, one reports the activation barrier and prefactor for diffusivity following the Arrhenius form,

$$\log_{10}D(T) = \log_{10}D_0 - \left(\frac{Q \cdot \log_{10}e}{k_B} \right) \frac{1}{T}, \quad (4.17)$$

where the Arrhenius parameters $\log_{10}D_0$ and Q denote the logarithm of the diffusion prefactor and the activation energy for diffusion, respectively. To propagate (highly correlated) uncertainty from the $D(T)$ data to uncertainty in the parameters Q and D_0 , we consider the determination of the parameters from the system of linear equations,

$$\begin{pmatrix} \log_{10}D(T_1) \\ \vdots \\ \log_{10}D(T_m) \end{pmatrix} = \begin{pmatrix} 1 & -\frac{\log_{10}e}{k_B T_1} \\ \vdots & \vdots \\ 1 & -\frac{\log_{10}e}{k_B T_m} \end{pmatrix} \begin{pmatrix} \log_{10}D_0 \\ Q \end{pmatrix}, \quad (4.18)$$

$$F = AX,$$

where F is an m dimensional vector of the logarithm of diffusion coefficients at distinct temperatures, A is the Vandermonde matrix of size $m \times 2$, and X is the two-dimensional vector of Arrhenius fitting parameters. Under the assumption that $\log_{10}D(T)$ follows a multivariate normal distribution for different temperatures, the covariance matrix of Arrhenius parameters Σ^X of size 2×2 is

$$\Sigma^X = (A^T A)^{-1} A^T \Sigma^F A (A^T A)^{-1}, \quad (4.19)$$

where Σ^F is the covariance matrix of $\log_{10}D(T)$ of size $m \times m$. In our case, where we find log-normally distributed diffusivities, we can use an analytic approximation based on the Jacobian matrix; $\log_{10}D(T)$ can be approximated as

$$\log_{10}D(\theta, T) \approx \log_{10}D(\bar{\theta}, T) + J \cdot (\theta - \bar{\theta}), \quad (4.20)$$

where J is the Jacobian matrix evaluated at $\bar{\theta}$, whose J_{ij} element is the partial derivative of $\log_{10}D(\theta, T_i)$ at temperature T_i with respect to the j th component of the θ vector: $\frac{\partial \log_{10}D(\theta, T_i)}{\partial \theta_j} \big|_{\theta=\bar{\theta}}$. The analytical covariance matrix of F is then

$$\Sigma^F = J \Sigma J^T, \quad (4.21)$$

where Σ is the previously defined covariance matrix of solute–vacancy energies.

4.4 Computational details

DFT calculations compute the solute–vacancy energy vector θ using the Vienna ab-initio simulation package VASP 5.4.4 [42]. The VASP software package performs electronic structure calculations based on plane-wave basis sets. We use the projector-augmented wave pseudopotentials [43] generated by Kresse [44] to describe the core electrons of 13 solutes and Mg atoms; the valence configurations are the same as used in the previous study [5] and summarized in Table 4.1. We use a $4 \times 4 \times 3$ Mg supercell containing 96 atoms with a $6 \times 6 \times 6$ gamma-centered Monkhorst–Pack k -point mesh for Ag, Al, Hf, Li, Mn, Sb, Sc, Sn, Ti, and Zn, while Ca, Ce, and La require a $5 \times 5 \times 3$ Mg supercell containing 150 atoms with a $5 \times 5 \times 6$ k -point mesh due to large vacancy relaxations near the solutes in 1p and 1b complexes. Methfessel–Paxton smearing [45] with an energy width of 0.25 eV is sufficient to integrate the density of states. We use the energy convergence tolerance of 10^{-8} eV for the electronic self-consistency cycle. We use a plane-wave energy cutoff of 500 eV which is sufficient to give an energy convergence of less than 1 meV/atom. All the atoms are relaxed using a conjugate gradient method until the force on each atom is less than 5 meV/Å. The climbing-image nudged elastic band [46] method with one intermediate image determines the transition state configurations and energies.

We perform DFT calculations with different exchange-correlation (XC) functionals using an efficient scheme to compute the covariance matrix of energies. We treat electron exchange and correlation for pure Mg using five different functionals—the local density approximation (LDA) [47], the generalized gradient approximations (GGA) by Perdew, Burke, and Ernzerhof (PBE) [48], Perdew–Wang-91 (PW91) [49], and PBE for solids (PBEsol) [50], and a strongly constrained and appropriately normed (SCAN) meta-GGA [51]. Table 4.2 lists the lattice parameters, vacancy formation energy, and vacancy migration barriers of bulk Mg for these five XC functionals. This table is used to compute the covariance in vacancy formation energy and vacancy migration barriers in bulk Mg due to XC functionals. We use PBE, LDA, and SCAN XC functional for 13 solutes (listed in previous paragraph and Table 4.1) to

Table 4.1 Electronic configurations for PAW pseudopotentials used for Mg and the 13 solutes that quantified the covariances in solute parameters.

Element	Valence	Element	Valence
Mg	$3s^2 3p^0$	Li	$2s^1 2p^0$
Ag	$5s^1 4d^{10}$	Mn	$3p^6 4s^2 3d^5$
Al	$3s^2 3p^1$	Sb	$5s^2 5p^3$
Ca	$3s^2 3p^6 4s^2$	Sc	$3p^6 4s^2 3d^1$
Ce	$6s^2 5d^1 4f^1$	Sn	$5s^2 5p^2$
Hf	$5p^6 6s^2 5d^2$	Ti	$3p^6 4s^2 3d^2$
La	$4d^{10} 4f^1$	Zn	$3d^{10} 4p^2$

Table 4.2 Prediction of the lattice parameters a and c , vacancy formation energy E_v^{form} , and vacancy migration barriers in the pyramidal $E_{\text{pyr}}^{\text{mig}}$ and basal $E_{\text{bas}}^{\text{mig}}$ directions for bulk HCP Mg using five XC functionals.

Property	LDA	PBE	PBEsol	PW91	SCAN	Experiments
a (Å)	3.13	3.19	3.17	3.19	3.17	3.19 [52]
c (Å)	5.09	5.19	5.16	5.19	5.16	5.17 [52]
E_v^{form} (eV)	0.85	0.81	0.87	0.76	0.95	0.58 [53], 0.79 [54], 0.81 [55]
$E_{\text{pyr}}^{\text{mig}}$ (eV)	0.43	0.42	0.43	0.40	0.49	0.45 [56], 0.59 [57]
$E_{\text{bas}}^{\text{mig}}$ (eV)	0.41	0.40	0.41	0.38	0.48	0.45 [56], 0.57 [57]

The DFT predictions of lattice parameters are similar within a 0.07 Å range, while E_v^{form} varies by 190 meV and the migration barriers vary by 100 meV. The last column lists the experimental measurements.

compute the covariance in solute-dependent energies. We make use of fully atomically relaxed supercells obtained using the PBE functional as a starting guess for the DFT calculations employing LDA and SCAN functional for computational efficiency. We also scale the PBE obtained geometries with the bulk Mg lattice parameters (a and c) corresponding to LDA or SCAN and compute the energy and the atomics forces of the scaled supercell. Instead of relaxing the atomic positions in the scaled supercell, we approximate the relaxation energy (E_{relax}) using

$$E_{\text{relax}} = -\frac{1}{2}F_{\text{atomic}}G F_{\text{atomic}}^T, \quad (4.22)$$

where G is the harmonic lattice GF of the supercell (the pseudoinverse of the force constant matrix of bulk Mg from PBE) and F_{atomic} is the atomic force vector computed from LDA or SCAN. So, the DFT energy using this approximate scheme is the sum of first ionic step energy and the relaxation energy computed using Eq. (4.22). We find an energy difference of less than 5 meV between our approximate and a fully relaxed calculation for Ag using SCAN functional for binding energies of 1p and 1b, and migration barriers of 1p-sol and 1b-sol. Our efficient scheme reduces the computational effort of 10 ionic steps on an average compared to regular DFT relaxation with a negligible sacrifice in accuracy. We use the above scheme to obtain binding energies and migration barriers for 13 solutes with three different exchange-correlation potentials in order to quantify the covariances of solute parameters.

4.5 Results and discussion

4.5.1 Distribution of parameters

We assume that the energies predicted by different XC functionals would obey a normal distribution and Fig. 4.3 shows the variance and the correlations in solute–vacancy energies computed using different sets of XC functionals. Solute transport

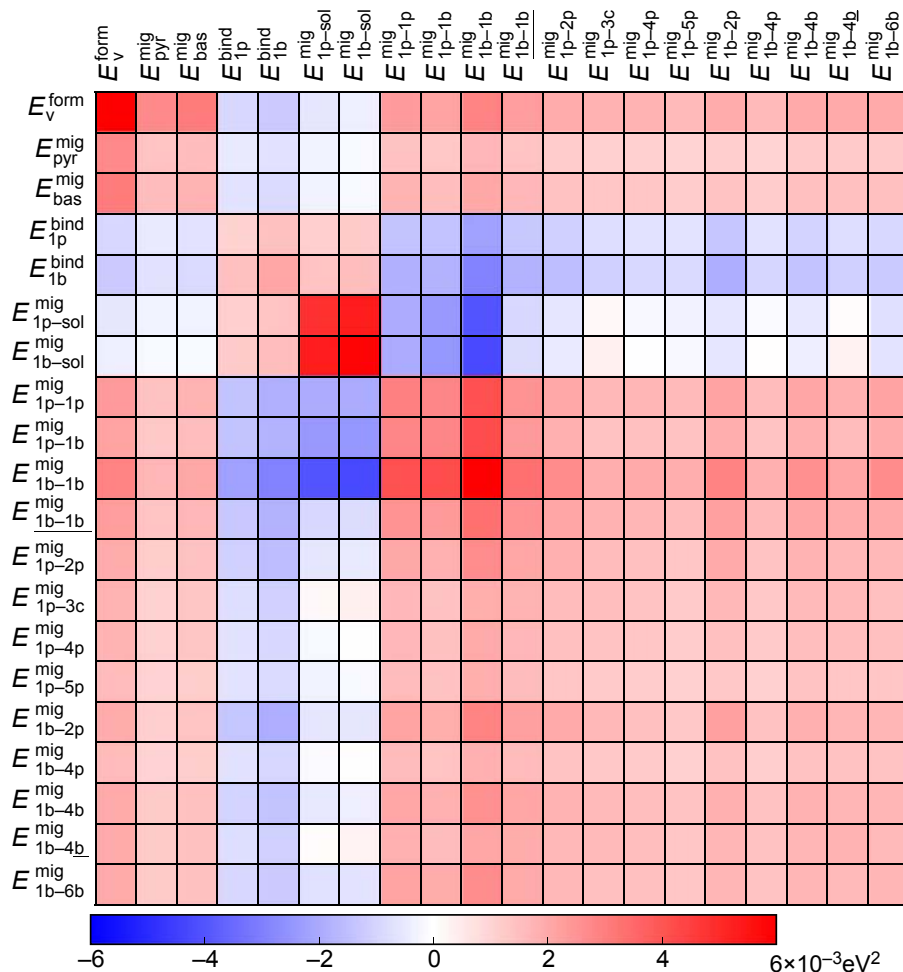


Figure 4.3 Covariance matrix of energies for 20 configurations in Mg. There are 3 solute-independent energies—vacancy formation energy and vacancy migration barriers in the pyramidal and basal directions in bulk Mg—and 17 solute-dependent energies—2 solute–vacancy binding energies and 15 vacancy migration barriers in the presence of a solute. The DFT data using three XC functionals (PBE, SCAN, and LDA) for 13 solutes is used to compute the covariance matrix. The vacancy formation energy, the solute–vacancy exchange barriers, and the 1b-1b vacancy reorientation barrier show the largest variance with values between 0.005 and 0.006 eV^2 . Refer to Figs. 4.1 and 4.2 for the geometries of these 20 configurations.

in Mg is determined by 20 energies consisting of 3 solute-independent energies and 17 solute-dependent energies. The solute-independent part of the covariance matrix is computed using the energies obtained from five XC functional for bulk Mg. The solute-dependent part of the covariance matrix is computed using the DFT energies for 13 solutes and employing three XC functionals as mentioned in Section 4.4.

To compute the covariances in the solute–vacancy interactions, we assume that the variations are *independent* of the particular solute being considered, so that our 13 solutes and 3 XC functionals are essentially random inputs. However, as each solute has its own solute–vacancy interaction, we subtract the PBE functional values from the SCAN and LDA values to compute the covariances, which reduce the number of effective degrees of freedom. The (i, j) entry of the covariance matrix Σ is

$$\Sigma_{ij} = \frac{1}{M-1} \left[\sum_{p=1}^M \theta_i^p \theta_j^p - \sum_{p=1}^M \theta_i^p \sum_{p=1}^M \theta_j^p \right], \quad (4.23)$$

where θ_i^p is the energy of the i th configuration (refer to Figs. 4.1 and 4.2 for the geometries of these 20 configurations) in the p th energy vector and M is the number of energy vectors. The vacancy formation energy, the solute–vacancy exchange barriers, and the 1b-1b vacancy reorientation barrier show the largest standard deviation of ≈ 70 meV, while the standard deviations in the energies of the other configurations lie between 10 and 50 meV. Note that we have computed our covariances using the distributions from 13 solutes; we now use the *mean values* for each solute from our previous study [5,58] and combine with these covariances to model uncertainties for 61 different solutes.

4.5.2 Distribution of diffusivities

Fig. 4.4 shows that the logarithm of diffusion coefficients ($\log_{10}D$) at different temperatures follows a normal distribution and different sampling parameters are required to converge to this distribution for all the solutes. We use Eq. (4.14) to separate the sampling of solute-dependent and solute-independent energies and use Eq. (4.16) to generate the distributions of $\log_{10}D$. Multinormal GH quadrature [59] integrates over the vacancy formation energy, and the vacancy migration barriers in pyramidal and basal directions in bulk Mg, while multivariate normal sampling integrates over the 17 solute-dependent energies. We find that faster solutes require a larger number of GH points (finer grids) i.e., 2500, 1600, 900, 400, and 100 for Ca, Li, Sn, Al, and Os, respectively, to converge diffusivities to log-normal distributions, otherwise coarser GH grids lead to multimodal distributions. Slower solutes are dependent on solute–vacancy exchange barriers requiring a large number of multivariate samples to integrate over solute-dependent energies; we use 50,000, 50,000, 10,000, 2500, and 1000 samples for Os, Al, Sn, Li, and Ca, respectively. We verify the normality of $\log_{10}D$ at different temperatures by computing the skewness, kurtosis, and the quantile–quantile plots of the distributions. The standard deviation of the $\log_{10}D$ distribution decreases with increasing temperature as thermal energy $k_B T$ reduces the effect of uncertainties in solute–vacancy energies. It should be noted that the normality of the distribution of the logarithm of the diffusion coefficients follows from the multivariate normal distribution of the uncertainty in parameters, and the domination of particular jumps in the diffusion network.

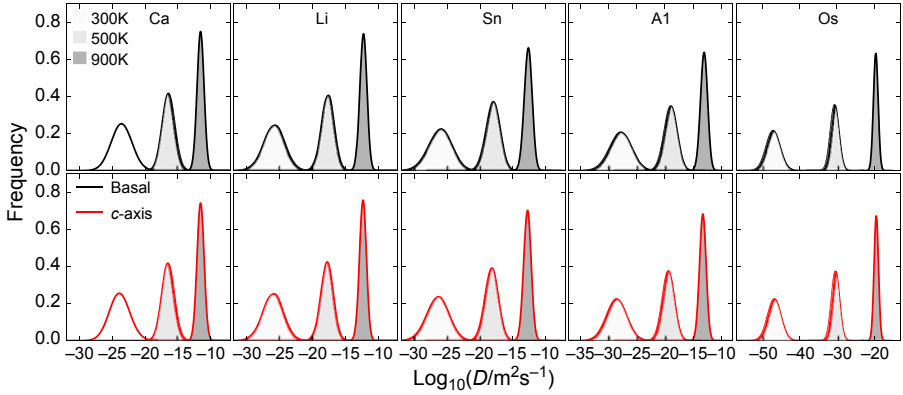


Figure 4.4 Distributions of the logarithm of diffusion coefficients $\log_{10}(D/\text{m}^2\text{s}^{-1})$ at 300K (light gray), 500K (gray), and 900K (dark gray) for Ca, Li, Sn, Al, and Os in Mg in the basal plane (black) and along the c -axis (red). The diffusion coefficients follow log-normal distributions and the widths decrease with temperature. The mean diffusivities of these five solutes are in the order $D_{\text{Ca}} > D_{\text{Li}} > D_{\text{Sn}} \approx D_{\text{Mg}} > D_{\text{Al}} > D_{\text{Os}}$ with respect to self-diffusion coefficient of Mg D_{Mg} . Faster solutes require a larger number of Gauss–Hermite quadrature points for solute-independent vacancy energetics and fewer multivariate samples for solute-dependent vacancy energetics compared to slower diffusing solutes to converge diffusivities to log-normal distributions.

The logarithm of diffusion coefficients obeys a multivariate normal distribution with respect to temperatures and we compute the covariance matrices of this distribution using stochastic sampling and an analytical method as discussed in Section 4.3. In the previous paragraph, we showed that our sampling scheme produces a normal distribution for $\log_{10}D$ at different temperatures. We also find that $\log_{10}D$ is positively correlated—Pearson correlation coefficient close to one—at different temperatures and obeys a multivariate normal distribution. We compute the covariance matrix of this multivariate distribution at eight temperatures between 300–923K using stochastic sampling and analytically using Eq. (4.21). The maximum relative difference for an entry in the covariance matrices between both of these methods is less than 5% for Ca, Li, Al, Sn, and Os. The analytical method is more computationally efficient than the sampling method because it only requires 40 diffusion calculations to compute the Jacobian for Eq. (4.21) using finite differences while sampling requires diffusion calculations for every stochastic sample. Since we find good agreement of covariance matrices between both the methods, we use the efficient analytical method to study uncertainties in the diffusion coefficients of 61 solutes.

We perform correlated error fits of solute diffusion coefficients with temperature using Eqs. (4.17)–(4.19) to compute the covariance matrix of Arrhenius parameters (Q and $\log_{10}D_0$). Fig. 4.5 shows that the standard deviation of the activation energy for diffusion lies between 90 and 115 meV for 61 solutes. The solute–vacancy exchange jumps 1b-sol and 1p-sol control the diffusion of solutes in the basal plane and along the c -axis for Ga, Ge, As, and the d -block solutes except Y and La [5]. Since the uncertainties in exchange barriers are the same for all the solutes (refer to Fig. 4.3),

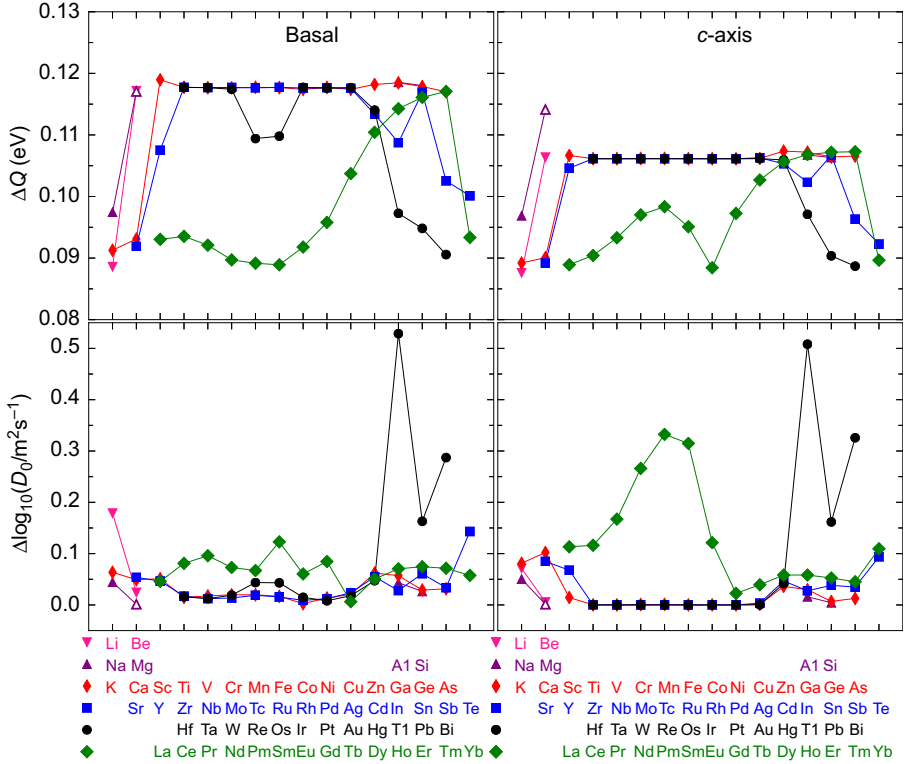


Figure 4.5 Uncertainties in the activation energy of diffusion ΔQ (top row) and the log of the diffusivity prefactor $\Delta \log_{10}(D_0/m^2s^{-1})$ (bottom row) in the basal plane and along the c -axis for 61 solutes in Mg. The activation energy uncertainties lies in a narrow interval of 90–120 meV for all the solutes, and the uncertainties in the diffusion prefactor are very small since the attempt frequencies are kept constant in our analysis. The solutes Tl, Pb, Bi, Li, Te, and the first half of the lanthanides have more than one vacancy transition rate dominating in the temperature interval of 300–923K, which gives rise to larger values of $\Delta \log_{10}D_0$.

the aforementioned 31 solutes show a similar standard deviation of 115 meV in the activation energy. In contrast, the diffusion of s -block solutes, lanthanides, Y, In, Sn, Sb, Te, Tl, Pb, and Bi depends on the vacancy exchanges with Mg atoms happening near the solute [5]. Since there are multiple types of vacancy exchanges with Mg atoms, the standard deviation of activation energy for these solutes varies between 90 and 115 meV. The standard deviation of the diffusion prefactor $\log_{10}D_0$ is negligible because the attempt frequencies of vacancy jumps are kept constant. In contrast, the s -block solutes, lanthanides, Y, In, Sn, Sb, Te, Tl, Pb, and Bi, show a nonzero standard deviation for $\log_{10}D_0$ due to competing vacancy rates across the fitting range of 300–923K.

Fig. 4.6 shows the computed solute diffusion coefficients against available experimental measurements. The solute–vacancy energetics obtained using the PBE XC functional informs the GF approach [11] to compute mean diffusion coefficient [5].

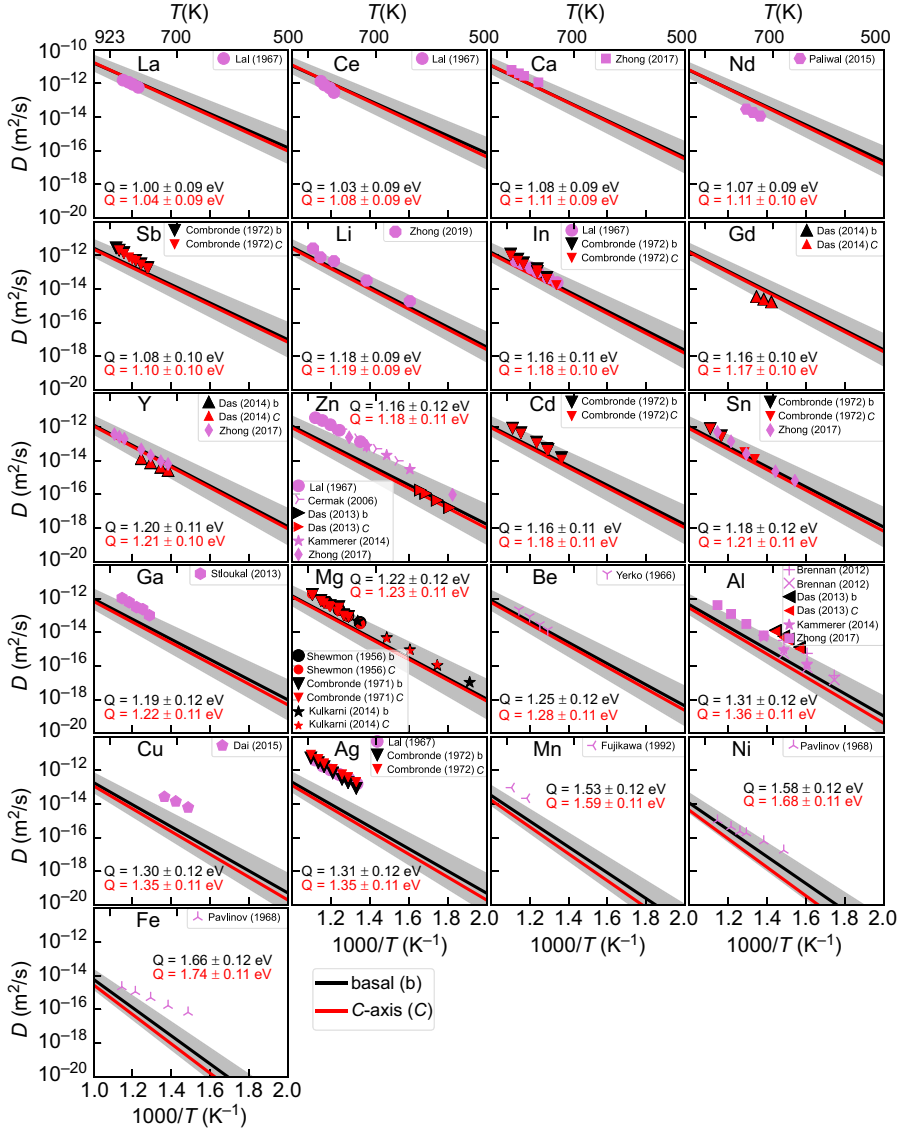


Figure 4.6 Solute diffusion coefficients D along with their error bars computed using the GF approach compared with the available experimental data. We arrange the Arrhenius plots of 20 solutes and Mg self-diffusion in decreasing order of computed diffusivity. Solid lines represent diffusion coefficients computed using the GF approach and symbols represent experimental measurements. Black and red denote diffusion in the basal(b) plane and along the c -axis, while pink symbols are the average diffusion coefficients from experimental polycrystalline measurements. The upper and lower bounds of the gray regions give the standard deviation of diffusion coefficients in the basal plane. We omit the uncertainties in diffusion coefficients along the c -axis since they are similar to the basal plane. We annotate the activation energies Q of diffusion along with their standard deviation in both directions. The experimentally measured diffusion coefficients fall within the computed error bars for all the solutes except Cu, Ag, Mn, and Fe.

The standard deviation of Arrhenius parameters shown in the last paragraph coupled with the mean diffusion coefficients is compared with the available experimental measurements [60–78]. The diffusion coefficient predictions are well within the computed error bars compared to the experimental measurements for 13 of the 17 solutes—La, Ce, Ca, Nd, Sb, Li, In, Gd, Y, Zn, Cd, Sn, Ga, Mg, Be, Al, and Ni. The disagreements for Cu, Ag, Mn, and Fe may suggest a diffusion mechanism other than vacancy mediated such as an interstitial mechanism or a combination of interstitial and vacancy mechanisms, since the experimental diffusion coefficients are larger than the theoretical predictions.

4.5.3 Distribution of drag ratios

Fig. 4.7 shows that the drag ratio distributions are not normal and have long tails on either side of the median. We use 36 GH points and 50,000 multivariate samples to obtain the drag ratio distribution in the temperature range of 300–923K for W, Li, Ca, Gd, and Zr. Drag ratios are positive due to the vacancy reorientations around the solute via inner or outer ring networks in HCP Mg [5]. The solutes W and Li have positive drag ratios due to faster vacancy reorientation rates in the inner ring networks, while Ca and Gd have positive drag ratios due to faster vacancy reorientation rates in the outer ring networks. The repulsive interaction between a vacancy and a Zr atom makes escape rates faster than the reorientation rates which lead to no drag. In case of W and to a lesser extent for Ca at 300K, the distribution is strongly peaked near one, which may be due to the insensitivity of vacancy reorientation around the solute to variations of 50–75 meV in solute–vacancy energies. The distribution for W, Ca, and Li spread out with temperature, while they narrow for Gd and Zr.

The skewness of the drag ratio distributions quantifies the nature of the tails and highlights the deviation from a normal distribution, as shown in Fig. 4.8. The drag ratio

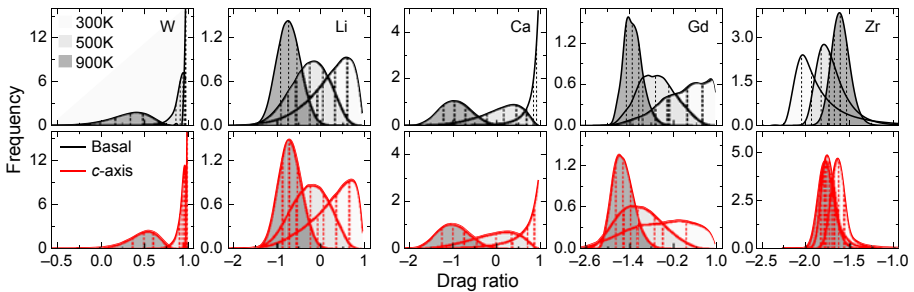


Figure 4.7 Distributions of the drag ratio at 300K (light gray), 500K (gray), and 900K (dark gray) for W, Li, Ca, Gd, and Zr in Mg in the basal plane (black) and along the *c*-axis (red). The three dashed vertical lines at each temperature represent lower quartiles, median, and upper quartiles of the drag ratio distribution. The drag ratio has a maximum value of one; hence, the distributions are not normal distributions. The drag ratio distributions for W and Ca at 300K are strongly peaked near one, while Li, Gd, and Zr have a spread in the distribution at 300K.

Fig. 4.8 quantifies the tails of the drag ratio distributions based on skewness.

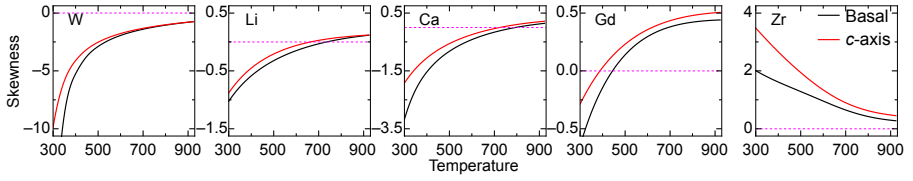


Figure 4.8 Skewness of the drag ratio distributions for W, Li, Ca, Gd, and Zr in Mg in the basal plane (black) and along the *c*-axis (red). A negative skewness indicates a longer tail on the left side compared to the right side of the distribution and vice versa. The drag ratio distributions remain negatively and positively skewed for W and Zr, respectively, in the temperature range of 300–923K. The skewness for Li, Ca, and Gd changes sign from negative to positive with temperature, i.e., the distribution of these three solutes is left-tailed at 300K, while right-tailed at 900K (c.f. Fig. 4.7).

distributions of W and Zr have long left and right tails in the temperature range of 300–923K, respectively, but the distribution becomes symmetric as temperature increases. In case of Li, Ca, and Gd, the distribution is left-tailed at lower temperatures and becomes right-tailed at higher temperatures.

Figs. 4.9–4.11 show the three quartiles of the drag ratio distributions for 61 solutes and we find that drag ratio is sensitive to the uncertainties in solute–vacancy energies with maximum uncertainty near the crossover temperature. We generate the drag ratio distributions using stochastic sampling in the temperature range of 300–923K. Figs. 4.9 and 4.10 show the drag distribution for solutes whose positive drag ratio is due to inner ring and outer ring networks, respectively, while Fig. 4.11 shows the solutes whose highly repulsive binding with the vacancy leads to no drag. The IQR—difference between the upper and lower quartiles—quantifies the spread of drag distributions. The drag ratio distribution is highly peaked at one (i.e., IQR of zero) near 300K for all the solutes in Fig. 4.9 except Al, Cr, V, Cd, and Li and for Sr, K, Te, Eu, La, and Sb in Fig. 4.10. We observe that IQR increases with temperature, achieving a maximum value near the median crossover temperature (where the drag ratio becomes zero) and then decreases with temperature for all solutes whose median of drag ratio distribution show a crossover. Note that the IQR maximas are flat and changes by only 0.01 within 100K temperature interval around the maxima. The maximum uncertainty in drag ratio near crossover may be because the variation in solute–vacancy energies changes the dominant mechanism since the mechanism for drag—vacancy motion around the solute through ring networks—and mechanism against drag—vacancy escape from the solute interaction range—cancels out at crossover. It is worth noting that the statistics we extract for each temperature describe the distribution of predictions for a given temperature, but there will be correlations between the predictions of drag ratios at different temperatures. This is similar to the correlation between predictions of diffusivity at different temperatures that we noted in Section 4.5.2. Given the non-normality of the distributions of drag ratios at each temperature, the best approach to quantifying the correlations across different temperatures would be empirical methods, like stochastic collocation [79].

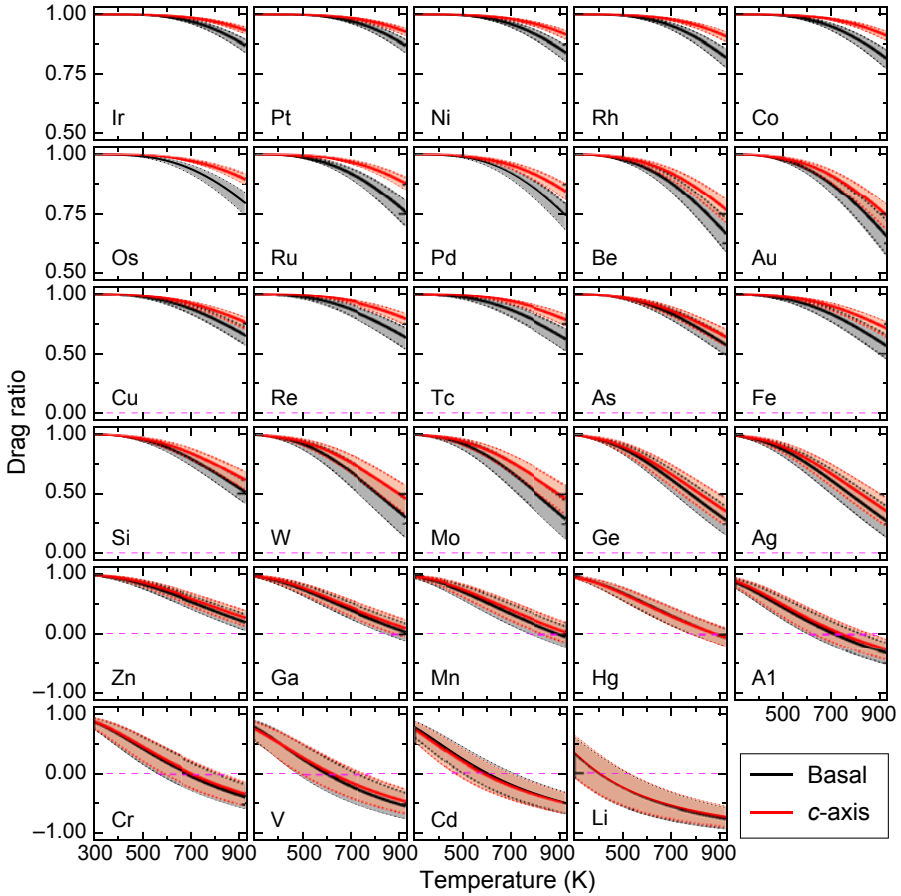


Figure 4.9 Three quartiles of the drag ratio distributions in the basal plane (black) and along the c -axis (red) for solutes where inner ring networks lead to reorientation of the vacancy around the solute. Solid lines represent the median of the drag ratio distributions and the dotted lines representing the upper and lower bounds of the gray or red regions correspond to the upper and lower quartiles of the drag ratio distributions, respectively. We arrange these 29 solutes in order of decreasing basal crossover temperature—the temperature at which the median of the drag ratio becomes zero—from left to right and top to bottom. The interquartile range (IQR)—width of the shaded regions—is narrow when the drag ratio is near one at low temperatures and the IQR increases with temperature as it approaches the crossover temperature.

4.6 Conclusion

We develop a computationally efficient methodology based on Bayesian sampling to quantify uncertainty in the diffusion coefficients and solute drag ratios and apply it to the vacancy-mediated solute transport in Mg. The uncertainties in DFT energies due to the exchange-correlation functional are used as a case study. We show that the solute diffusivities obey a multivariate log-normal distribution across different

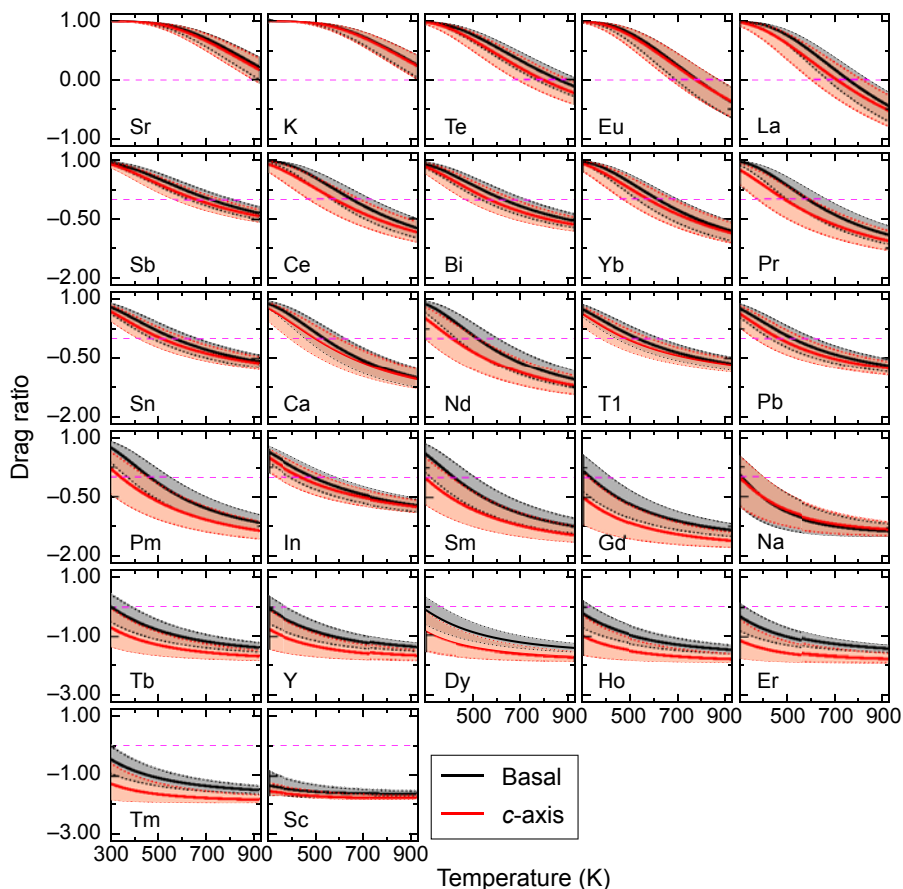


Figure 4.10 Three quartiles of the drag ratio distributions in the basal plane and along the c -axis for solutes where outer ring networks lead to reorientation of the vacancy around the solute. For Sr, K, Te, Eu, La, Sb, Ce, Bi, and Yb, their attractive binding energies of greater than 100 meV with a vacancy coupled with faster outer ring network rates compared to escape rates lead to a narrow distribution of drag ratio at low temperatures. The remaining solutes—Pr to Sc—have smaller attractive or repulsive binding with vacancy which lead to wide distribution of drag ratios at low temperatures. Near crossover temperature, the spread of the drag ratio distribution is maximum and decreases or becomes constant at higher temperatures.

temperatures and compute their covariance matrix using two approaches—a stochastic and a computationally efficient analytical method—which agree well. We quantify uncertainty in Arrhenius parameters through a correlated error fit and find that the standard deviation of the activation energy of diffusion lies between 90 and 120 meV for all the 61 solutes with small uncertainties in diffusion prefactors caused only by changes in dominant diffusion pathways. A nonzero uncertainty in diffusion prefactor for Tl, Pb, Bi, Li, Te, and the first half of the lanthanides indicates that more than one vacancy transition rate dominates in the temperature interval of 300–923K. We find

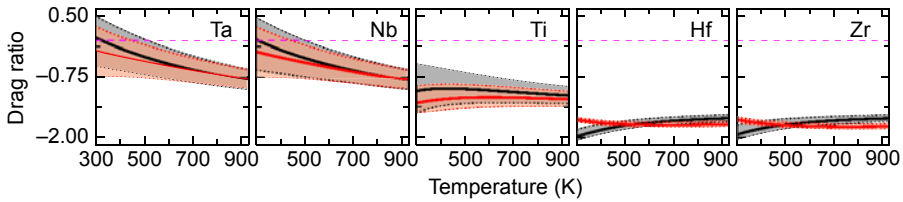


Figure 4.11 Three quartiles of the drag ratio distributions in the basal plane and along the c -axis for solutes whose vacancy reorientation rates in inner and outer ring network are similar. These five solutes have high repulsive interactions with vacancy (> 0.2 eV) leading to negative median of drag ratio above 300K except for Ta. The solutes Ta, Nb, and Ti show the maximum spread in drag ratio distribution near 300K because it is the closest temperature to crossover. The spread of the distributions decreases with temperature and becomes constant at higher temperatures for Hf and Zr.

that the experimentally measured diffusivities fall within the computed error bars for most solutes. The drag ratios are not normally distributed and are sensitive to the variation in vacancy reorientation barriers and solute–vacancy binding energies. The IQR quantifies the spread of the drag ratio distributions, and we observe that the IQR is maximum near the crossover temperature, signifying the maximum uncertainty in drag ratio.

Our methodology of uncertainty quantification for solute transport coefficients is general and can be extended to other crystal lattices, such FCC and BCC, as well as to other defect-mediated diffusion such as interstitial mechanisms. In our analysis, we ignore the uncertainty in attempt frequency and defect formation entropies which is expected to have minimal impact on the accuracy of uncertainty quantification of the diffusion prefactors. In the future, the distribution of parameters could be considered using the BEEF exchange-correlation functional and is worth investigation in future studies [80]. Finally, the inclusion of uncertainties in computationally generated transport databases will help to ascertain their reliability and robustness.

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Data-driven acceleration of first-principles saddle point and local minimum search based on scalable Gaussian processes

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5.1 Introduction

Establishing the process—structure—property linkage is the first and the most crucial step in materials design. Integrated computational materials engineering (ICME) tools can be utilized to numerically study the process—structure and the structure—property linkage, from nanoscale to macroscale. Particularly, first-principles methods at the nanoscale, such as density functional theory (DFT) [1], are attractive when there is a lack of experimental data to construct empirical models. For a complex material system, which involves a large representative volume and multiple chemical components, the material behaviors are difficult to predict. Because there can be numerous stable and metastable states as well as transition states in-between in the system. Searching for the metastable and transition states in materials is the key to design novel materials such as phase-change materials for information storage and energy storage, shape-memory polymers or alloys, as well as materials for extreme conditions with superior properties to avoid structural degradation and the chemical corrosion.

At the nanoscale, phase transitions can be inferred from the free energy or potential energy surface (PES) of material systems. The PES can be regarded as a high-dimensional hypersurface formed in the space of atomic configurations in the simulation cell. A minimum energy path (MEP) [2,3], describing the transition process from one stable or metastable state to another, is the lowest energy path which connects multiple local minima on the PES. The activation energy that the material system needs to overcome to finish the transition is determined by the energy difference between the maximum potential energy on the MEP and the energy of the initial state. The maximum potential energy on the MEP is obtained from a saddle point on the PES. From the activation energy, the transition rate can be calculated based on transition state theory (TST) [4]. Thus, finding the MEP is an important step to predict how often transitions occur. It also provides the information of how stable a configuration in

the material system is. The knowledge of both stable and transition states is important for establishing structure—property linkage in computational materials design.

In theory, the PES can be constructed by exhaustively calculating the potential energy levels for all configurations with first-principles DFT. However, there are challenges in first-principles PES construction. They are as follows. First, the PES does not have a simple analytical form. Numerical methods such as interpolation or regression are needed to construct a surrogate for the PES. Nevertheless, the dimension of the configuration space is typically very high, since the dimension scales linearly with the number of atoms in the simulation cell (dimension $d = 3N$ for N atoms). Constructing the surrogate PES model in a high-dimensional space requires a large number of sampling points to cover the space with enough density. The number of samples scales exponentially in the order of $O(s^d)$ for d -dimensional space with s samples in each dimension. Each sample corresponds to a DFT calculation, which itself is already computationally expensive. As a result, current computational schemes of DFT cannot satisfy the density requirement. Surrogate models constructed with sparse samples will be inherently inaccurate and lead to spurious predictions of stable and transition states.

Second, all simulation models have model-form and parameter uncertainty involved, even in first-principles simulation. The sources of model-form and parameter uncertainty in first-principles calculation include major assumptions such as Hartree—Fock self-consistency method and the Born—Oppenheimer approximation, as well as the approximation of the exchange-correlation energy. The Hartree—Fock method assumes that the electrons move independently and repel each others based on the average positions, and thus can be approximated using a single Slater determinant. The Born—Oppenheimer approximation assumes that the lighter electrons adjust adiabatically to the motion of the heavier atomic nuclei, and thus their motions can be separated. A zero-temperature ground state of the system is also assumed in DFT calculation. In addition, models with multiple fidelities have been involved in approximating the exchange-correlation energy in DFT, forming the rungs in a Jacob's ladder, increasing in complexity from local spin-density approximation to generalized gradient approximation (GGA), meta-GGA, hyper-GGA, exact exchange and compatible correlation, and exact exchange and exact partial correlation [5,6]. Furthermore, pseudopotentials have been regularly applied in DFT to reduce computational burden. In pseudopotential-based DFT calculations, the nuclear potential and core electrons of an atom are replaced by a significantly softer potential on the valence electrons, thus substantially reducing the number of basis functions used to approximate. As a result, the success of popular DFT codes which use plane-wave basis sets, including VASP [7–10], Quantum-ESPRESSO [11,12], and ABINIT [13–16], is dependent on the availability of good pseudopotentials [17]. Furthermore, the DFT calculation is also dependent on a good guess for the initial electron density. If the initial electron density is too wrong, the DFT calculation may not converge or converge to the wrong solution. Numerical treatments such as k-point sampling and orbital basis selection also introduce model-form uncertainty. Research efforts have been made to quantify uncertainty for DFT calculations. For example, Jacobsen et al. [18,19] estimated the distribution of errors in exchange-correlation functionals with the Bayesian approach. Pernot et al. [20] predicted systematic errors associated with the exchange-correlation functionals of different crystal structures using regression analysis. McDonnell et al. [21]

employed Bayesian analysis and direct least-squares optimization to assess the information content of the new data with respect to a model. Schunck et al. [22] provided a comprehensive literature review on quantifying model discrepancy with experimental data in nuclear DFT. Dobaczewski et al. [23] proposed a simple guide to quantify uncertainty in nuclear structure models. Lejaeghere et al. [24] conducted a benchmark study to compare 15 solid-state DFT codes, using 40 different potentials or basis set types, to assess the quality of the Perdew–Burke–Ernzerhof equations of state for 71 element crystals.

Because of the uncertainty described above, along with the research effort in literature in quantifying them, the system energy prediction using first-principles calculation is not exact. Significant discrepancies between simulated and actual systems exist. Therefore, model-form and parameter uncertainties in both surrogate model and first-principles calculation pose great challenges for constructing PES and searching MEP from DFT calculations for materials design. Uncertainty quantification (UQ) becomes particularly important in such calculations in order to assess the credibility of the predictions.

Various MEP and saddle point search methods have been developed. Comprehensive reviews were provided by Henkelman et al. [25], Schlegel [26], Alhat et al. [27], and Lasrado et al. [28]. In general, the methods for finding MEPs can be categorized as either chain-of-states methods or other methods. Chain-of-states methods rely on a collection of images that represent intermediate states of the atomic structure as it transforms from initial to final configurations along the transition path. These discrete states are chained to each other after the search converges, and the transition path and saddle point are obtained. The most commonly used chain-of-states methods include nudged elastic band (NEB) methods [29,30] and string methods [31,32]. Other methods for finding MEPs include the conjugate peak refinement method [33], the accelerated Langevin dynamics method [34], and the Hamilton–Jacobi method [35]. The methods for searching saddle points can also be categorized in two groups: local search and global search methods. Widely used local search methods include the ridge method [36] and the dimer method [37]. Popular global search methods include Dewar–Healy–Stewart (DHS) method [38] and activation-relaxation technique (ART) [39]. All of the above methods require prior knowledge of either the reactant or product, or both, in order to search for an MEP. In addition, they can search only one MEP or one saddle point at a time with one initial guess of the transition path. For large systems in an ultrahigh-dimensional searching space, the energy landscape is very complex, and there are numerous local minima and saddle points on the PES. The efficiency of depicting a global picture of such complex PES is very important. Therefore, efficient searching methods that can simultaneously locate multiple local minima and saddle points on the PES are needed, without the prior knowledge of the stable states of the material system.

When constructing PES, we need to cope with the challenges of computational load and high-dimensional configuration spaces. Surrogates or metamodels can improve the efficiency of configuration space exploration. Without relying only on expensive physics-based simulations, a surrogate model can be evaluated very efficiently. Examples of surrogate metamodels include polynomial regression [40], support vector regression [41], moving least-squares regression [42,43], radial basis functions [44], neural networks [45], Gaussian process (GP) method [46], and inverse distance weighting [47].

Here, GP regression is applied to assist local minimum and saddle point search. GP is a common choice for the surrogate, because of its rigorous mathematical formulation, active learning for model construction, tractable convergence rate, and UQ capability. In particular, the posterior variance in GP can be used to quantify the uncertainty of the predictions. Although a versatile tool, classical GP modeling employs a sequential sampling approach and the computational bottleneck is the calculation of the inverse of the covariance matrix for model update. When the number of data points n reaches a few thousands, the efficiency of GP modeling decreases monotonically. The well-known computational bottleneck of GP is due to its covariance matrix of size $n \times n$, which costs $\mathcal{O}(n^2)$ to store, and $\mathcal{O}(n^3)$ to compute the inverse matrix during the fitting process (cf. [Section 5.3.3](#)). At $\mathcal{O}(10^4)$ number of data points, the classical GP is generally no longer computationally affordable. Several modifications have been proposed to improve the scalability of the GP approach. Notable examples include fixed-rank GP [48], fast GP algorithm [49], multifidelity co-kriging [50,51], and cluster GP [52,53].

In this work, a local minimum and saddle point search method of the high-dimensional PES is developed based on a physics-based symmetry-enhanced local GP method, which is called GP-DFT. The curse of dimensionality is mitigated using physics-based symmetry invariance properties, in which the atomic position and velocities of the same chemical elements can be shuffled combinatorially without changing the potential energy prediction. The objectives of the proposed method are twofold. The first objective is to accelerate the searching method through the use of GP as a metamodel for potential energy prediction during some parts of the searching process. The second objective is to mitigate the negative impact of the curse of dimensionality, by enhancing the classical GP metamodel with a physics-based symmetry-enhanced GP-DFT metamodel. The searching process begins with a limited number of DFT calculations. Once this number reaches a threshold, a physics-based symmetry-enhanced GP metamodel, GP-DFT is constructed. In the GP-DFT metamodel, multiple local and overlapping GPs are constructed. The large dataset is dynamically assigned to the GP-DFT, as the searching process advances. The potential energy predictions based on the GP-DFT is used to locate new sampling locations for DFT calculations. After DFT calculations are ran, the GP-DFT sequentially updates with new data points included, and the searching method switches back to the GP-DFT metamodel. The “real-surrogate-real” approach in the searching method continues until some stopping criteria are satisfied. The advantages of the proposed searching method using GP-DFT are the significantly improved computational efficiency, which eliminates a large number of potential energy calculations through DFT. Furthermore, the divide-and-conquer approach in GP-DFT resolves the computational bottleneck in classical GP formulation, further improving the computational efficiency. Lastly, a physics-based symmetry-enhanced feature, which is constructed based on physical knowledge about the material system, is injected into GP-DFT to mitigate the curse of dimensionality in high-dimensional space. The posterior variance in GP-DFT is used as a measure to quantify uncertainty during searching the process.

In this chapter, [Section 5.2](#) provides a literature review on traditional searching method. The concurrent searching method in our previous work is introduced in [Section 5.3.1](#). As an extension of the concurrent searching method, curve swarm searching method is described in [Section 5.3.2](#). [Section 5.3.3](#) describes the integration of GP to efficiently estimate the potential energy in the searching process from [Section 5.3.1](#). [Section 5.3.4](#) shows three synthetic benchmark examples to demonstrate the power and efficiency of the curve swarm searching method and the concurrent search method assisted by a GP surrogate model to approximate the PES. [Section 5.4](#) provides the GP-DFT formulation for high-dimensional and large dataset problem. [Section 5.5](#) applies the searching method with GP-DFT to an example of hydrogen diffusion in body-centered cubic iron, which demonstrates the scalability of the proposed GP-DFT framework, in contrast to the computational bottleneck of classical GP. [Section 5.6](#) provides a discussion, and [Section 5.7](#) concludes this chapter.

5.2 Literature review

The challenge for phase transition simulation is to search the transition rate which is determined by the activation energy between two states. An activation energy barrier always exists between two states. In 1931, Eyring and Polanyi [4] proposed the TST as a means to calculate the transition rates using the activation energy to characterize reactions. Most of the simulation methods developed recently are based on the TST and harmonic transition state theory (hTST) [54]. Some variants of TST (variational transition state theory [55] and reaction path Hamiltonian [56]) are also used. The general procedure to simulate a phase transition process is as follows. First a PES is generated. Then an MEP which is the most probable physical pathway of transition among all possible ones is located. Finally, the activation energy is obtained by finding the maximum energy on the MEP and the transition rate is calculated using TST. Subsequently, the phase transition simulation can be done using KMC, accelerated molecular dynamics [34], or other simulation methods. The accuracy of the simulation depends on the accuracy of the rate constants. In other words, it depends on the accuracy of the activation energy. The research on transition pathway search and saddle point search aims to find the accurate MEP and the saddle point.

To search saddle points on a PES, a number of algorithms [25–28,57–61] were developed in the past few decades. The algorithms can generally be categorized into two groups: single-ended methods and double-ended methods. Single-ended methods start with one configuration to search the saddle point on a PES without locating the corresponding MEP. Double-ended methods are to locate the saddle point and corresponding MEP between two stable states.

The major group of single-ended methods is eigenvector-following methods [62–71] that follow the eigenvector of Hessian matrix with local quadratic approximations of the PES. Newton–Raphson method [62] optimizes the energy iteratively along the eigenvector directions using Newton–Raphson optimizer. Surface walking algorithms [63–68] determine the walking steps by introducing Lagrange multipliers [63], a trust radius [64,66], and parameterized step vector [67,68]. Partitioned rational

function optimization method [65] makes a local rational function approximation to the PES with augmented Hessian matrix. Frontier mode-following method [69] identifies the uphill direction to the saddle point by following more than one eigenvectors. Hybrid eigenvector-following methods [70,71] update the eigenvectors of the Hessian matrix using a stand shifting technique and minimize the energy in tangent space using conjugate gradient minimization.

Other single-ended methods are summarized as follows. The distinguished coordinate method [72–74] defines one internal coordinate as the reaction coordinate and iteratively minimizes the energy level along all other internal coordinates within a gradually converging lower and upper bounds of the reaction coordinate. The gradient norm minimization method [75] identifies the transition states by minimizing the Euclidian norm of the gradient of the potential energy function using a generalized least-squares technique. The constrained uphill walk method [76,77] employs simplex method to minimize the energy over a set of hypersphere surfaces, the center of which are several points on or near the reaction path. Image function methods [78–80] formulate an image function with the local minima located at position of the saddle points on the original PES. The gradient-only method [81] starts at the bottom of a valley and traces to a saddle point in the ascent direction that is defined based on gradient information. The ART method [39] can travel between many saddle points using a two-step process; an image first jumps from a local minimum to a saddle point and then back down to another minimum. The reduced gradient following [82,83] and reduced PES model [84] methods use intersections of zero-gradient curves and surfaces, with saddle point search occurring within the subspace of these curves or surfaces. The interval Newton method [85] is capable of finding all stationary points by solving the equation of vanishing gradient.

The most popular double-ended methods are chain-of-states methods [29–32,86–104] including the NEB [29,30,32,96–99,102–104], string methods [31,32,98,100,101], and other methods [86–95]. Chain-of-states methods rely on a collection of images that represent intermediate states of the atomic structure as it transforms from initial to final configurations along the transition path. These discrete states are chained to each other after the search converges, and the transition path and saddle point are obtained. The most common one among these methods is the NEB [29], which relies on a series of images connected by springs. To increase the resolution at the region of interest (ROI) and the accuracy of saddle point energy estimates, the NEB method omits the perpendicular component of the spring force, as well as the parallel component of the true force due to the gradient of the potential energy. In some cases, this method produces paths with unwanted kinks or may not have any images that are directly on the saddle point. The improved tangent NEB [30] and doubly NEB [96] methods reduce the appearance of kinks by generating a better estimate of the tangent direction of the path and reintroducing a perpendicular spring force component. The adaptive NEB [97] method increases the resolution around the saddle point adaptively to improve the efficiency and accuracy of NEB. The free-end NEB method [102] only requires knowledge of either the initial or final state, rather than both. The climbing image NEB [96] allows the image with the highest energy to climb in order to locate the saddle point. A generalized solid-state NEB (G-SSNEB) [104] was developed with a modified approach to estimate spring forces and perpendicular

projection to search MEP for the process of solid–solid transformations which have both atomic and unit-cell degrees of freedom involved. Eigenvector-following optimization can be applied to the result of NEB to locate actual saddle points, and the resolution of ROI can be increased by using adaptive spring constants [103].

The string methods [31,32] represent the transition path continuously as Splines that evolve and converge to the MEP. As opposed to NEB, the number of points used in the String method can be modified dynamically. The growing string [98] takes advantage of this by starting with points at the reactant and product, and then adding points which meet at the saddle point. The quadratic string method [100] is a variation that uses a multiobjective optimization approach. The string and NEB methods are comparable in terms of computational efficiency [105]. In addition to NEB and string methods, other chain-of-states methods have been developed to find transition paths. Gaussian chain method [87] minimizes the average value of the potential energy along the path by formulating an objective function. Self-penalty walk (SPW) method [89] reformulates the Gaussian chain objective function by adding a penalty function of distance. Locally updated planes method [90,91] minimizes the energy of each image in all directions except their corresponding tangent directions estimated at the position of each images along the path. The variational Verlet method [69] formulates an objective function similar to the Gaussian chain objective function to locate dynamical paths. Sevick–Bell–Theodorou method [93] optimizes the energy with a constraint of fixed distance between images. Path energy minimization method [94] modifies the SPW objective function by including a high value of exponential index that increase the weight of the image with highest energy along the path.

In addition to chain-of-states methods, other double-ended methods have been developed to search transition paths. The ridge [36] and dimer [37,106] methods use a pair of images to search for the saddle point. DHS method [38] searches the saddle point by iteratively reducing the distance between reactant and product images. Step and slide method [107] uses an image from the initial and final states. Energy levels of each are increased gradually, and the distance between them is minimized while remaining on the same isoenergy surface. Concerted variational strategy method [108] employs Maupertuis' and Hamilton's principles to obtain a transition path that will be further refined using conjugate residual method [109] to locate the saddle point. Conjugate gradient methods [110–112] are based on conjugate gradient function minimization. Conjugate peak refinement method [33] finds saddle points and the MEP by searching the maximum of one direction and the minima of all other conjugate directions iteratively. Accelerated Langevin dynamics method [34] is a stochastic transition path sampling method that involves activation and deactivation paths described by Langevin equations. Hamilton–Jacobi method [35] relies on the solution of a Hamilton–Jacobi type equation to generate the MEP. Missing connection method [113] identifies multistep paths between two local minima by connecting one minimum to its adjacent minimum one by one. Each intervening transition states is located by using the doubly NEB methods. For each cycle, the next targeted minimum that will be connected is determined by the criteria of minimum distance in Euclidean distance space using Dijkstra algorithm. Synchronous transit method [57,111,114] estimates the transition states and refines the saddle point by combining the conjugate gradient method and the quasi-Newton minimization method. Intersection surface method

[115] formulates an intersecting surface model based on the quadratic basin approximations around the two local minima on the original PES. The minima of the intersecting surface are good approximation to the positions of saddle points on the original PES. Contingency curve method [116] formulates a bi-Gaussian model for the PES. The transition path is represented by using the equipotential contour contingency curve that connects two local minima and the corresponding saddle points.

5.3 Concurrent search of local minima and saddle points

5.3.1 Concurrent searching method

A double-ended concurrent searching method was proposed by He and Wang [117] to simultaneously locate multiple local minima and saddle points along a transition pathway on the PES, without knowing the initial and final stable states of the material system. The Bézier curve formulation was adopted to model the transition path from one local minima to another as a Bézier curve. In each convex polygon wrapping the Bézier curve, two end control points are converged to two local minima, while one intermediate control point climbs up to find the saddle point. A constrained degree elevation and reduction scheme is implemented to ensure that the control points are distributed evenly along the path.

To search multiple local minima and saddle points that may exist between two end points, a curve subdivision scheme is used to progressively break one Bézier curve to two Bézier curves. The searching process is conceptually divided into three stages. The first stage is the single transition pathway search. The second stage is the multiple transition pathway search. And the last one is the climbing process to locate the actual saddle points. Fig. 5.1 illustrates the subdivision scheme for the Bézier curve with five control points, where p_0 and p_4 are the two end control points to locate the local minima while one of the three intermediate control points p_1 , p_2 , and p_3 is chosen as the breaking point. Table 5.1 lists all eight possible cases, from which the decision is made according to the angles θ_i 's between the PES slope $-\nabla V(p_i)$ and the connected control points at control point p_i , as well as energy levels. Fig. 5.2 and Table 5.2 present the illustration and the subdivision scheme for the Bézier curves with six control points, respectively. It is noted that the subdivision scheme is only utilized in the second stage of the searching algorithm.

In the first stage, the two end control points are driven to two local minima using the conjugate gradient method. The intermediate control points are relaxed along their corresponding conjugate directions with positive eigenvalues of the Hessian matrix. In the second stage, the searching method locates all local minima between two end control

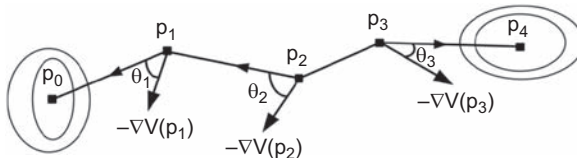
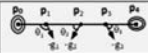
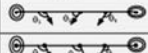
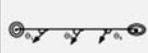
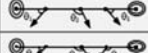
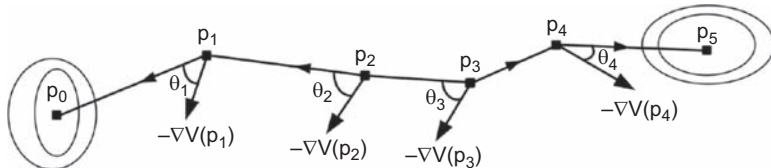


Figure 5.1 Illustration for multiple pathway search with five control points.

Table 5.1 Curve subdivision scheme for five control points.

Eight Cases	Greater (>) or smaller (<) than $\pi/2$			Breakable ?
	θ_1	θ_2	θ_3	
1 	>	<	<	Break at $\mathbf{p}_2$
2 	>	<	>	Break at $\mathbf{p}_2$
3 	>	>	>	Break at $\mathbf{p}_2$
4 	>	>	<	If $V(\mathbf{p}_1) > V(\mathbf{p}_2) > V(\mathbf{p}_3)$, the curve is defined as unbreakable; Otherwise, break at $\mathbf{p}_1$.
5 	<	<	>	If $V(\mathbf{p}_3) > V(\mathbf{p}_2) > V(\mathbf{p}_1)$, the curve is defined as unbreakable; Otherwise, break at $\mathbf{p}_3$.
6 	<	<	<	If $V(\mathbf{p}_1) < V(\mathbf{p}_2)$ and $V(\mathbf{p}_3) < V(\mathbf{p}_2)$, the curve is defined as unbreakable; Otherwise, break at $\mathbf{p}_2$.
7 	<	>	<	Same as case 6
8 	<	>	>	Break at $\mathbf{p}_2$

**Figure 5.2** Illustration for multiple pathway search with six control points.

points, which are obtained from the first stage. To find all the local minima between the two end control points, a curve subdivision scheme is developed to check if another potential local minimum between two local minima exists. If a minimum does exist, the potential local minimum is further driven to the local minimum using the conjugate gradient method, and the initial Bézier curve is broken into two Bézier curves, separating at the middle local minimum. The searching method continues to break all Bézier curves until no local minimum is found between two end control points of any curve. This process continues until each curve crosses only two adjacent energy basins. In the third stage, the control point with maximum potential energy prediction climbs up to locate the actual saddle point between two local minima. Similar to the first stage, a set of conjugate directions are constructed for each intermediate control point. The control point with the maximum potential energy prediction along each transition pathway is maximized along the direction corresponding to a negative eigenvalue, and relaxed along all other conjugate directions. All the other intermediate control points are only relaxed in all the conjugate directions except for the one with the

Table 5.2 Curve subdivision scheme for six control points.

Sixteen Cases		Greater (>) or smaller (<) than $\pi/2$				Breakable?
		θ_1	θ_2	θ_3	θ_4	
1		>	<	<	>	Break at $\mathbf{p}_2$
2		>	<	>	>	Break at $\mathbf{p}_2$
3		>	>	>	>	Break at $\mathbf{p}_2$
4		>	>	<	>	Break at $\mathbf{p}_2$
5		>	<	<	<	Break at $\mathbf{p}_2$
6		>	<	>	<	Break at $\mathbf{p}_3$
7		>	>	>	<	Break at $\mathbf{p}_3$
8		>	>	<	<	If $V(\mathbf{p}_1) > V(\mathbf{p}_2) > V(\mathbf{p}_3) > V(\mathbf{p}_4)$, the curve is defined as unbreakable; otherwise, break at $\mathbf{p}_2$
9		<	>	<	>	Break at $\mathbf{p}_3$
10		<	>	>	>	Break at $\mathbf{p}_3$
11		<	<	<	>	Break at $\mathbf{p}_3$
12		<	<	>	>	If $V(\mathbf{p}_4) > V(\mathbf{p}_3) > V(\mathbf{p}_2) > V(\mathbf{p}_1)$, the curve is defined as unbreakable; otherwise, break at $\mathbf{p}_4$
13		<	<	<	<	If $V(\mathbf{p}_3) > V(\mathbf{p}_4)$ and $V(\mathbf{p}_2) > V(\mathbf{p}_1)$, the curve is defined as unbreakable; otherwise, if $V(\mathbf{p}_2) < V(\mathbf{p}_1)$, break at $\mathbf{p}_2$, else break at $\mathbf{p}_3$
14		<	<	>	<	If $V(\mathbf{p}_3) > V(\mathbf{p}_2) > V(\mathbf{p}_1)$, the curve is defined as unbreakable; otherwise, break at $\mathbf{p}_3$
15		<	>	>	<	Break at $\mathbf{p}_2$
16		<	>	<	<	If $V(\mathbf{p}_2) > V(\mathbf{p}_3) > V(\mathbf{p}_4)$, the curve is defined as unbreakable; otherwise, break at $\mathbf{p}_2$

negative eigenvalue. It is noteworthy that the searching method has not yet been implemented to execute in parallel. In theory, the execution can be massively parallelized to improve computational efficiency.

5.3.2 Curve swarm searching method

The major limitation of single-path searching methods is that they may miss some important transition paths within a region. For a complicated PES, it is also possible

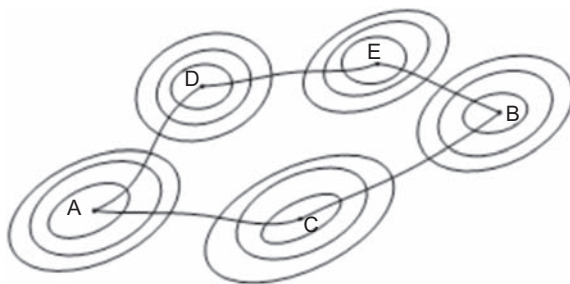


Figure 5.3 Illustration for two possible transition paths between two states.

that more than one path exist between two stable states. For instance, as illustrated in Fig. 5.3, there are two paths A–D–E–B and A–C–B between two stable states A and B. With the use of this method, only one path can be found. All potential MEPs between two stable states should be located to provide a global view of the energy landscape. Since the concurrent search method is also a local method, the result sensitively depends on the initial guess of the transition path. A path identified by local search methods may not be the actual MEP, and consequently this results in the overestimation of the energy barrier between two states.

To extend the current searching method and provide a global view of the PES, a curve swarm searching method was proposed by He and Wang [118,119] to exhaustively locate the local minima and saddle points on a PES within a searching area. It uses multiple groups of Bézier curves, each of which represents a multistage transition path. At the initial stage, each group includes only one curve representing one initial transition path. The curve in one group will gradually be divided into multiple curves to locate multiple local minima and saddle points along the transition path. At the final stage, each group includes multiple curves with their end points connected together and located at multiple local minima. In addition, each curve has one intermediate point located at the saddle point position.

The central issue in the curve swarm searching method is to maintain cohesion and to avoid collision between groups during the searching process. Cohesion means that groups should stay relatively close to each other to explore a PES thoroughly, thus locating all the local minima and saddle points. If two adjacent groups stay too far away from each other, some intermediate space between them may not be explored. Collision means that more than one group search the same area on a PES. Collision should be avoided to prevent repetitive efforts, thus maintaining a global view and reducing computational cost. To simultaneously maintain cohesion and avoid collision between groups, a collective potential model was introduced to describe the collective behavior among groups. In other words, collective forces are introduced between groups, which can be either attractive or repulsive. The forces are applied to control points in each group. If two curves are too close to each other, the repulsive force is applied to the control points of the curves; otherwise, attractive force is applied. The flow chart of curve swarm searching method is shown in Fig. 5.4.

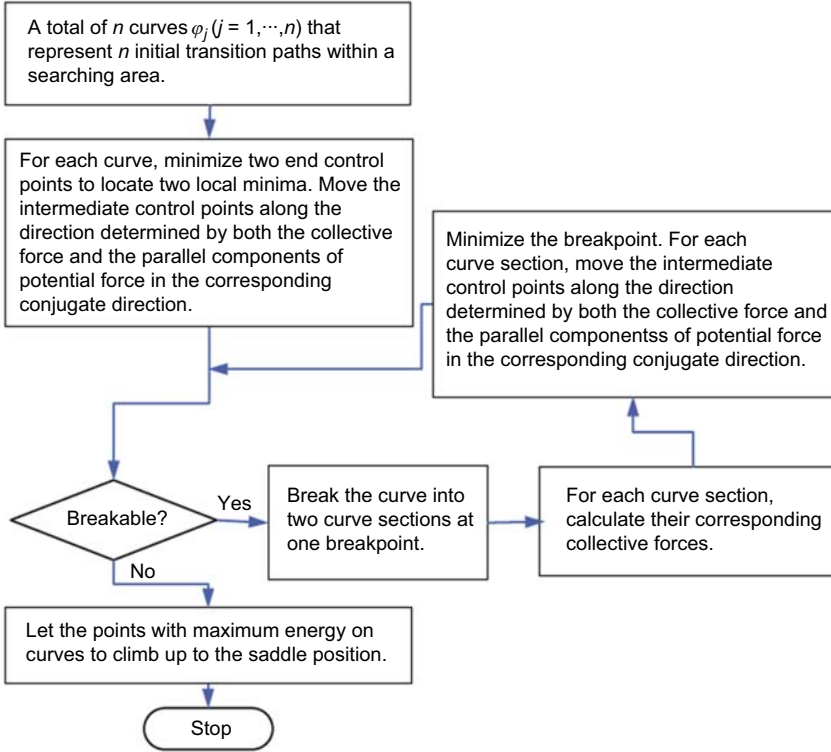


Figure 5.4 Flow chart of the curve swarm searching method.

5.3.3 Concurrent searching method assisted by GP model

To reduce the computational overhead and accelerate the searching method, a GP surrogate model was used to approximate the high-dimensional PES in the work of He and Wang [120]. In this section, the GP formulation is briefly reviewed and the integration of GP surrogate model is discussed.

Comprehensive reviews on GP are provided by Brochu et al. [121] and Shahriari et al. [122]. Here, we adopt the notion from Shahriari et al. [122] and summarize the GP formulation. Assume that f is a function of $\mathbf{x}$, where $\mathbf{x} \in \mathcal{X}$ is the d -dimensional input. A $GP(\mu_0, k)$ is a nonparametric model over functions f , which is fully characterized by the prior mean functions $\mu_0(x) : \mathcal{X} \mapsto \mathbb{R}$ and the positive-definite kernel, or covariance function $k : \mathcal{X} \times \mathcal{X} \mapsto \mathbb{R}$. In GP regression, it is assumed that $\mathbf{f} = f_{1:n}$ is jointly Gaussian, and the observation $\mathbf{y}$ is normally distributed given $\mathbf{f}$, leading to

$$\mathbf{f} | \mathbf{X} \sim \mathcal{N}(\mathbf{m}, \mathbf{K}), \quad (5.1)$$

$$\mathbf{y} | \mathbf{f}, \sigma^2 \sim \mathcal{N}(\mathbf{f}, \sigma^2 \mathbf{I}), \quad (5.2)$$

where $m_i := \mu(\mathbf{x}_i)$, and $K_{ij} := k(\mathbf{x}_i, \mathbf{x}_j)$. Eq. (5.1) describes the prior distribution induced by the GP.

The covariance kernel k is a user choice of modeling covariance between inputs. One of the most widely used kernel is the squared exponential kernel, where f is implicitly assumed to be smooth. The covariance kernel is described mathematically as

$$\mathbf{K}_{i,j} = k(\mathbf{x}_i, \mathbf{x}_j) = \theta_0^2 \exp\left(-\frac{r^2}{2}\right), \quad (5.3)$$

where $r^2 = (\mathbf{x} - \mathbf{x}')^T \mathbf{\Gamma} (\mathbf{x} - \mathbf{x}')$, and $\mathbf{\Gamma}$ is a diagonal matrix of d squared length scale θ_i .

The hyperparameters θ is determined by maximum likelihood estimation method, where the log marginal likelihood function is

$$\begin{aligned} \log p(\mathbf{y}|\mathbf{x}_{1:n}, \theta) = & -\frac{1}{2} (\mathbf{y} - \mathbf{m}_\theta)^T (\mathbf{K}^\theta + \sigma^2 \mathbf{I})^{-1} (\mathbf{y} - \mathbf{m}_\theta) - \frac{1}{2} \log |\mathbf{K}^\theta + \sigma^2 \mathbf{I}| \\ & - \frac{n}{2} \log(2\pi). \end{aligned} \quad (5.4)$$

Numerical optimization of the log marginal likelihood function yields the hyperparameters θ for the GP for the current dataset. Because the optimization process involves computing and storing the inverse of the covariance matrix, the algorithmic complexity is at $\mathcal{O}(n^3)$ and the data storage cost is at $\mathcal{O}(n^2)$.

Let the dataset $\mathcal{D} = (\mathbf{x}_i, y_i)_{i=1}^n$ denote a collection of n noisy observations and $\mathbf{x}$ denote an arbitrary input of dimension d . Under the formulation of GP, given the dataset $\mathcal{D}_n$, the prediction for an unknown arbitrary test point is characterized by the posterior Gaussian distribution, which can be described by the posterior mean and posterior variance functions, respectively, as

$$\mu_n(\mathbf{x}) = \mu_0(\mathbf{x}) + \mathbf{k}(\mathbf{x})^T (\mathbf{K} + \sigma^2 \mathbf{I})^{-1} (\mathbf{y} - \mathbf{m}), \quad (5.5)$$

and

$$\sigma_n^2 = k(\mathbf{x}, \mathbf{x}) - \mathbf{k}(\mathbf{x})^T (\mathbf{K} + \sigma^2 \mathbf{I})^{-1} \mathbf{k}(\mathbf{x}), \quad (5.6)$$

where $\mathbf{k}(\mathbf{x})$ is the covariance vector between the test point $\mathbf{x}$ and $\mathbf{x}_{1:n}$.

The integration of GP model to the searching method is implemented through the “real-surrogate-real” approach. On the one hand, the GP provides an efficient way to search for the saddle points. On the other hand, the GP model needs to be refined by querying sampling locations where potential energy prediction is uncertain. The main objective of the GP approach is to switch back and forth between the DFT calculations and the surrogate models during the search.

The “real-surrogate-real” approach is implemented by several thresholds in the searching methods. For example, if the number of certain functional evaluations passes these thresholds, the functional evaluations are performed using the GP, instead of the expensive DFT calculations. At certain point, the searching method switches back to

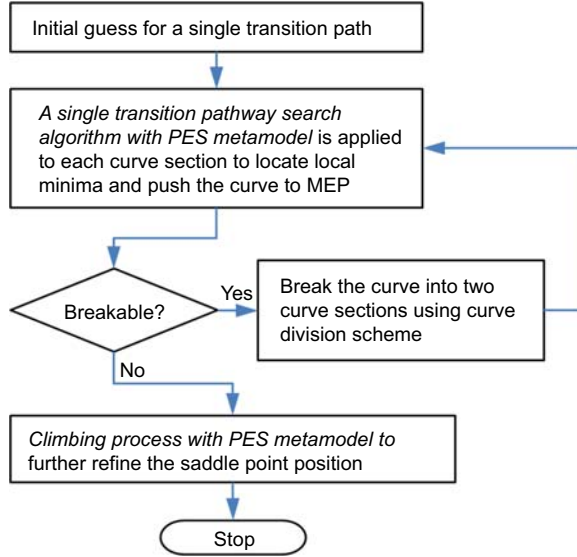


Figure 5.5 Flowchart of the searching method with metamodel involves three stages. The first and second stages are combined into a single transition pathway search, and third stage is the climbing process. A GP model approximating PES is utilized in all three stages to accelerate the searching process.

the DFT calculations to check the accuracy of the GP prediction and further update the GP model. Fig. 5.5 presents the workflow of the searching method using GP surrogate model. The “real-surrogate-real” approach is involved in all three stages of the searching method, described as follows.

In the first stage, the searching method updates the positions of the end control points based on DFT calculations using the conjugate gradient method and the positions of intermediate control points by moving them along conjugate directions until a number of observations equals to a threshold. The GP model is then constructed to approximate the high-dimensional PES, and the searching method relies on a sampling scheme to locate two local minima, which correspond to the two end control points. For each end control point, distributed samples are drawn uniformly in a local region, defined by the current locations of the end control points and a hypercube with the side length

$$a = \sqrt{2}c\min(d_{\text{pre}}, d_{\text{neighbor}}), \quad (5.7)$$

where $c \in (0, 1]$ is a constant, $d_{\text{pre}} = \|\mathbf{x}^{(i)} - \mathbf{x}^{(i-1)}\|$ is the distance between the positions of the end points in the current iteration i and previous iteration $(i-1)$. $d_{\text{neighbor}} = \|\mathbf{x}_{\text{end}}^{(i)} - \mathbf{x}_{\text{neighbor}}^{(i)}\|$ is the distance between the end point and its neighboring control point. The definition of the hypercube length is necessary to ensure that the new end control point will not jump to a position that is too far away from the closest local minimum and prevent the formation of possible loops at the end of the curve.

The work flow of the second stage of the searching method using GP is presented in Fig. 5.6. In the second stage, the potential energy prediction in the line search along the conjugate directions is also evaluated based on the actual DFT calculations until another threshold is met. Line search is one of the main components in the searching method, as it is involved in all stages, and is used to determine the minimum or maximum along each conjugate direction. The searching method updates the positions

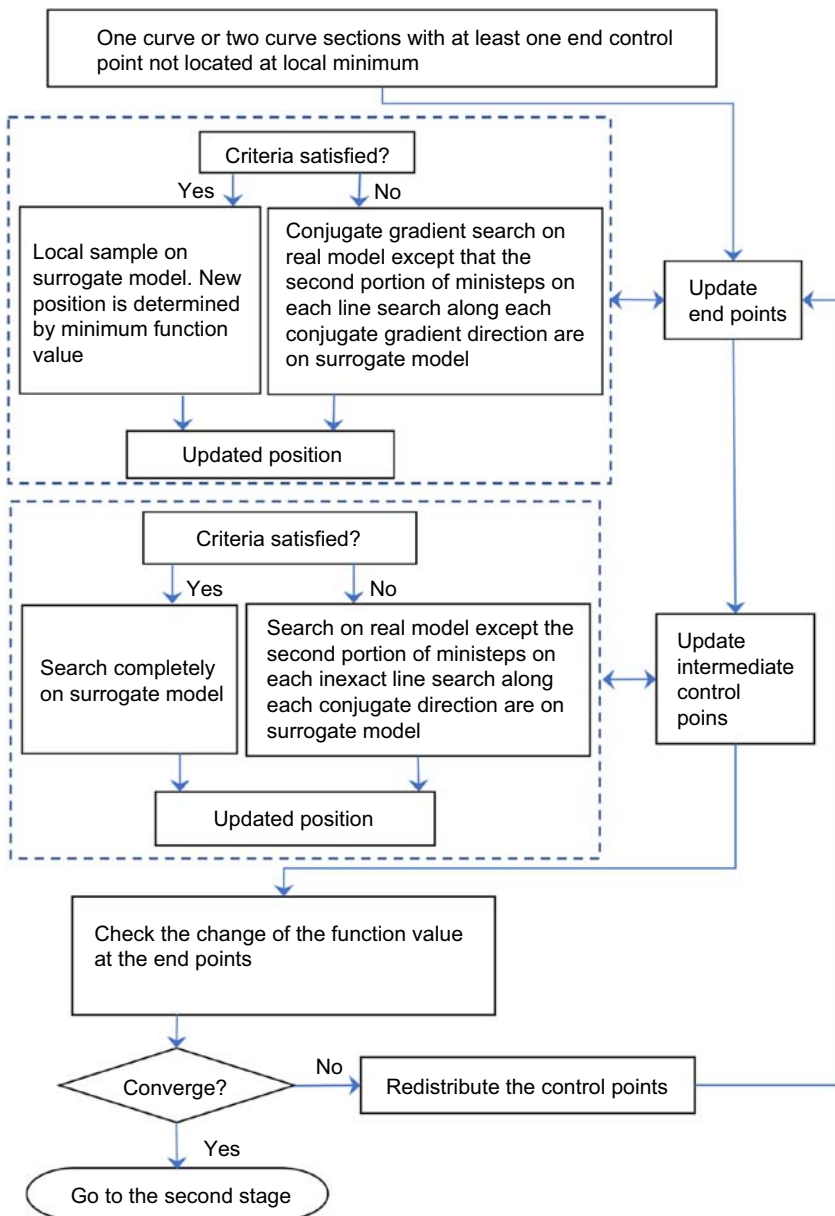


Figure 5.6 Flowchart for single transition pathway search method using GP model.

of the end control points based on the actual DFT calculations using the conjugate gradient method and the positions of the intermediate control points by moving them along conjugate directions until a predefined number of observations are met. After that, when more potential energy predictions are required, the GP model is used to approximate the PES to reduce the computational cost. The intermediate control points move along the conjugate directions with all the potential energy predictions evaluated on the GP model.

In the third stage, the control point with the maximum energy climbs up along a conjugate direction and all other intermediate control points are minimized along their corresponding conjugate directions with positive eigenvalues. The construction of the conjugate directions is based on DFT calculations, except for some functional evaluations during the line search are conducted using the GP model until a threshold is satisfied. After that, the climbing process depends solely on the GP model.

5.3.4 Benchmark on synthetic examples

The effectiveness of curve swarm searching method in [Section 5.3.2](#) is demonstrated with some test functions. Meanwhile, the concurrent searching method, described in [Section 5.3.1](#), is compared with the accelerated searching method using GP models in [Section 5.3.3](#). Three test functions are used as benchmark examples in this section, including LEPS potential, Rastrigin function, and Schwefel function [[117–119](#)]. [Fig. 5.7](#) shows the definitions and surface plots of the test functions used to demonstrate the accuracy and efficiency of searching methods.

[Fig. 5.8](#) presents the comparison results between concurrent searching method without applying collective forces and curve swarm searching method, using the Rastrigin function as the test function. [Fig. 5.8\(a\)](#) shows that two curves (e.g., the first and second curve, and the third and fourth curve) may duplicate the search efforts and find the same result when there is no communication among curves. [Fig. 5.8\(b\)](#) shows that the collective force introduced in the curve swarm searching method pushed those two curves away. As a result, as shown in [Fig. 5.8\(e\)](#), the curve swarm searching method locates 35 local minima and 35 saddle points, whereas only 26 local minima and 29 saddle points are located by concurrent searching method without applying collective forces. There are 49 local minima and 56 saddle points in total. The scalability and convergence of swarm searching method is tested by gradually increasing the number of the initial curves on the PES. [Fig. 5.8\(c\)](#) shows a near quadratic relationship between the total CPU time and the total number of initial curves which is acceptable in terms of computational efficiency. [Fig. 5.8\(d\)](#) shows the result of convergence test. It shows that the total number of located local minima converges when the number of initial curves approaches 17. However, the total number of located saddle points keeps increasing, which means that it needs more initial curves to locate all the saddle points in the area.

[Fig. 5.9](#) presents the comparison results between concurrent searching method without applying collective forces and curve swarm searching method, using Schwefel function as the test function. [Fig. 5.9\(a\)](#) and [\(b\)](#) shows that the collective force introduced in the curve swarm searching method can maintain cohesion and avoid collision

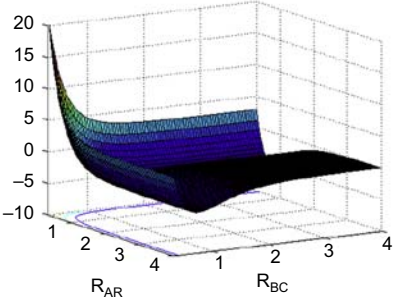
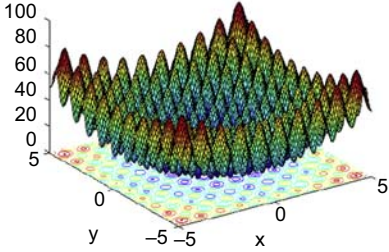
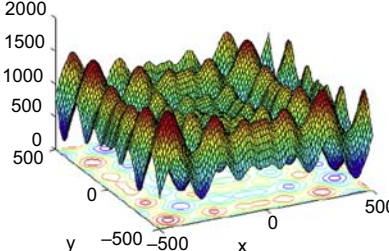
Function	Definition	Graphic in two dimension
LEPS potential	$V^{LEPS}(r_{AB}, r_{BC})$ $= \frac{Q_{AB}}{1+a} + \frac{Q_{BC}}{1+b} + \frac{Q_{AC}}{1+c} - \left[\frac{J_{AB}^2}{(1+a)^2} + \frac{J_{AB}^2}{(1+a)^2} + \frac{J_{AB}^2}{(1+a)^2} \right. \\ \left. - \frac{J_{AB}J_{BC}}{(1+a)(1+b)} - \frac{J_{BC}J_{AC}}{(1+b)(1+c)} - \frac{J_{AB}J_{AC}}{(1+a)(1+c)} \right]^{1/2}$ where $Q(r) = \frac{d}{2} \left(\frac{3}{2} e^{-2\alpha(r-r_0)} - e^{-\alpha(r-r_0)} \right)$ $J(r) = \frac{d}{4} \left(e^{-2\alpha(r-r_0)} - 6e^{-\alpha(r-r_0)} \right)$	
Rastrigin	$f(\mathbf{x}) = 10n + \sum_{i=1}^n [x_i^2 - 10 \cos(2\pi x_i)]$	
Schweffel	$f(\mathbf{x}) = 418.9829n - \sum_{i=1}^n x_i \sin \sqrt{ x_i }$	

Figure 5.7 Test functions.

of curve groups. As shown in Fig. 5.9(c), the curve swarm searching method is able to identify more local minima and saddle points than the ones located by concurrent searching method.

Fig. 5.10 presents the comparison results between concurrent searching method and the accelerated searching method assisted by GP model, using the synthetic LEPS potential function as the test function. Fig. 5.10(a) and (b) shows the visualization of the initial and final locations of the curve using the concurrent searching method and the accelerated searching method using GP, respectively. Both have very similar final results using two curves during the searching process. Fig. 5.10(c) compares the

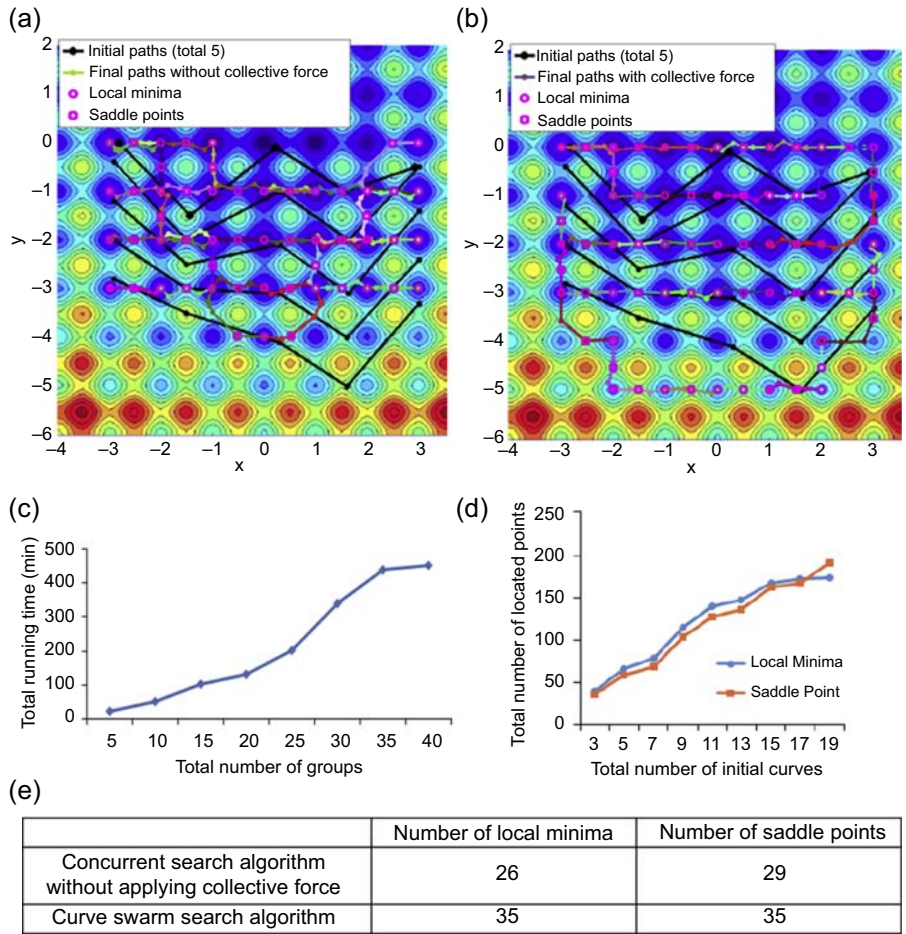


Figure 5.8 Benchmark results with Rastrigin function: (a) concurrent searching method without applying collective forces, (b) curve swarm searching method with collective forces, (c) scalability test, (d) convergence test, and (e) the number of identified local minima and saddle points.

two searching methods with the number of functional calls or DFT simulations, where “Con” denotes the concurrent search algorithm, “Krig” denotes the new search algorithm integrated with kriging, “Pos *” means the initial position * in the figure, N_f is the number of function evaluation at each initial position, N_p is the number of identified final paths, and N/path is the average number of function evaluations to locate one final path. It clearly shows that the GP integration in the concurrent searching method significantly improves the efficiency.

Figs. 5.11 and 5.12 show the qualitative and quantitative analysis of the comparison between the concurrent searching method and the GP-assisted searching method, using 2D Rastrigin and Schwefel functions as the test functions, respectively. The efficiency of the GP model as the surrogate in searching for saddle points can be clearly seen.

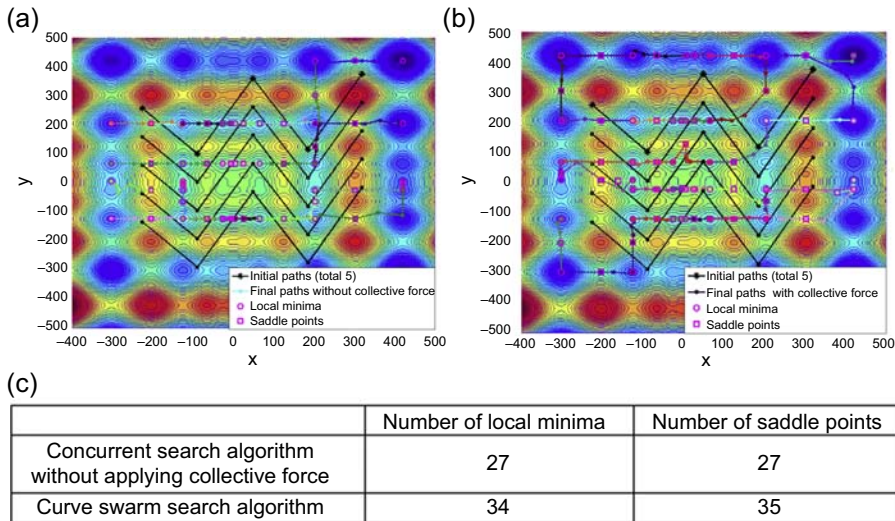


Figure 5.9 Benchmark results with Schwefel function: (a) concurrent searching method without applying collective forces, (b) curve swarm searching method, and (c) the number of identified local minima and saddle points.

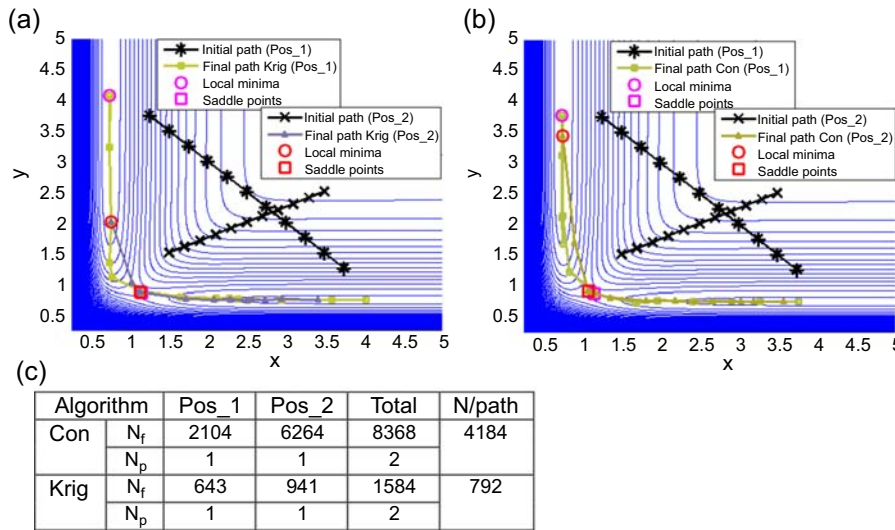


Figure 5.10 Benchmark results by example of LEPS potential function: (a) searching method using true prediction, (b) searching method using GP prediction, and (c) quantitative comparison of the efficiency between two searching methods.

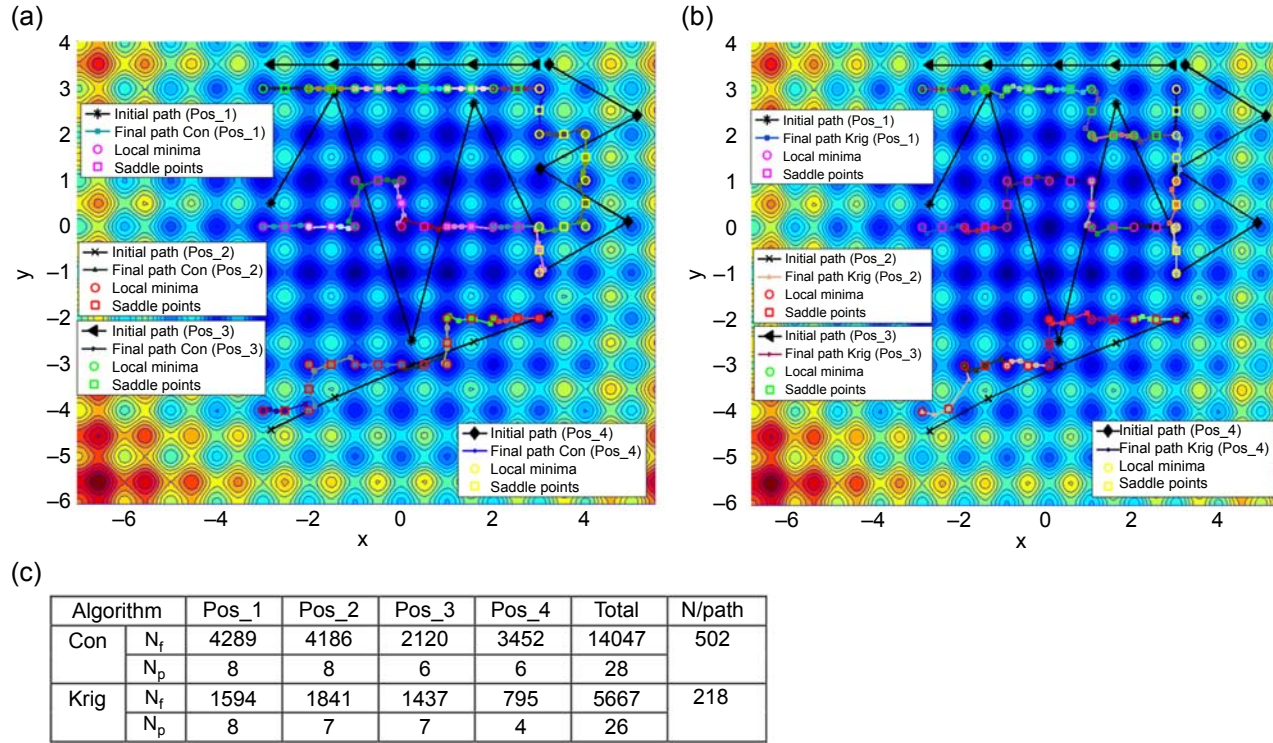


Figure 5.11 Benchmark results by example of Rastrigin function: (a) searching method using true prediction, (b) searching method using GP prediction, and (c) quantitative comparison of the efficiency between two searching methods.

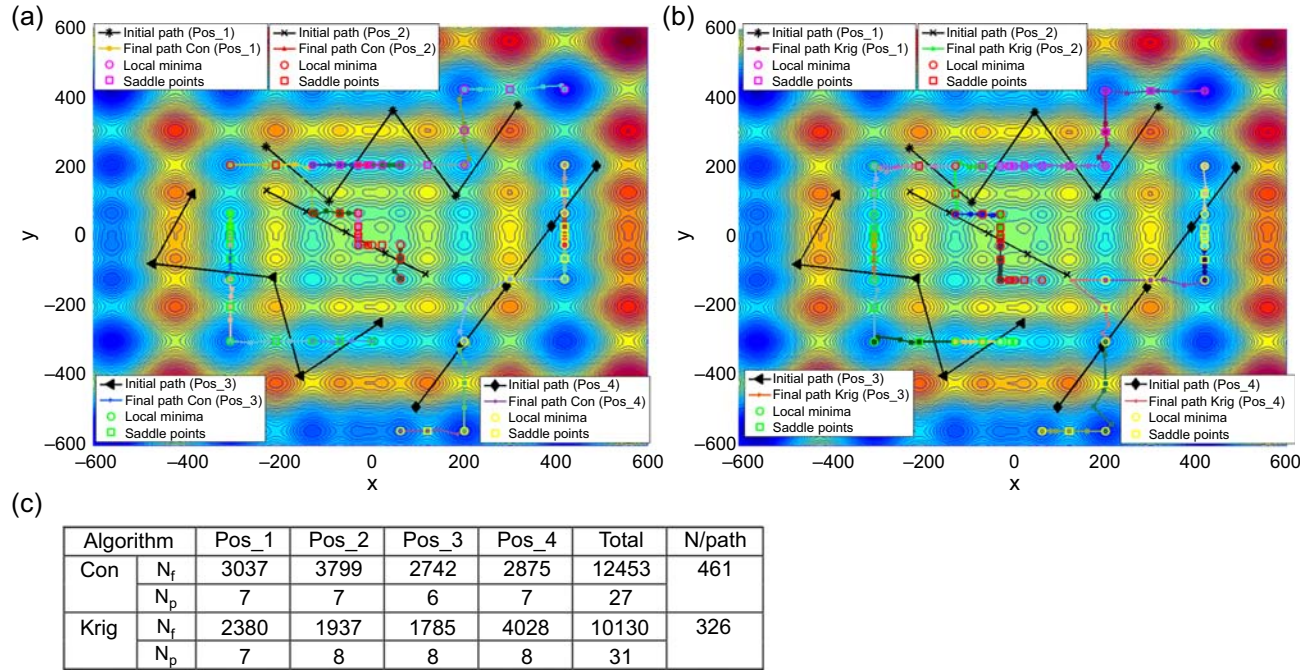


Figure 5.12 Benchmark results by example of Schwefel function: (a) searching method using true prediction, (b) searching method using GP prediction, and (c) quantitative comparison of the efficiency between two searching methods.

Furthermore, the searching methods are verified numerically through three synthetic examples, by searching for the saddle points and local minima that connect together and form a set of Bézier curves.

In this section, analytic functions are used to benchmark and verify the implementation before moving to an actual system. GP-DFT is essentially a machine learning surrogate model for PES and comparable to SNAP [123], HIP-NN [124], and GAP [125], which are all well-known and revolutionary methods in molecular dynamic field. GP-DFT is similar to GAP, but it focuses more on the MEP and saddle point problem instead of molecular dynamics problem. It is also emphasized that the efficiency of GP-DFT is heavily dependent on how well the GP-DFT approximates the underlying potential. In the benchmark study, 2D Rastrigin and Schwefel functions, which are highly nonlinear and multimodal, are used to thoroughly investigate the efficiency of the searching algorithm. Due to the highly nonlinear and multimodal behaviors of these two functions, the improvement ratio N/path is only 2.30 and 1.41, as shown in Figs. 5.11(c) and 5.12(c), for the Rastrigin and Schwefel functions, respectively. However, for simple functions, such as LEPS potential, as presented in Fig. 5.10(c), the N/path ratio is 5.28, showing a strong efficiency of searching on the surrogate model GP-DFT. In summary, the efficiency strongly depends on how well GP-DFT can approximate the underlying function, and a thorough benchmark study is needed to draw a conclusion.

5.4 GP-DFT: a physics-based symmetry-enhanced local Gaussian process

In this section, we describe a physics-based symmetry-enhanced local GP model, called GP-DFT, which exploits the symmetry invariance property of typical DFT calculations during the searching process [126]. The advantages of the GP-DFT model are twofold. The physics-based knowledge is injected to exploit the symmetry invariance property of the material system so that the curse of dimensionality in the high-dimensional PES is mitigated. Second, the GP-DFT is scalable and computationally efficient, compared to the classical GP model. The scalability is a key to search for the saddle points and local minima on the high-dimensional PES.

5.4.1 Symmetry invariance in materials systems

In a material system, an atom is invariant to its own kind in terms of nanoscale atomistic simulations, such as MD simulation and DFT calculations. In MD simulation, the potential energy of the simulation cell does not change when the positions and velocities of two identical atoms are swapped simultaneously. For ground-state DFT calculations, where atomistic velocities are negligible at 0 K temperature, swapping the positions of two identical atoms does not change the potential energy prediction. This symmetry property helps generate $n!$ samples with different inputs, but identical DFT calculation of energy levels. This physical knowledge can be used to significantly reduce the number of samples to construct a high-dimensional PES.

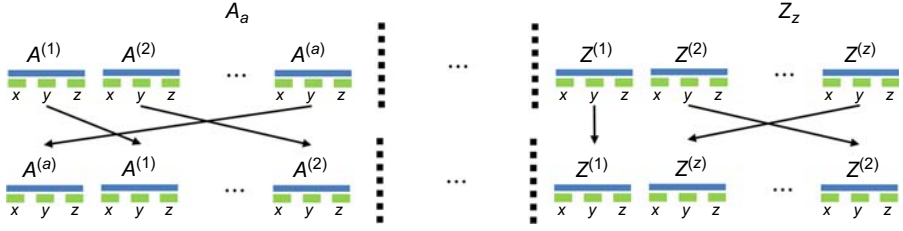


Figure 5.13 A possible permutation of the original input with identical potential energy prediction using DFT calculations for a complex material system.

Fig. 5.13 illustrates the concept of rearranging atomistic positions without alternating potential energy prediction in ground-state DFT for a material system. Let us assume that the chemical composition of the material system is $A_a, B_b, \dots, Z_z$ and enumerate the superscript for each component as the chemical composition of the material system. Suppose that there are a atoms of type A, where atoms $A^{(1)}, A^{(2)}, \dots, A^{(a)}$ are described by their positions (x, y , and z) in the 3D Cartesian system. The atomistic positions of a atoms A, b atoms B, etc., are the inputs of the ground-state DFT calculations. Fig. 5.13 shows one possible permutation of the original input, where atom $A^{(1)}$ is relocated to the position of atom $A^{(2)}$, atom $A^{(2)}$ is relocated to the position of atom $A^{(a)}$, atom $A^{(a)}$ is relocated to the position of atom $A^{(1)}$, atom $Z^{(2)}$ is relocated to the position of atom $Z^{(z)}$, atom $Z^{(z)}$ is relocated to the position of atom $Z^{(2)}$, but the potential energy output is the same for the DFT calculations. For a complex material system as in Fig. 5.13, it is possible to create $(a!b!\dots z!)$ permutations with identical potential energy DFT calculations.

The permutation principle can be used to produce many symmetric configurations that yield the same potential energy of DFT calculations and increase the number of observations for the GP surrogate model. With the large number of permutations, the GP model then can be used to accurately approximate the high-dimensional PES. However, blind usage of the symmetry property would result in a computational bottleneck of the classical GP model, where the cost of storage and computation are evaluated at $\mathcal{O}(n^2)$ and $\mathcal{O}(n^3)$, respectively. Thus, efficient exploitation of the symmetry property is needed and is presented in the next section with the formulation of GP-DFT.

5.4.2 Efficient exploit of symmetry property

Even though the symmetry property is very useful in approximating the high-dimensional PES with the GP model, in practice, the formulation of the classical GP model does not allow the number of observations to go beyond 10^4 data points. Thus, a special treatment is needed to avoid the excessively large dataset. We propose a sorting method, embedded within the GP-DFT framework, to exploit the symmetry property without exhausting the GP model. The main idea is to carefully select a few points using the symmetry property that best support the GP formulation.

Fig. 5.14 illustrates the sorting process to obtain three fictitious DFT inputs which correspond to the same potential energy prediction. In Fig. 5.14, the first DFT input is

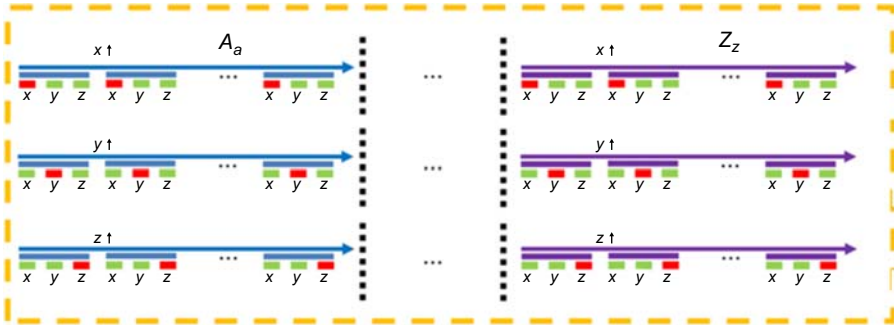


Figure 5.14 Sorting an input for DFT calculations to create three unique inputs that minimize the distance in constructing GP model.

sorted according to the x -coordinates of its vectorization, i.e., $A^{(1)} \leq A^{(2)} \leq \dots \leq A^{(a)}, \dots, Z^{(1)} \leq \dots \leq Z^{(z)}$. In the same manner, the second and third DFT inputs are sorted according to its y - and z -coordinates, respectively. The potential energy prediction using three sorted DFT inputs are evaluated using the GP model. Among these three GP predictions, the one with lowest posterior variance is picked.

The advantages of sorting step are twofold. First, the distances between the sorted DFT inputs are minimized, improving the usage of GP kernel. Recall that the Gaussian kernel, described in Eq. (5.3), is calculated based on the Euclidean distance, ℓ_2 -norm between two vectorized DFT inputs. The minimization of ℓ_2 -norm distance can be mathematically proven through the rearrangement inequality. Second, by avoiding to create a gigantic dataset which goes beyond the capability of GP modeling, the PES dataset is kept at a computationally tractable level, and the efficiency of the GP model construction is maintained.

Theorem (rearrangement inequality [127]).

Let $\mathbf{X}, \mathbf{Y}$ be the sorted configuration of $\mathbf{x}, \mathbf{y}$, respectively, i.e., $\{x_i\}_{i=1}^n = \{X_i\}_{i=1}^n$, $\{y_i\}_{i=1}^n = \{Y_i\}_{i=1}^n$, and

$$X_i \leq X_j \quad \text{and} \quad Y_i \leq Y_j \quad \text{for every} \quad i, j \quad 1 \leq i \leq j \leq n,$$

then $\|\mathbf{X} - \mathbf{Y}\|_2^2 = \arg \min_{\sigma(\mathbf{x}, \mathbf{y})} \|\mathbf{x} - \mathbf{y}\|_2^2$, where $\sigma(\mathbf{x}, \mathbf{y})$ is the set of all possible permutations.

By introducing the sorting function to reorder the DFT input, $(a!b!\dots z!)$ possible combinations are reduced to three. Yet, the effectiveness of GP modeling is preserved. However, for a complex material system with high-dimensional configuration space, as the searching method advances, it is likely to go beyond the scalability threshold, 10^4 number of data points. In order to scope with the scalability, a local GP scheme to dynamically decompose the large dataset is devised to avoid the scalability issue.

5.4.3 Dynamic clustering algorithm for GP-DFT

In Section 5.4.2, by sorting the x -, y -, and z -coordinates separately, from one DFT input, we rearrange and add three equivalent DFT inputs to construct the meta-model GP-DFT. In this section, we present a dynamic clustering algorithm to scope

with the scalability issue, by dynamically decomposing a large dataset for the high-dimensional PES to construct the GP-DFT surrogate model. The algorithm is similar to other local GP algorithms, such as van Stein et al. [52] and Nguyen et al. [53].

Algorithm 1. Sequential construction of clusters given k initial clusters.

Input: new data point $\{\mathbf{x}_{\text{new}}, y_{\text{new}}\}$

```

1  if cluster( $k$ ) $N_{\text{data}} \leq N_{\text{thres}}$  then
2    Add new data point into the last cluster:
3    cluster( $k$ ) $X \leftarrow [\mathbf{x}_{\text{new}}; \text{cluster}(k)X]$ 
4    cluster( $k$ ) $y \leftarrow [y_{\text{new}}; \text{cluster}(k)y]$ 
5    Remove last data point from cluster( $k$ ) $X$  and cluster( $k$ ) $y$ 
6    Increase the counter: cluster( $k$ ) $N_{\text{data}} \leftarrow \text{cluster}(k)N_{\text{data}} + 1$ 
7    if  $N_{\text{fit}} | \text{cluster}(k)N_{\text{data}}$  then
8      Fit the hyperparameter  $\theta$  for every  $N_{\text{fit}}$  of new data points
9    end if
10 else
11   Create ( $k + 1$ ) cluster:
12   cluster( $k + 1$ ) $y \leftarrow \text{cluster}(k)y$ 
13   cluster( $k + 1$ ) $X \leftarrow \text{cluster}(k)X$ 
14   Add new data point into the last cluster:
15   cluster( $k$ ) $X \leftarrow [\mathbf{x}_{\text{new}}; \text{cluster}(k)X]$ 
16   cluster( $k$ ) $y \leftarrow [y_{\text{new}}; \text{cluster}(k)y]$ 
17   Remove last data point from cluster( $k$ ) $X$  and cluster( $k$ ) $y$ 
18   Reset the counter: cluster( $k + 1$ ) $N_{\text{data}} \leftarrow 1$ 
19   Increase the number of cluster:  $k \leftarrow k + 1$ 
20 end if

```

The work flow of the decomposition scheme is shown in Algorithm 4.3. The large PES dataset is decomposed into k smaller clusters, where each cluster corresponds to a local GP. The $(k + 1)$ -th cluster is constructed solely depending on the next to the k -th cluster.

In each cluster, there is a counter of the unique data points N_{data} . If the counter exceeds the predefined threshold for the cluster size N_{thres} , then the new cluster $k + 1$ is created in the following manner. First, the counter N_{data} for the new cluster is reset to 1. Second, the remaining missing data $(N_{\text{thres}} - N_{\text{data}})$ are borrowed from the previous cluster k . Finally, when a new data point is added, one of the borrowed data points is replaced with the new one until the number of unique data points N_{data} reaches the threshold N_{thres} . Then, a new cluster is created again.

As previously mentioned, on each cluster, a local GP model is built. After certain number of steps N_{fit} on each cluster, the hyperparameters θ are recalculated by optimizing the maximum likelihood estimation function. The centroids $\mathbf{c}_k$'s are also updated. It is noteworthy to mention that all the DFT inputs of GP-DFT are sorted independently according to the x -, y -, and z -coordinates.

5.4.4 Prediction using multiple local GP

In this section, a weighted linear average scheme is presented to combine the local GP predictions for the potential energy. Algorithm 4.4 shows the work flow in calculating the predictions, after k local GP clusters are constructed.

Algorithm 2. Prediction using weighted GP from all clusters.

Input: location $\mathbf{x}$, k clusters, and their centroids $\mathbf{c}_l$, $1 \leq l \leq k$

Output: the prediction $\hat{\mathbf{y}}$ at location $\mathbf{x}$ using k clusters

```

1 for  $l \leftarrow 1, k$  do
2   Compute the distance from  $\mathbf{x}$  to all clusters' centroids:
3    $d_l^2 \leftarrow \mathbf{x} - \mathbf{c}_l^2$ 
4   if  $\min_l \{d_l\}_{l=1}^k \neq 0$ 
5     Compute the weights with a radial basis function  $f_{\text{RBF}}(\cdot)$ :
6      $w_l \leftarrow f_{\text{RBF}}(d_l)$ 
7   else
8     Insert a penalized term  $d_{\text{avg}}$  to stabilize  $f_{\text{RBF}}(\cdot)$ 
9     Compute the weights:
10     $w_l \leftarrow f_{\text{RBF}}(d_{\text{avg}}, d_l)$ 
11  end if
12 end for
13 Normalize the weights:
14   $w_l \leftarrow \frac{w_l}{\sum_{l=1}^k w_l}$ 
15 Compute the prediction:
16   $\hat{\mathbf{y}} \leftarrow \sum_{l=1}^k w_l \bar{\mathbf{y}}^{(l)} \triangleright \bar{\mathbf{y}}^{(l)}$  is the GP prediction of  $l$  cluster at  $\mathbf{x}$ 

```

To predict the potential energy $\hat{\mathbf{y}}$ at location $\mathbf{x}$, given k clusters and a local GP model on each cluster, the prediction is given in the form of weighted average as

$$\hat{\mathbf{y}} = \sum_{l=1}^k w_l \bar{\mathbf{y}}_l, \quad (5.8)$$

where $\sum_{l=1}^k w_l = 1$, and $\bar{\mathbf{y}}_l$ is the GP posterior mean of the l -th cluster. Here, the local weight w_l is computed based on a radial basis function $f_{\text{RBF}}(\cdot)$ of the distance d from the query point $\mathbf{x}$ to the centroid of the l -th cluster $\mathbf{c}_l$, i.e., $d = |\mathbf{x} - \mathbf{c}_l|$, for example, inverse distance weight $w_l \propto \frac{1}{d_l^2}$, or Gaussian weight $w_l \propto e^{-\epsilon d_l^2}$. The main principle for choosing an appropriate weight function is that the closer the location to the centroid of the l -th cluster, the more accurate prediction one can obtain from this GP prediction. As the searching method advances, the location point $\mathbf{x}$ for prediction tends to be away from the initial dataset. With the formalism of dynamic and sequential construction scheme for the cluster, only the last few clusters contribute meaningful predictions to the location $\mathbf{x}$.

In case the prediction is at the centroid of one or several clusters, a penalizing term is inserted to the denominator to avoid numerical instabilities. The posterior variance can be computed as

$$\hat{\sigma}^2 = \sum_{l=1}^k w_l^2 \bar{\sigma}_l^2, \quad (5.9)$$

where σ_l^2 is the posterior variance of the l -th local GP cluster, assuming that data in clusters are independently sampled.

5.5 Application: hydrogen embrittlement in iron systems

In this section, the proposed methods are applied to study the hydrogen embrittlement in iron systems, Fe_8H and FeTiH . A MATLAB and VASP [7–10] interface is developed to couple the implementation of the searching methods and the potential energy calculations.

5.5.1 Hydrogen embrittlement in FeTiH

FeTi experiences transition from a body-centric structure to an orthorhombic state where it can hold two hydrogen (H) atoms. FeTi has CsCl-type structure which corresponds to $Pm\bar{3}m$ space group with a lattice parameter of 2.9789 Å. Fig. 5.15(a) shows four unit cells of the FeTi structure at its initial state, where the unit cell is a body-centered structure with the Ti atoms at the center and Fe atoms at the corners. Fig. 5.15(b) shows one of the possible final states when two H atoms are absorbed in each unit cell forming the structure of FeTiH . It is noted that because periodic boundary condition is applied on the simulation cell, the computational domain is invariant with respect to translation. And either Fe or Ti can be at the center of the simulation cell. The unit cell of FeTiH is an orthorhombic structure of dimension $a = 2.956$ Å, $b = 4.543$ Å, and $c = 4.388$ Å. The Fe atoms occupy the corner and the center position of the front and back face. The Ti atoms reside at the center of the rest of faces and the H atoms are located on two side faces. Notice that Fig. 5.15(b) shows two unit cells of FeTiH , which correspond to four unit cells of FeTi .

The unit cell for both initial and final structures is defined as $a = 2.956$ Å, $b = 4.543$ Å, and $c = 4.388$ Å. The coordinate of the intermediate images are obtained by linear interpolation of the coordinate of the initial and final images. To demonstrate the capability of the concurrent searching method to locate stable states, we slightly

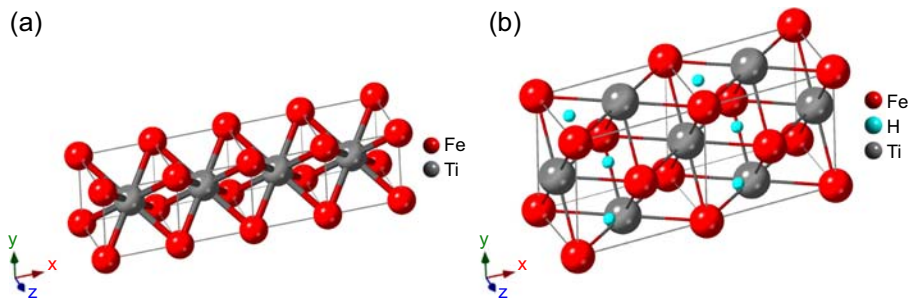


Figure 5.15 Comparison between FeTi and FeTiH . (a) FeTi bcc structure with lattice constant of 2.9789 Å. (b) A possible FeTiH stable orthorhombic structure of dimension $a = 2.956$ Å, $b = 4.543$ Å, $c = 4.388$ Å.

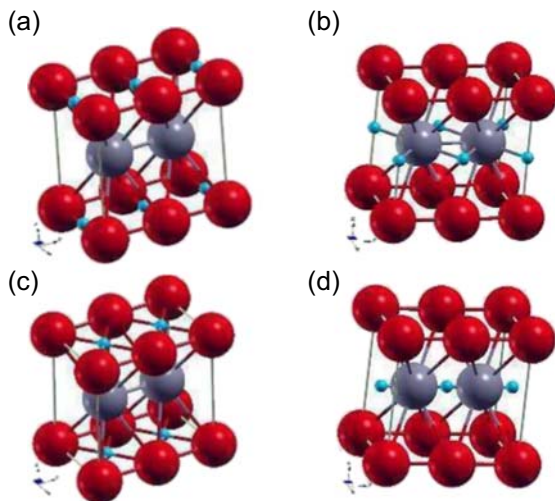


Figure 5.16 Initial structures of FeTiH with H atoms located at the (a) Fe–Fe bridge along the first primitive lattice vector, (b) Fe–Fe bridge along the third primitive lattice vector, (c) center of the (001) surface, and (d) center of the (010) surface.

shift the hydrogen atoms from the equilibrium positions as the initial images, which are shown in Fig. 5.16. Four corresponding initial guesses of transition paths are formed on the PES hypersurface, and the concurrent searching method is then performed.

The total energy of the system and the forces on each atom are calculated based on DFT calculation using VASP. The projector-augmented wave potentials, specifically LDA potentials, are used here. The convergence test for the k-point sampling with respect to the total energy shows that $26 \times 13 \times 13$ gamma-centered grid of k-point sampling is adequate for study of FeTiH structure. Here, to reduce the computational time, we use a k-point sampling of $4 \times 2 \times 2$ for all the three scenarios. The relaxation of the electronic degree of freedom is stopped if the total free energy change and the change of eigenvalues between two steps are both smaller than 10^{-4} . First order Methfessel–Paxton scheme is utilized, where the smearing width is left to a default value of 0.2 eV.

The located MEPs for the four initial curves are plotted in terms of total energy (eV) with respect to the reaction coordinates which are shown in Fig. 5.17. Here, reaction coordinate which is an abstract one-dimensional coordinate to represent the progress of the atomic configuration along the transition path is used to show the relative distribution of the images along the path. The E_I and E_S are the total energy at the initial states and transition states (i.e., saddle points with highest energy or global saddle points along the transition path). The ΔE represents the activation energy. The square markers in red are the local minima and the round markers in blue are the saddle points. The asterisk markers are intermediate images along the MEPs. Each curve section in different color represents a substage transition path. For example, in Fig. 5.17(b), there

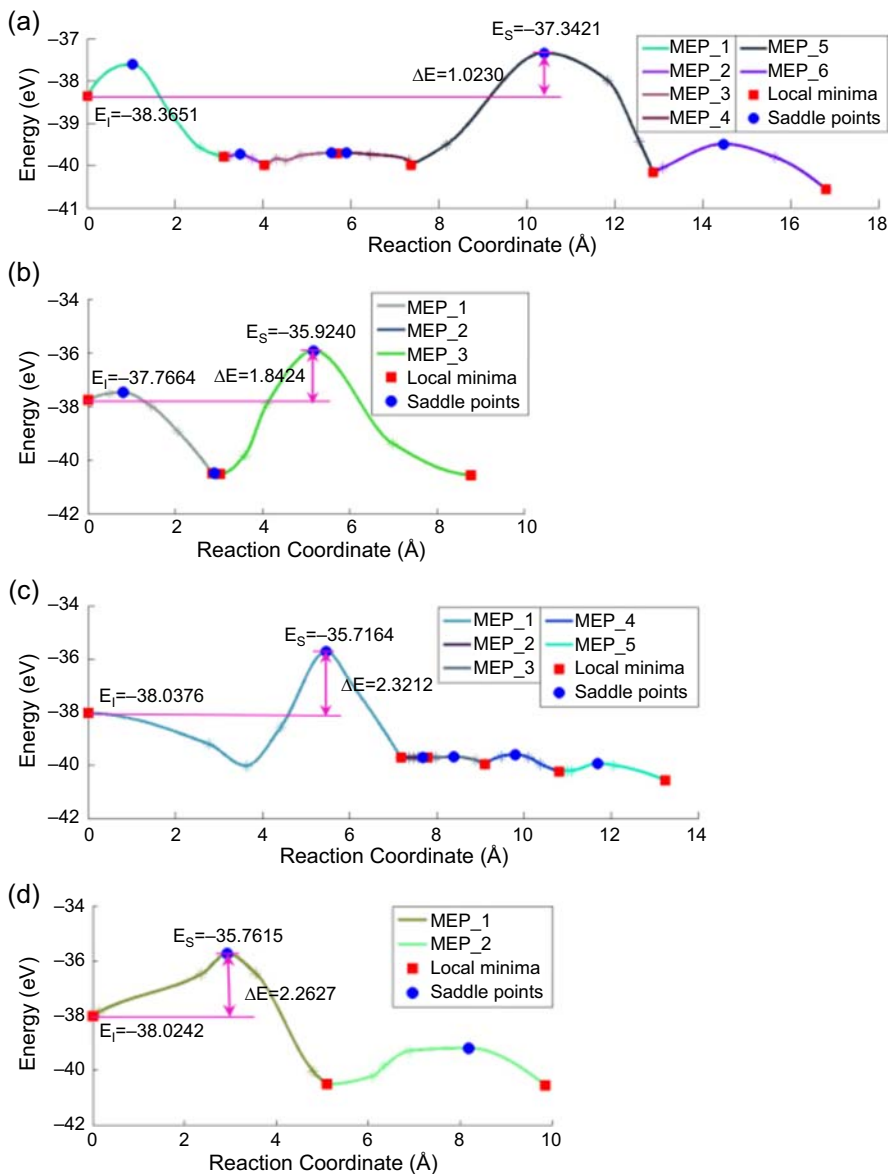


Figure 5.17 Minimum energy paths obtained by the concurrent search algorithm for hydrogen diffusion in the FeTiH structure starting from different initial structures with hydrogen locating at (a) the Fe-Fe bridge along the first primitive lattice vector, (b) Fe-Fe bridge along the third primitive lattice vector, (c) center of the (001) surface, and (d) center of the (100) surface, to the same final orthorhombic structure.

are three substage curves which are shown in blue, dark green, and purple. For the first initial curve, the algorithm locates six MEPs with seven local minima and six saddle points which are shown in Fig. 5.17(a). The activation energy ΔE is the energy difference between the saddle point with highest energy (i.e., global saddle point along the transition path) and the initial state. The global saddle point is the one on the fifth MEP with the total energy of -37.3421 eV. The total energy of the initial structure is -38.3651 eV. Thus, the activation energy for the transition from the initial structure with hydrogen atoms located at the Fe–Fe bridge along the first primitive lattice vector to the final orthorhombic structure (i.e., FeTiH_tran_a) is 1.0230 eV.

Similarly, for the second initial curve, the algorithm locates three MEPs with four local minima and three saddle point which are shown in Fig. 5.17(b). The total energy for the initial structure is -37.7664 eV and for the global saddle point is -35.9240 eV. The activation energy for the transition from the initial structure with hydrogen locating at the Fe–Fe bridge along the third primitive lattice vector to the final orthorhombic structure (i.e., FeTiH_tran_b) is 1.8424 eV. For the third initial curve, the algorithm locates five MEPs with six local minima and five saddle points which are shown in Fig. 5.17(c). The total energy for the initial structure and saddle point is -38.0376 eV and -35.7164 eV. The activation energy for the transition from the initial structure with hydrogen locating at the center of the (001) surface to the final orthorhombic structure (i.e., FeTiH_tran_c) is 2.3212 eV. For the fourth initial curve, the algorithm locates two MEPs with three local minima and two saddle points which are shown in Fig. 5.17(d). The total energy for the initial structure is -38.0242 eV and for the saddle point is -35.7615 eV. The activation energy for the transition from the initial structure with hydrogen locating at the center of the (010) surface to the final orthorhombic structure (i.e., FeTiH_tran-d) is 2.2627 eV.

The experimental result of the activation energy for the diffusion of hydrogen in the β phase FeTiH is 1.0 ± 0.05 eV per H_2 [128]. The transition process from the initial structure in Fig. 5.16(a) with hydrogen located at the Fe–Fe bridge along the first primitive lattice vector to the final structure has the lowest energy barrier with the activation energy of 1.023 eV. The difference between the calculated activation energy and the experimental one is only 2.3% . The activation energies for the other three transitions starting from the initial positions in Fig. 5.16(b–d) are all higher than the experimental one. The result can be explained as follows. First, the formation of the β phase FeTiH includes two steps which are (1) adsorption of the free hydrogen onto the free surface of iron–titanium alloy FeTi and (2) the hydrogen diffusion in the FeTiH system. The transition paths obtained here are possible diffusion paths which could happen in step 2, depending on external conditions. The initial structures of these transition processes are the final products of the adsorption process of step 1. The theoretical study using DFT calculation shows that there are many possible hydrogen adsorption sites on the free surface of iron–titanium alloy, and the hydrogen position in the initial structure in Fig. 5.16(a) is one of the favorite adsorption sites [129]. This explains that the transition FeTiH_tran-a has a higher probability of occurring in physical world than the rest three transitions. In other words, the process captured by the experiment will most likely be the transition FeTiH_tran-a. Second, according to the hTST, the lower the activation energy for one transition is, the higher the probability that the transition will occur.

This also explains that the transition in the experiment will be the FeTiH-tran-a. In addition, this indicates that the activation energies of the other three transitions should be higher than the transition FeTiH-tran-a; otherwise, the transition with the lowest activation energy should occur during the experiment. In summary, the computational results for the hydrogen diffusion process here match well with the experimental results. Compared to single-path search, exploring many possible paths simultaneously can increase the chance of finding the real transition path and reducing the error of activation energy estimation.

Figs. 5.18–5.21 show the detailed transition paths for the atoms in one unit cell along the MEPs in transitions FeTiH-tran-a, FeTiH-tran-b, FeTiH-tran-c, and

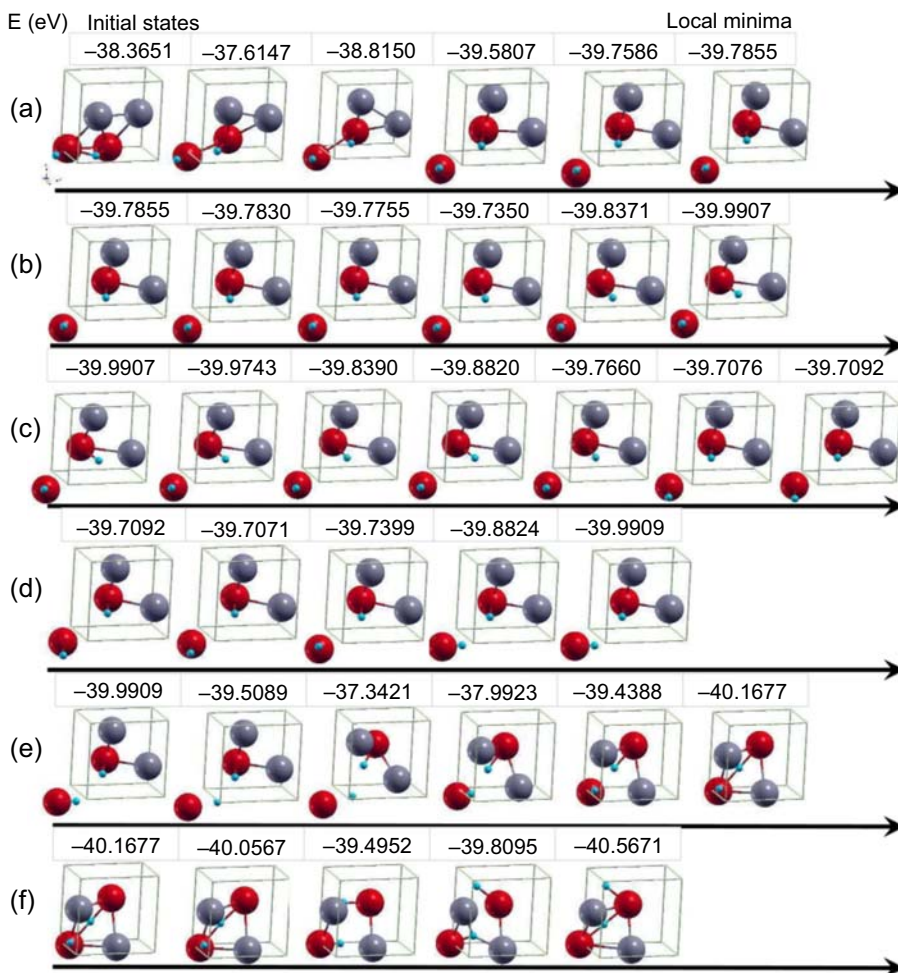


Figure 5.18 Detailed atomic configuration transition of hydrogen atoms in FeTiH for FeTiH-tran-a: (a) MEP-1, (b) MEP-2, (c) MEP-3, (d) MEP-4, (e) MEP-5, and (f) MEP-6 obtained by the concurrent search algorithm.

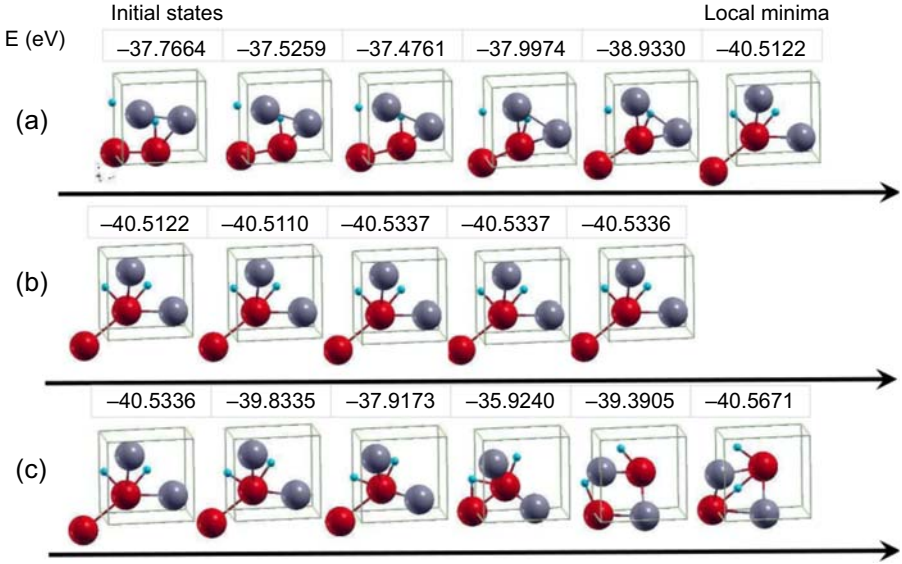


Figure 5.19 Detailed atomic configuration transition of hydrogen atoms in FeTiH for FeTiH-tran-b: (a) MEP-1, (b) MEP-2, and (c) MEP-3 obtained by the concurrent search algorithm.

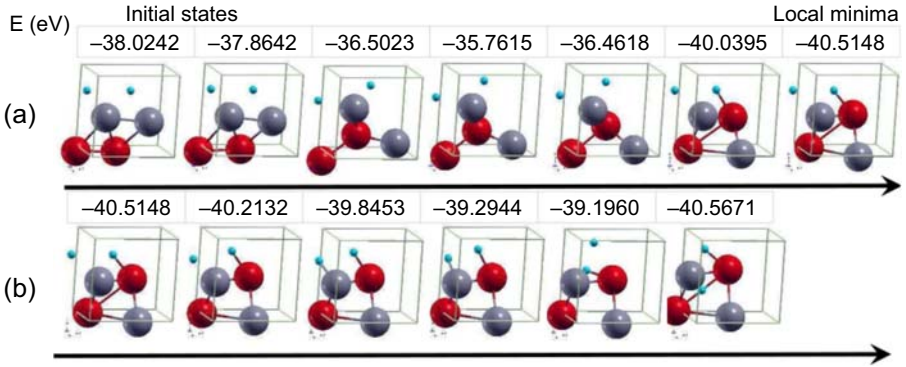


Figure 5.20 Detailed atomic configuration transition of hydrogen atoms in FeTiH for FeTiH-tran-c: (a) MEP-1 and (b) MEP-2 obtained by the concurrent search algorithm.

FeTiH-tran-d, respectively. The energy levels of the intermediate images are also shown, which correspond to the markers in Fig. 5.17. The energy values in bold text are the local minima, and the energy values in bold italic text are the saddle points.

5.5.2 Hydrogen embrittlement in pure bcc iron, Fe^8H

Here we study the diffusion process of hydrogen atoms in pure body-centered iron with a lattice parameter of 2.86 Å. There are two possible sites that H atoms reside

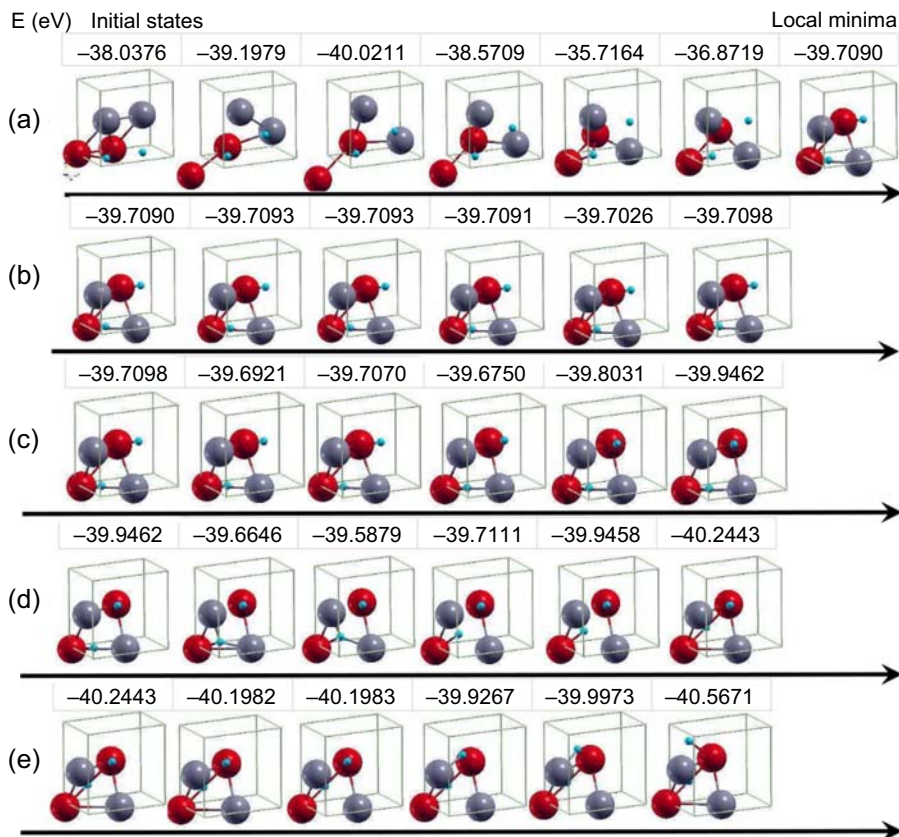


Figure 5.21 Detailed atomic configuration transition of hydrogen atoms in FeTiH for FeTiH-tran-d: (a) MEP-1, (b) MEP-2, (c) MEP-3, (d) MEP-4, and (e) MEP-5 obtained by the concurrent search algorithm.

in the body-centered iron. One is octahedral site, and the other is tetrahedral site which are shown in Fig. 5.22(a) and (b). The big black dots represent the metal atoms in a body-centered unit cell. The small blue dots in Fig. 5.22(a) are the octahedral site and those in Fig. 5.22(b) are tetrahedral site. Both experimental and theoretical studies have been conducted to uncover the favorite site for hydrogen. Some [130–132] found that hydrogen atoms prefer to reside at the tetrahedral site, whereas others [133] showed that the preferable site is the octahedral site. Some studies [134] discovered that there is no preference between these two sites. Here, we use a supercell with four unit cells which include a total of eight Fe atoms. Since it is generally believed that hydrogen has low solubility in body-centered iron, we assume that there is only one hydrogen atom in the supercell (Fe^8H). We study the diffusion process of the hydrogen from one octahedral site to the tetrahedral site and two other octahedral sites within the supercell.

The lattice parameter for the unit cell (Fe^8H) is set to be $a = 5.72 \text{ \AA}$, $b = 2.86 \text{ \AA}$, and $c = 5.72 \text{ \AA}$ for both initial and final structures. Fig. 5.23 shows the initial structure

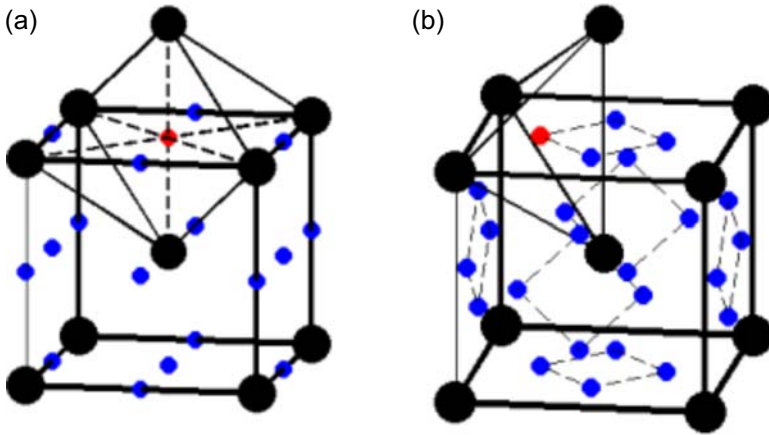


Figure 5.22 The interstitial sites in a body-centered lattice with metal atoms (*large black dot*): (a) octahedral site (*small blue dot*) and (b) tetrahedral site (*small blue dot*).

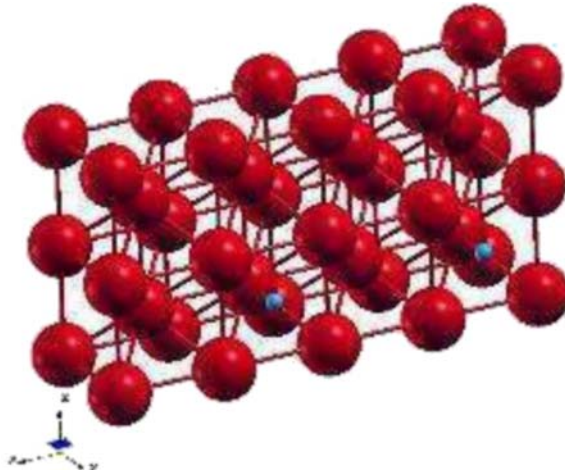


Figure 5.23 Two unit cell of the initial structure with hydrogen residing on the octahedral site.

with hydrogen residing on one of the octahedral site. The total energy of the system and the forces on each atom are calculated based on DFT calculation using VASP. The projector-augmented wave potentials, specifically LDA potentials, are used here. The convergence test for the k-point sampling with respect to the total energy shows that $13 \times 26 \times 13$ gamma-centered grid of k-point sampling is adequate for study of Fe^8H structure. Here, to reduce the computational time, we use a k-point sampling of $2 \times 4 \times 2$ for all the three scenarios. The relaxation of the electronic degree of freedom is stopped if the total free energy change and the change of eigenvalues between two steps are both smaller than 10^{-4} . First order Methfessel–Paxton scheme is utilized, where the smearing width is left to a default value of 0.2 eV. Fig. 5.24 shows three possible final structures with hydrogen residing on the (a) tetrahedral site on the (100) surface, (b) octahedral site on the (001) surface, and

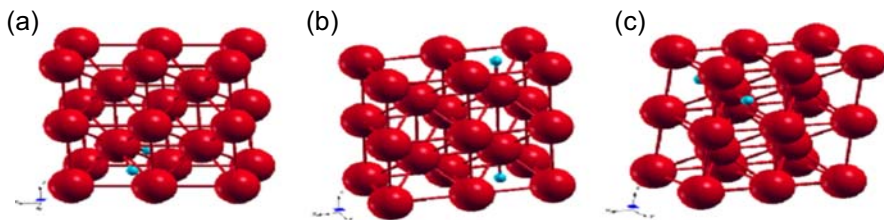


Figure 5.24 Final structure with hydrogen residing at (a) tetrahedral site on the (100) surface, (b) octahedral site on the (001) surface, and (c) octahedral site on the (100) surface.

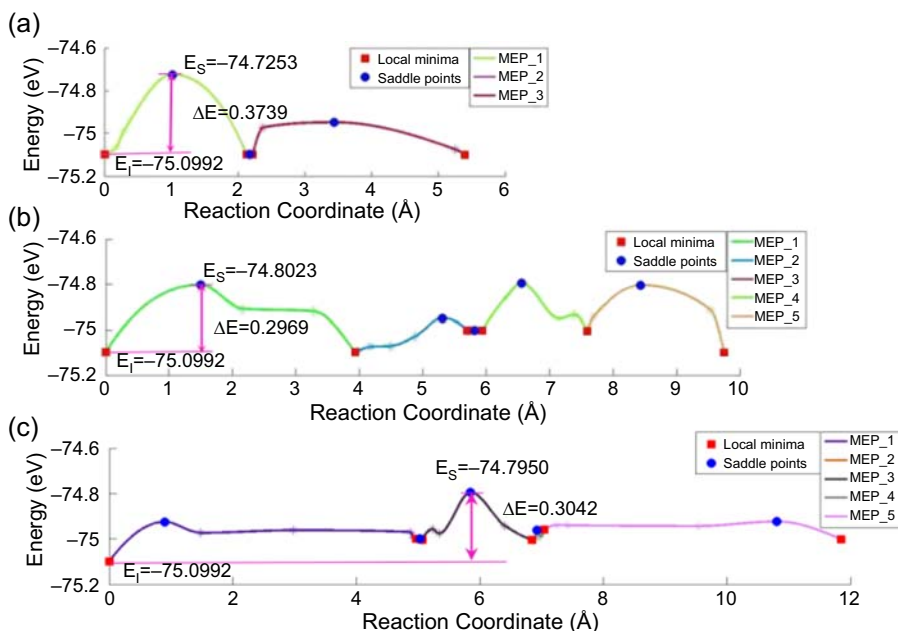


Figure 5.25 Minimum energy paths obtained by the concurrent search algorithm for hydrogen diffusion in Fe⁸H structure starting from the initial structure to final structures with hydrogen residing at (a) tetrahedral site on the (100) surface, (b) octahedral site on the (001) surface, and (c) octahedral site on the (100) surface.

(c) octahedral site on the (100) surface. The coordinates of the intermediate images are obtained by linear interpolation of the coordinate of the initial and final states. To demonstrate the algorithm's capability to locate stable states, we slightly shift the hydrogen atoms from the equilibrium positions which are shown in Figs. 5.23 and 5.24. For the purpose of convenient reference to the four transition paths in the following paragraphs, we refer the transition from the initial structures in Fig. 5.23 to the final structures in Fig. 5.24(a)–(c) as Fe⁸H-tran-a, Fe⁸H-tran-b, and Fe⁸H-tran-c, respectively.

The located MEPs for the three initial curves are plotted in Fig. 5.25, where the total energy (eV) with respect to the reaction coordinate is shown. For the first initial curve,

the algorithm locates three MEPs with four local minima and three saddle points which are shown in Fig. 5.25(a). The global saddle point is the one on the first MEP with the total energy of -74.7253 eV. The total energy of the initial structure is -75.0992 eV. Thus, the activation energy for the transition from the initial structure to the final structure with hydrogen residing at tetrahedral site on the (100) surface (i.e., $\text{Fe}^8\text{H-tran-a}$) is 0.3739 eV. For the second initial curve, the algorithm locates five MEPs with six local minima and five saddle points which are shown in Fig. 5.25(b). The total energy for the initial structure is -75.0992 eV. The global saddle point is the one on the first MEP with the total energy of -74.8023 eV. The activation energy for the transition from the initial structure to the final structure with hydrogen residing on the octahedral site on the (001) surface (i.e., $\text{Fe}^8\text{H-tran-b}$) is 0.2969 eV. For the third initial curve, the algorithm locates five MEPs with six local minima and five saddle points which are shown in Fig. 5.25(c).

The total energy for the initial structure is -75.0992 eV. The global saddle point is the one on the third MEPs with the total energy of -74.7950 eV. The activation energy for the transition from the initial structure to the final structure with hydrogen residing at the octahedral site on the (100) surface (i.e., $\text{Fe}^8\text{H-tran-c}$) is 0.3042 .

The experimental results for the activation energy of the hydrogen diffusion in the iron are significantly affected by the impurities of the iron used for the study. Thus, the activation energy from the experiments conducted by 10 research groups around the world are scattered from 0.035 to 0.142 eV, which are included in by Hayashi and Shu [135]. The small activation energy indicates that the hydrogen atoms can diffuse easily in iron. The results for all three transitions are out of the range with a higher activation energy, which does make sense since the algorithm could locate the transition paths with higher activation energy.

Figs. 5.26–5.28 present the detailed transition paths for one unit cell along the MEPs in the transition $\text{Fe}^8\text{H-tran-a}$, $\text{Fe}^8\text{H-tran-b}$, and $\text{Fe}^8\text{H-tran-c}$, respectively.

5.5.3 Hydrogen embrittlement in pure bcc iron, Fe^8H , using GP-DFT

In this example, we use the physics-based model to improve the searching method with GP by a simple observation: if two atoms of the same kind, i.e., Fe, swap their positions, the calculated potential energy in the simulation cell is the same. Therefore, the enumeration labeling does not affect the output results. This hypothesis has been examined and the observation was confirmed. However, in GP model, the distance between designed sites has a significant impact on its interpolation results. That is, the shorter distance the inputs are compared to each other, the higher the resolution that GP model can achieve. In this Fe^8H system, there are $8! = 40,320$ geometric configurations that yield the same potential energy.

In this simulation, the cluster size N_{data} is set at 721. The cluster size is chosen so that it is less than 1000, but very close to the least common multiple of 2, 3, 4, 5, and 6 so that the N_{fit} parameter for fitting procedure can be easily chosen from these numbers. The number of DFT calculations is 1598. For every $N_{\text{fit}} = 4$ steps, the hyperparameters in the last cluster are updated.

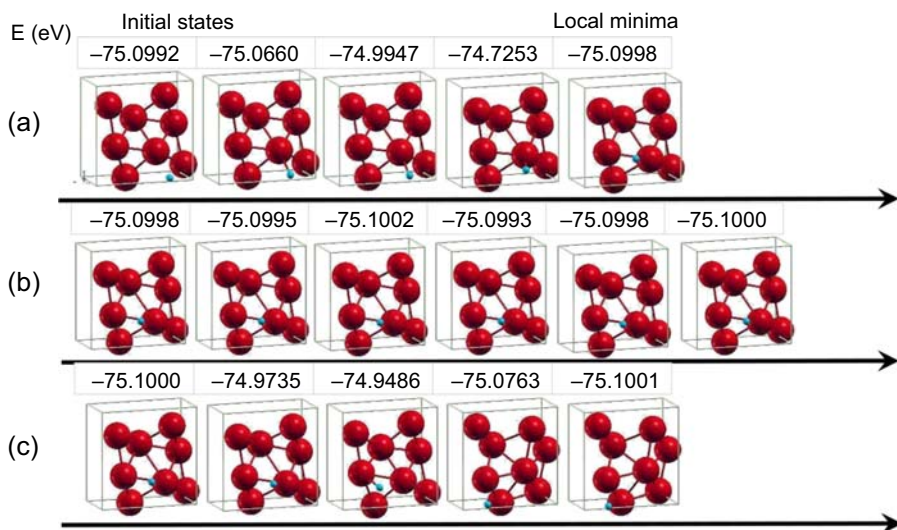


Figure 5.26 Detailed atomic configuration transition of hydrogen atoms in Fe-8H for Fe-8H-tran-a: (a) MEP-1, (b) MEP-2, and (c) MEP-3 obtained by the concurrent search algorithm.

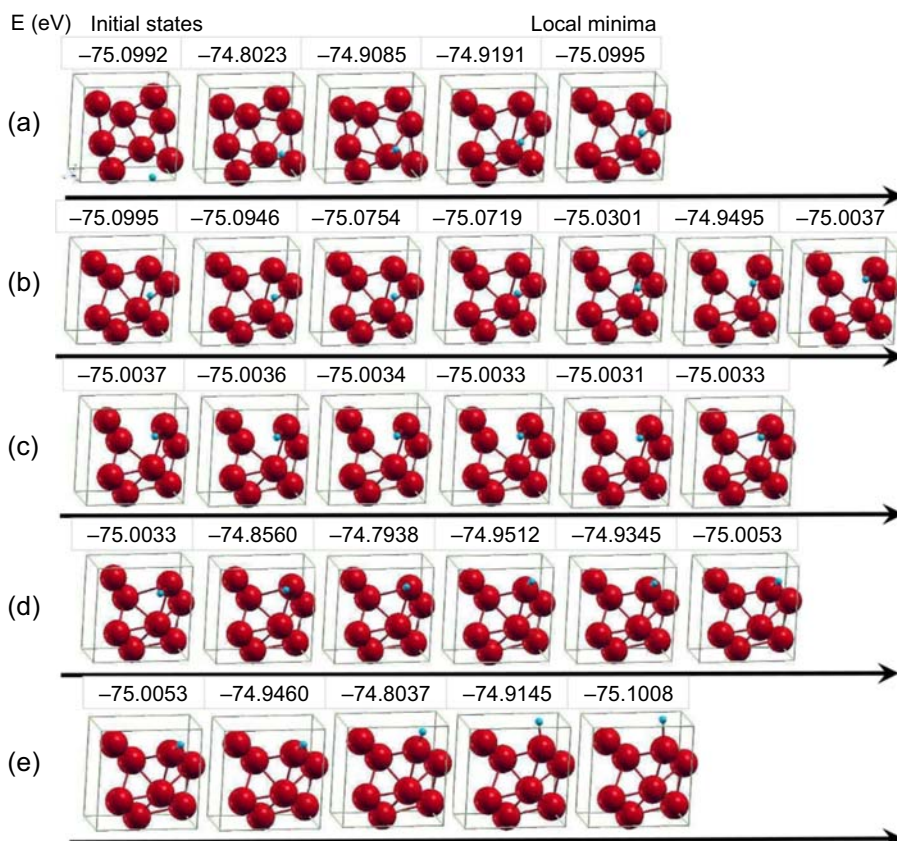


Figure 5.27 Detailed atomic configuration transition of hydrogen atoms in Fe-8H for Fe-8H-tran-b: (a) MEP-1, (b) MEP-2, (c) MEP-3, (d) MEP-4, and (e) MEP-5 obtained by the concurrent search algorithm.

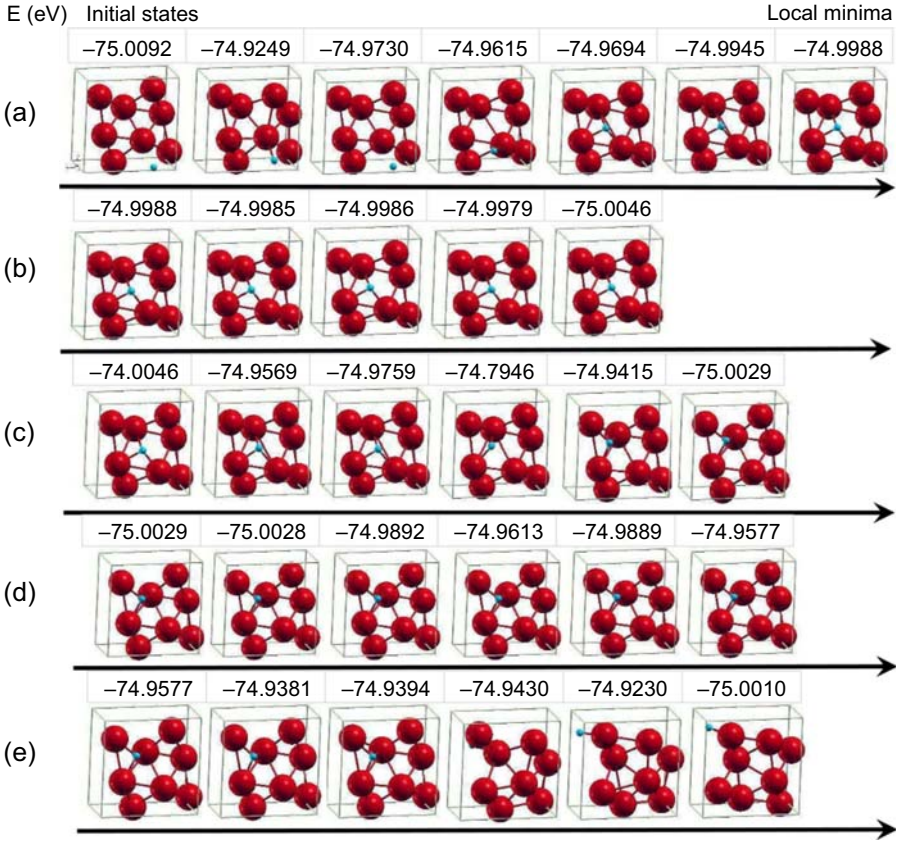


Figure 5.28 Detailed atomic configuration transition of hydrogen atoms in Fe-8H for Fe-8H-tran-c: (a) MEP-1, (b) MEP-2, (c) MEP-3, (d) MEP-4, and (e) MEP-5 obtained by the concurrent search algorithm.

In our study, the variances of clusters are roughly of the same scale, and the exponential weights decay rapidly to zero without the shape parameters in the exponent, leading to numerical instability issues. Thus, the inverse distance weight function is used to compute the weight, i.e., $w_l = \frac{1}{d_l^2}$, where d_l is the distance from the query point to the l -th cluster. The penalized parameter d_{avg}^2 is set at $0.25 \cdot \left(\max_l \{d_l\}_{l=1}^k \right)^2$. The uncertainty of the searching method, particularly the predicted energy levels at local minima and saddle points, and the MEP are assessed based on Eq. (5.9). The GP-DFT model not only helps to predict the potential energy from DFT calculations but also its first partial derivatives with respect to each of the atom positions.

Fig. 5.29 shows the transition pathways obtained by the searching method using the GP-DFT model. The corresponding configurations at different states are also presented corresponding with the local minima and saddle points of the transition path. Table 5.3 presents the potential energy of the local minima, saddle points, and control points

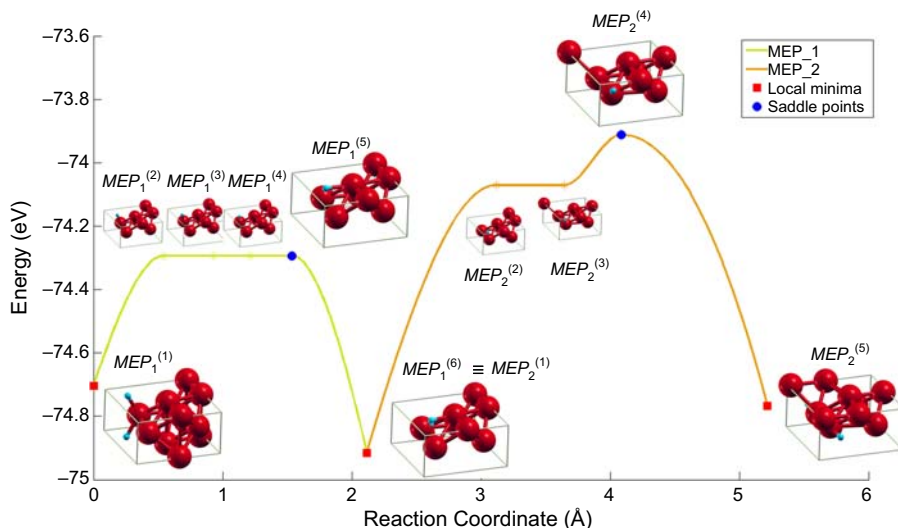


Figure 5.29 Transition pathway with local minima and saddle points from initial to final states and its corresponding configurations for Fe^8H system. The saddle points are denoted as *circles*, whereas the local minima are denoted as *squares*.

along the curve of MEP_1 and MEP_2 . The uncertainty associated with the saddle point energy is also indicated by the posterior variance or standard deviation (Std. Dev.). The activation energy is calculated to be 1.004 eV. The computational time is about 31 h, using four processors for parallel DFT calculations. The covariance matrix size is 721×721 for each of the two clusters. The GP-DFT framework breaks the covariance matrix in the classical GP into several covariance matrices, one for each GP model on each cluster. The covariance matrix has a fixed constant size. By doing so, the fitting hyperparameters can be calculated at a cheaper computational price.

5.6 Discussions

As mentioned in [Section 5.3.2](#), the single-path searching method can miss some important paths between two stable states when the dimension of PES is high. The ideal case is that all the possible paths on the PES are located, which can give us a better overview of the energy landscape of the system. Once all of the local minima and saddle points are identified, the transition path that requires the least energy can be located accurately. Exploring the complete energy landscape however is a challenge to the single-path searching methods. The result can be sensitively dependent on the initial path that is chosen to start with. Different initial guesses for the transition path are necessary in order to locate all the transition paths on the PES. This trial procedure is computationally expensive. One trial with different initial guesses from previous trials may locate some transition paths which are already identified by the previous trials, since for each trial they can converge to several transition paths, particularly

Table 5.3 Potential energy of the configurations in Fig. 5.29 and their standard deviations.

		Configuration number					
		1	2	3	4	5	6
Potential energy	MEP ₁	−74.7027	−74.2947	−74.2945	−74.2943	−74.2942	−74.9158
	Standard deviation	3.2652	3.2825	3.2951	13.5816	13.5033	3.3306
	MEP ₂	−74.9158	−74.0713	−74.0712	−73.9122	−74.7660	
	Standard deviation	3.3306	13.4424	13.3451	13.2758	12.9051	

for the complex PES in the high-dimensional search space. As a result, it is difficult to assess whether all the transition paths are located or not. To solve this issue, the curve swarm algorithm is developed to exhaustively search the local minima and saddle points within a searching area simultaneously.

The curve swarm algorithm improves the accuracy of searching. Yet the searching process is still challenging because of its high computational cost. A large number of energy evaluations are needed for DFT. A fundamental issue in most of saddle searching algorithms is that there is a lack of memory of searching history. The searching history can help guide the searching process and improve the efficiency. Therefore, surrogate modeling is a good tool to keep the searching history in memory by building a response surface globally. GP modeling is applied to build the surrogate. At the same time, it keeps track of the uncertainty level. Searching the minima and saddle points can be on the surrogate with very fast evaluation instead of running DFT simulation each time. Constructing GP models in high-dimensional space requires a large number of samples and the expensive computation of the inverse of the covariance matrix prohibits GP modeling in large problems. In the proposed GP-DFT scheme, a parallel and distributed GP modeling approach and physics-based dimensionality reduction are taken to mitigate the scalability issue.

Several advantages of the GP-DFT framework are highlighted as follows. First, GP-DFT exploits the symmetry property of the material system by injecting physical knowledge. GP-DFT rearranges the DFT inputs by sorting them independently according to the coordinates, and thus creating three sampling locations for one DFT calculations. The sorting step is crucial to avoid the scalability issue and maximize the capability of GP formulation at the same time. Second, a dynamic clustering scheme is devised to sequentially construct a local GP cluster and combine them using a weighted linear average scheme. The clustering scheme is built on the divide-and-conquer approach to solve for the scalability issue, which is the main computational bottleneck for GP framework. Third, GP-DFT is a data-driven (or machine learning) approach so that the searching method is accelerated through the “real-surrogate-real” feature. In addition, the concurrent searching method parallelizes the traditional searching method. Thus, the new searching algorithm is accelerated with two distinct features: parallel search and searching on a surrogate model. Fourth, the GP-DFT is enhanced with UQ feature, so that the error bar can be estimated for the prediction. Finally, the searching process can be embarrassingly parallelized by the curve swarm algorithm, as opposed to a single curve approach, including one single-ended and double-ended method. The curve swarm algorithm, along with the data-driven GP-DFT surrogate approach, provides two types of acceleration to improve the efficiency of the searching process. Dislocations at the atomic level are represented by atomic entities, such as atomic positions do not break symmetry as long as the atoms are identical in the DFT simulation. The symmetry that we use in this context does not mean the same with symmetry in materials, particularly in crystal, such as point groups or Laue symmetry.

Compared to other surrogate models, the GP model is chosen because of two reasons. First, it is an adaptive data-driven approach that is capable of quantifying uncertainty. Only a few possess this capability. Second, it is well known for its

accuracy in approximation because of a rigorous mathematical foundation, namely the best linear unbiased predictor.

While the idea of using GP models to support saddle point search is promising with the advantages of computational time and the simple reconstruction of PES, there are several challenges in the current state of the search method. First, even though the GP-DFT can compute the energy level quickly compared to the classical DFT method, the uncertainty associated with GP-DFT is typically higher because GP-DFT has significantly fewer data points, hence a larger standard deviation. Additionally, the uncertainty is amplified in high-dimensional PES. However, the location of saddle points is assured by the gradients of PES, whose gradient vectors contain mostly zero components. The scalability and accuracy of GP framework remains the most important problem in large-scale dataset. There is trade-off between scalability and accuracy, in the sense that if the scalability is improved, the accuracy is likely to degrade, and vice versa. The proposed GP-DFT surrogate model for searching saddle points with DFT calculations has good scalability, yet only achieves the intermediate level of accuracy. Future work is needed to improve the accuracy aspect of the GP-DFT, including the choice of weights in GP-DFT. Another future extension is the consideration of stochastic GP [136], where input uncertainty is included and composite GP [137], where the global trend and local details are captured separately.

The accuracy of GP-DFT strongly depends on the number of training points. The larger the dataset is, the more accurate the GP-DFT is. At the exact training locations, the difference between the GP-DFT and the full DFT calculations or the prediction error is zero. In addition, the error also depends on the locations of the training points and how far away the unknown input from the whole training dataset is. Asymptotically, when the number of training points reaches infinity, the prediction error is zero. For convergence rate, we refer interested readers to the seminal work of Rasmussen [138] on GP.

However, there are also several shortfalls of GP-DFT. One of the main drawbacks is that the GP-DFT model is nontransferable, in the sense that if the GP-DFT is trained using one particular DFT simulation, it is not transferable to another DFT simulation even with the same set of chemical elements. The issue is rooted with the atomic positions as the representation of GP-DFT. If the number of atoms changes, a new GP-DFT model is required from scratch. Thus, the capability of GP-DFT is limited and unappealing for any scale-bridging problems, such as bridging from DFT to molecular dynamics. One way to remove this limitation is to integrate the bispectrum descriptor as in GAP [125,139] and SNAP [123]. The bispectrum of the neighbor density mapped onto the three spheres forms the basis for SNAP and GAP, which have been shown to be invariant under rotation and translation. These properties make the bispectrum descriptor suited for atomic computational materials models with the periodic boundary condition, posing an interesting direction for future work. The interatomic force, which is the directional derivative of the PES, can also be included during the process of constructing GP-DFT. However, including derivatives in GP is nontrivial and poses as another potential direction for future work.

5.7 Conclusion

In this chapter, a curve swarm saddle point searching method is developed, and the efficiency is further improved with distributed GP surrogate modeling to accelerate the searching process. Two computational materials examples of hydrogen embrittlement in metal are used to demonstrate the effectiveness of the proposed method.

The curve swarm searching method shows a global approach to search for minima and saddle points on PES. The coordination between curves ensures the completeness of searching results with all possible transition paths. At the same time, the incorporation of GP framework into saddle point search is achieved where the efficiency of the algorithm is significantly improved. The additional benefit of GP modeling is that the uncertainty associated with the predicted potential energy level is quantified simultaneously.

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Bayesian calibration of force fields for molecular simulations

6

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6.1 Introduction

Over the last three decades, molecular simulation has become ubiquitous in scientific fields ranging from molecular biology to chemistry and physics. It serves as a tool to rationalize experimental results, providing access to the dynamics of a system at the atomistic and molecular level [1], and predictions of macroscopic properties of materials [2]. As computational hardware and software capabilities increase, molecular simulations are becoming increasingly more important as a tool to complement experiments and have become an invaluable asset for insight, prediction, and decision making by scientists and engineers. This increased importance is associated with an ever-increasing need to interpret quality of the predictions of the complex molecular systems. In the context of *Virtual Measurements*, as proposed by Irikura et al. [3], we remark that *for the output of a molecular simulation to be considered equivalent to an experimental measurement, it must include both a value of the quantity of interest (QoI) and a quantification of its uncertainty*. In turn, uncertainty can be defined [4] as a “parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.” Uncertainty quantification (UQ) is essential for building confidence in model predictions and helping model-based decisions [5]. Monitoring uncertainties in computational physics/chemistry has become a key issue [6], notably for multiscale modeling [7]. Reliable predictions at coarser scales imply the rational propagation of uncertainties from finer scales [8,9]; however, accounting for such uncertainties requires access to a significant computational budget.

The sources of uncertainty in molecular simulations can be broadly categorized as follows:

- *Modeling* (e.g., the choice of the particular force fields)
- *Parametric* (e.g., the 6–12 exponents and the σ , ϵ parameters in the Lennard-Jones (LJ) potentials)

- *Computational* (e.g., the effects of the particular thermostats and non-Hamiltonian time integrators)
- *Measurement* (involving the stochastic output of the simulations for various QoIs).

In this chapter, we focus on Modeling and Parametric uncertainties introduced by the force fields employed in molecular simulations. A force field is a model to represent the energy of the system as a function of the atomic coordinates and empirically determined parameters. In other words, the force field defines the potential energy surface (PES) on which the system evolves in a molecular simulation. In recent years, mathematical descriptions of force fields have also been proposed in nonexplicit form by employing machine learning algorithms such as neural networks [10–12].

Macroscopic properties of systems studied through molecular simulations are obtained using the laws of statistical mechanics through the use of algorithms, mainly Monte Carlo or Molecular Dynamics, that sample the PES of the system. Molecular simulations may involve large numbers of molecules (up to a few trillions of atoms currently) and may reach time scales (up to few microseconds currently) that are presently inaccessible with quantum mechanics. At the same time the output of molecular simulations hinges on the effective representation of the (electronic) degrees of freedom that are removed from the quantum mechanics simulations.

One of the major challenges of molecular simulation is the specification of the inter-particle interaction potentials, both in terms of the functional shape and the respective parameter values. Even for force fields where the parameters have a physical meaning (for example, the power of six in the LJ potential), their values are often not directly accessible by experiments, nor by computational chemistry. They need to be calibrated on a set of reference (experimental or calculated) properties. Force field calibration is an exacting and intuitive task and is sometimes considered as an “art.” Most of the time, the previous experience of the researcher is required to provide a reasonable initial guess of the parameters, which are then refined locally, either by trial and error, or using optimization methods [13–15]. Calibration is also difficult because the simplicity of the mathematical expressions used in force fields for efficient computations often leads to the impossibility to correctly fit different properties with a unique set of parameters [16,17]. The “best” parameter set is then often the result of a subjective compromise between representing the various data chosen for the calibration. Validation of the force field thus obtained is made by computing properties not used for calibration and comparing them with experimental data [14,18].

The effect of parameters on property predictions is sometimes estimated through sensitivity analysis [14,19–21]. Until very recently, there was no attempt to compute the uncertainties on those properties that are due to the force field parameters. This lack of interest is due in part to the belief that *measurement* uncertainties of molecular simulation (inherited from the stochastic nature of Monte Carlo and molecular dynamics simulations) were greater than *parametric* uncertainties. However, the increase in computational power has greatly reduced the former, without affecting the latter, thus making the parametric errors a significant contribution to the uncertainty budget [17]. A second reason for the scarcity of literature on parametric uncertainties in molecular simulation is the difficulty in estimating the uncertainties on the force field

parameters. This requires an extensive exploration of the parameter space, which is often inaccessible due to limited computational resources. Force field calibration was, and still is, mostly based on deterministic least-squares optimization [22].

Uncertain quantities can be represented by probability density functions (PDFs) [4,23], which grounds uncertainty management in the theory of probabilities and provides a sound mathematical framework for their consistent treatment. Parameter calibration is an inference process, for which probability theory provides a computation framework through Bayes' rule. When compared to least-squares-based calibration procedures, the Bayesian approach presents several decisive advantages: (a) it exposes clearly the statistical assumptions underlying the calibration process; (b) it enables the implementation and calibration of complex statistical models (e.g., hierarchical models, model selection ...); and (c) it provides directly information on parameter identification through the shape of the PDF.

In the context of molecular simulations, Bayesian inference has been introduced in 2008 by Cooke and Schmidler [24], who calibrated the protein dielectric constant to be used in electrostatic calculations in order to reproduce helicities of small peptides. Since then, several research groups have brought significant contributions to the use of Bayesian calibration aiming at the estimation of force field parameter uncertainties and their impact on property predictions.

This chapter begins with an overview of Bayesian calibration in Section 6.2, focusing on the “standard” approach (Section 6.2.1), its limitations (Section 6.2.2), as well as advanced schemes (Section 6.2.3). Then, in Section 6.3, we discuss computational aspects focusing on metamodels (Section 6.3.2) and approximation of intractable posteriors (Section 6.3.3) necessary to make Bayesian strategies compatible with the high cost of molecular simulations. The main topics treated in the previous sections are summarized in Fig. 6.1. In Section 6.4, we describe representative applications to show what has been learned during the last decade. Finally, in Section 6.5, we present conclusions and perspectives.

6.2 Bayesian calibration

This section introduces Bayesian inference and the general concepts used in Bayesian data analysis [25–27]. It presents also some basic and commonly used statistical models and hypotheses, only to better show their limitation in the context of force field calibration and the necessity to design more advanced calibration schemes.

6.2.1 The standard Bayesian scheme

6.2.1.1 Bayes' theorem

In general, a force field calibration problem involves searching for the value(s) of the parameters $\vartheta = \{\vartheta_i\}_{i=1}^{N_\vartheta}$ of a given computational model $F(x; \vartheta)$ that minimizes the difference between model predictions and a set of reference data $\mathbf{D} = \{d_i\}_{i=1}^{N_D}$ in specified (macroscopic, observable) physical conditions (temperature, pressure, etc.) defined by $\mathbf{X} = \{x_i\}_{i=1}^{N_D}$.

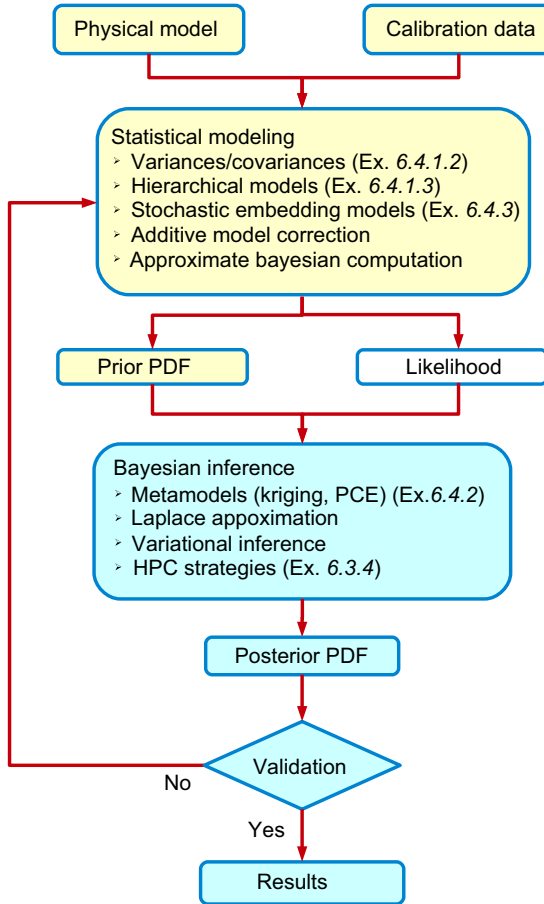


Figure 6.1 Flowchart of the Bayesian calibration process, underlining the main topics developed in this chapter. The section numbers of application examples are given in *italics*.

In contrast to deterministic least-squares fitting resulting in a single set of parameter values, in a Bayesian perspective the parameters are considered as random variables ϑ with associated PDFs that incorporate both prior knowledge and constraints by reference data through the model. Bayesian calibration gives the estimation of the conditional distribution of the parameters that fit the available data given a choice of calibration model M , $p(\vartheta|\mathbf{D}, \mathbf{X}, M)$. By M , we denote the full calibration model under consideration, i.e., the computational model F , and a statistical model presented below.

Bayes' rule relates the data and *prior* assumptions on the parameters into the *posterior* density of the target parameters. The *posterior* PDF of the parameters, knowing the data and model, is

$$p(\vartheta|\mathbf{D}, \mathbf{X}, M) = \frac{p(\mathbf{D}|\vartheta, \mathbf{X}, M)p(\vartheta|M)}{p(\mathbf{D}|\mathbf{X}, M)}, \quad (6.1)$$

where $p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M})$ is the *likelihood* of observing the data given the parameters and model, $p(\boldsymbol{\vartheta}|\mathbf{M})$ is the *prior density* of the parameters reflecting our knowledge *before* incorporating the observations, and $p(\mathbf{D}|\mathbf{X}, \mathbf{M})$ is a normalization factor, called the *evidence*. The denominator is typically ignored when sampling from the posterior since it is a constant, independent of $\boldsymbol{\vartheta}$; however, this factor has to be estimated if one wishes to compare different models (see [Section 6.2.1.3](#)).

The choice of a prior PDF is an important step in Bayesian data analysis, notably when the data provide weak constraints on (some of) the parameters. Data influence the resulting posterior probability only through the likelihood $p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M})$, which involves the difference between the reference data $\mathbf{D}$ and the model predictions $F(\mathbf{X}; \boldsymbol{\vartheta})$.

In general, given the complexity of the model, the posterior density is not known in closed form and one has to resort to numerical methods to evaluate it (see [Section 6.3.1](#)).

From the model to the likelihood. A widely adopted approach in data analysis is to express the difference between a reference value of the data d_i and the respective model prediction $F_i(\boldsymbol{\vartheta}) \doteq F(\mathbf{x}_i; \boldsymbol{\vartheta})$ using an additive noise model

$$d_i = F_i(\boldsymbol{\vartheta}) + \varepsilon_i, \quad (6.2)$$

where ε_i is a zero-centered random variable. This expression is a *measurement model*, expressing that the observed datum is a random realization of a generative process centered on the model prediction. This formulation is assuming that the model $F(\mathbf{x}; \boldsymbol{\vartheta})$ *accurately* represents the true, physical process occurring with fixed, but unknown, parameters. This is a strong assumption, which is usually wrong, because every model of a physical process involves some approximation. This is one of the main deficiencies of this approach, which will be treated at length in the following sections. Nevertheless, this is a commonly used method due to its simplicity.

The next common modeling assumption, especially if the data come from various experiments, is to assume the errors to be independent normal random variables with zero mean, i.e., $\varepsilon_i \sim \mathcal{N}(0, \sigma_i^2)$, where σ_i^2 is the variance of the errors at x_i . Based on [Eq. \(6.2\)](#), an equivalent formulation is $d_i \sim \mathcal{N}(F_i(\boldsymbol{\vartheta}), \sigma_i^2)$, which yields the following expression for the likelihood

$$\begin{aligned} p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M}) &= \prod_{i=1}^{N_D} p(d_i|\boldsymbol{\vartheta}, x_i, \mathbf{M}), \\ &= \prod_{i=1}^{N_D} (2\pi\sigma_i^2)^{-1/2} \exp\left(-\frac{(d_i - F_i(\boldsymbol{\vartheta}))^2}{2\sigma_i^2}\right), \\ &= \left[\prod_{i=1}^{N_D} 2\pi\sigma_i^2\right]^{-1/2} \exp\left(-\frac{1}{2} \sum_{i=1}^{N_D} \frac{(d_i - F_i(\boldsymbol{\vartheta}))^2}{\sigma_i^2}\right). \end{aligned} \quad (6.3)$$

The value of σ_i depends on the error budget and the available information. As ε_i is the difference of two quantities, its variance is the sum of the variances of d_i and $F_i(\boldsymbol{\vartheta})$ [4]. Typically, one would write

$$\sigma_i^2 = u_{d_i}^2 + u_{F_i(\boldsymbol{\vartheta})}^2, \quad (6.4)$$

where $u_{d_i} \doteq u(d_i)$ is the uncertainty attached to d_i , and $u_{F_i(\boldsymbol{\vartheta})}$ is the *measurement* uncertainty for model prediction $F_i(\boldsymbol{\vartheta})$. In this formulation, the only parameters are those of the model F .

When no value of u_{d_i} is available, it is convenient to make the assumption that the reference data uncertainty is unknown and identical for all data of a same observable. Depending on the heterogeneity level of the reference dataset, one then has one or several additional parameters $\boldsymbol{\tau} = \{\tau_i\}_{i=1}^{N_\tau}$ to be identified, and the likelihood becomes

$$p(\mathbf{D}|\boldsymbol{\vartheta}, \boldsymbol{\tau}, X, M) = \left[\prod_{i=1}^{N_D} 2\pi\sigma_i^2(\boldsymbol{\tau}) \right]^{-1/2} \exp\left(-\frac{1}{2} \sum_{i=1}^{N_D} \frac{(d_i - F_i(\boldsymbol{\vartheta}))^2}{\sigma_i^2(\boldsymbol{\tau})}\right), \quad (6.5)$$

with

$$\sigma_i^2(\boldsymbol{\tau}) = \tau_{j=I(i)}^2 + u_{F_i(\boldsymbol{\vartheta})}^2, \quad (6.6)$$

where $I(i)$ is a pointer from the datum index i to the adequate index in the set of unknown uncertainty parameters $\boldsymbol{\tau}$.

Although this is a very convenient and commonly used setup, akin to the ordinary least-squares procedure for regression with unknown data variance [28], one should be aware that it can become problematic, especially if the model is inadequate, i.e., it is not able to fit properly the data (more on this in [Section 6.2.2.1](#)).

By noting $\mathbf{R}(\boldsymbol{\vartheta})$ the vector of N_D differences between the model and data, and $\boldsymbol{\Sigma}_R$ the corresponding covariance matrix, one gets a compact notation for the likelihood in the case of a normal additive noise:

$$p(\mathbf{D}|\boldsymbol{\vartheta}, X, M) \propto |\boldsymbol{\Sigma}_R|^{-1/2} \exp\left(-\frac{1}{2} \mathbf{R}(\boldsymbol{\vartheta})^T \boldsymbol{\Sigma}_R^{-1} \mathbf{R}(\boldsymbol{\vartheta})\right), \quad (6.7)$$

where the proportionality symbol means that a multiplicative constant has been omitted. $\boldsymbol{\Sigma}_R$ is the sum of the covariance matrix for the reference data $\boldsymbol{\Sigma}_D$ and the covariance matrix of the measurement errors of the model $\boldsymbol{\Sigma}_F$, and $|\boldsymbol{\Sigma}_R|$ is its determinant. So far, especially in [Eqs. \(6.3\) and \(6.5\)](#), $\boldsymbol{\Sigma}_R$ has been considered as diagonal, with elements $\Sigma_{R,ij} = \sigma_i^2 \delta_{ij}$. Whenever available, covariances of the reference data should be included in the nondiagonal part of $\boldsymbol{\Sigma}_D$.

The prior PDF. In order to complete the definition of the posterior PDF, one needs to define the prior PDF, encoding all the available information on the parameters not

conditioned to the data to be analyzed. Mathematical and physical constraints (e.g., positivity) are introduced here through the choice of adapted PDFs [27].

The most common choice in absence of any information on a parameter might be a uniform distribution, or a log-uniform one in case of a positivity constraint (so-called *noninformative* priors). A normal distribution would typically be used to encode a known mean value and uncertainty [23]. An essential consideration at this stage is to ensure that the prior PDF captures intrinsic correlations between parameters (e.g., a sum-to-zero constraint).

Estimation and prediction. The posterior PDF is used to generate statistical summaries of the target parameters. Point estimations can be obtained by the mode of the posterior PDF, or *Maximum a posteriori* (MAP),

$$\hat{\boldsymbol{\vartheta}} = \underset{\boldsymbol{\vartheta}}{\operatorname{argmax}} p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, M), \quad (6.8)$$

and/or the *mean value* of the parameters,

$$\overline{\boldsymbol{\vartheta}}_i = \int d\boldsymbol{\vartheta} \vartheta_i p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, M), \quad (6.9)$$

which are different for nonsymmetric PDFs.

The parameter variance, $u_{\boldsymbol{\vartheta}^2}$, and covariances, $\operatorname{Cov}(\vartheta_i, \vartheta_j)$, are also derived from the posterior PDF:

$$\operatorname{Cov}(\vartheta_i, \vartheta_j) = \int d\boldsymbol{\vartheta} \left(\vartheta_i - \overline{\vartheta}_i \right) \left(\vartheta_j - \overline{\vartheta}_j \right) p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, M), \quad (6.10)$$

$$u_{\vartheta_i} = \operatorname{Cov}(\vartheta_i, \vartheta_i)^{1/2}. \quad (6.11)$$

If the posterior PDF has a shape different from the ideal normal multivariate distribution, other statistical summaries might be useful, but one should also consider contour or density plots of the PDF, which are important diagnostics to assess problems of parameter identification (multimodality, nonlinear correlations, etc.).

Predictions of a QoI $A(\boldsymbol{\vartheta})$ is made through the estimation of the PDF of the QoI averaged over the posterior PDF of the parameters

$$p(A=a|\mathbf{D}, \mathbf{X}, M) = \int d\boldsymbol{\vartheta} p(A=a|\boldsymbol{\vartheta}) p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, M), \quad (6.12)$$

where $p(A=a|\boldsymbol{\vartheta})$ is a PDF describing the dependence of the QoI on $\boldsymbol{\vartheta}$. If A is a deterministic function of the parameters, then $p(A=a|\boldsymbol{\vartheta}) = \delta(\mathbf{a} - A(\boldsymbol{\vartheta}))$, where δ is the Dirac delta function. The posterior-weighted integrals used for estimation and prediction are generally evaluated by the arithmetic mean on a representative sample of the posterior PDF (Monte Carlo integration).

6.2.1.2 Validation

As the Bayesian calibration process will always produce a posterior PDF independently of the quality of the fit, it is essential to perform validation checks, notably of the statistical hypotheses used to build $p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M})$. A posterior PDF failing these tests should not be considered for further inference. In particular, the uncertainties on the parameters and their covariances would be unreliable.

Residuals analysis. In a valid statistical setup, *the residuals at the MAP*, $\mathbf{R}(\hat{\boldsymbol{\vartheta}})$, *should not display serial correlation* along the control variable(s), which is usually assessed by visual inspection of plots of the residuals [17] and their autocorrelation function. Serial correlation in the residuals is a symptom of model inadequacy and should not be ignored.

Moreover, *the variance of the residuals should be in agreement with the variance of the data and model*. Ideally, the Birge ratio at the MAP,

$$r_B(\hat{\boldsymbol{\vartheta}}) = \left(\frac{1}{N_D - N_{\boldsymbol{\vartheta}}} \mathbf{R}(\hat{\boldsymbol{\vartheta}})^T \boldsymbol{\Sigma}_R^{-1} \mathbf{R}(\hat{\boldsymbol{\vartheta}}) \right)^{1/2}, \quad (6.13)$$

should be close to 1 [29]. The Birge ratio might be too large when the model does not fit the data or when the variances involved in $\boldsymbol{\Sigma}_R$ are underestimated, but it can also be too small when these variances are overestimated.

Note that if the calibration model contains adjustable uncertainty parameters ($\boldsymbol{\tau}$ in Eq. 6.5), their optimization might ensure that $r_B(\hat{\boldsymbol{\vartheta}}, \hat{\boldsymbol{\tau}}) \simeq 1$, but would not guarantee that the residuals have no serial correlation [30].

Posterior predictive statistics and plots. The posterior predictive density for the value $\tilde{d}$ at a new point $\tilde{x}$ is [27]

$$p(\tilde{d}|\tilde{x}, \mathbf{D}, \mathbf{X}, \mathbf{M}) = \int d\boldsymbol{\vartheta} p(\tilde{d}|\tilde{x}, \boldsymbol{\vartheta}, \mathbf{M}) p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, \mathbf{M}). \quad (6.14)$$

$\tilde{x}$ is used to generate high-probability (typically 0.9 or 0.95) prediction bands from which one can check the percentage of data effectively recovered by the model predictions [31]. Plots of high-probability bands for the model's residuals as function of the control variable(s) are particularly informative for model validation [30].

6.2.1.3 Model selection

Let us consider a set of alternative models $\mathbf{M} = \{\mathbf{M}^{(i)}\}_{i=1}^{N_M}$, parameterized by $\boldsymbol{\vartheta}^{(i)}$, for which one wants to compare the merits in reproducing the reference data $\mathbf{D}$. The posterior probability of model $\mathbf{M}^{(i)}$ is estimated by applying Bayes' rule

$$p(\mathbf{M}^{(i)}|\mathbf{D}, \mathbf{X}) = \frac{p(\mathbf{D}|\mathbf{X}, \mathbf{M}^{(i)}) p(\mathbf{M}^{(i)})}{\sum_{i=1}^{N_M} p(\mathbf{D}|\mathbf{X}, \mathbf{M}^{(i)}) p(\mathbf{M}^{(i)})}, \quad (6.15)$$

where $p(M^{(i)})$ is the prior probability of model $M^{(i)}$ and the evidence $p(D|X, M^{(i)})$ is obtained by

$$p(D|X, M^{(i)}) = \int d\vartheta^{(i)} p(D|\vartheta^{(i)}, X, M^{(i)}) p(\vartheta^{(i)}|M^{(i)}). \quad (6.16)$$

This approach has been used in Refs. [32–36] to compare the performances of different models. Computation of the evidence terms is costly, and high-performance computing (HPC) is generally necessary. On the other hand, the TCMCMC algorithm [37], which will be described in [Section 6.3.1](#), offers an estimator for the evidence term.

6.2.2 Limitations of the standard scheme

As in all calibration process, the underlying statistical hypotheses have to be checked, and the Bayesian approach offers no guarantee against model misspecification. In particular, the common hypothesis of i.i.d. errors should be carefully scrutinized.

In fact, the simple likelihood scheme presented above ([Eq. 6.7](#)) is often unable to deal properly with the specificities of the calibration of force field parameters, i.e., the corresponding posterior PDF does not pass some of the validation tests. These tests might help to point out the deficiency sources(s), which concern the calibration dataset and its covariance matrix (improper Birge ratio values) or the force field model (serial correlation of the residuals) or both.

6.2.2.1 Modeling of the error sources

A convenient feature of the standard model is the possibility to infer uncertainty parameter(s) (τ in [Eq. 6.5](#)) in order to ensure that $r_B(\hat{\vartheta}, \hat{\tau}) \simeq 1$, i.e., to obtain a unit variance of the weighted residuals.

The applicability of this approach relies essentially on the independence of the errors, to be validated by the absence of serial correlation in the residuals. Otherwise, τ is absorbing model errors in addition to data uncertainty. In the absence of dominant measurement uncertainty, model errors present strong serial correlations, which is in conflict with the standard scheme's i.i.d. hypothesis. In these conditions, using the uncertainty parameters τ as “error collectors” should not be expected to produce reliable results. It is essential to devise a detailed scheme of error sources in order to get unambiguous identification and modeling of all contributions.

6.2.2.2 Data inconsistency

Experimental data. In force field calibration, one is often confronted with multiple versions of reference data, produced by different teams in similar or overlapping experimental conditions. It is frequent that some measurement series are inconsistent, in the sense that values measured with different methods, instruments, or by different

teams (*reproducibility conditions* [4]) are not compatible within their error bars. This might be due to an underestimation of measurement uncertainty, for instance, taking into account only the *repeatability component*, and ignoring nonrandom instrumental error sources.

Depending on the context, this problem can be dealt with in several (nonexclusive) ways [17]:

- pruning the dataset, which should be reserved to experts in the specific data measurements fields;
- scaling the data covariance matrix Σ_D by factor(s) which might be parameter(s) of the calibration process. This assumes that the initial uncertainty assessments are incorrect (this approach is a common practice in the metrology of interlaboratory comparisons [29,38,39]); or
- using data shifts, to be calibrated along with ϑ , in order to reconcile discrepant data series by compensation of measurement biases [29,30].

Theoretical data. Data might also come from deterministic reference theoretical models (e.g., equations-of-state, as used by the NIST database for the properties of fluids [40]), in which case they are not affected by random errors, and the uncertainty statement issued by the data provider quantifies the representative amplitude of errors of this model with respect to its own calibration data [40,41]. A *reductio ad absurdum* in this case would be to fit the model's results with their declared error bars by the generative model itself, which would produce numerically null residuals, invalidating the Birge ratio test.

This type of data violates the errors independence hypothesis. One way to take it into account would be to design a data covariance matrix Σ_D , but there is generally no available information to establish it reliably.

To our knowledge, this point has generally been overlooked in the force field calibration literature, probably because the uncertainty budget is often dominated by other error sources (numerical simulation uncertainty, and/or model inadequacy). It might, however, readily occur when uncertainty scaling is used to compensate for data inconsistency [29] or model inadequacy [30]. Besides, as the quality of force fields and computational power increase, the problem will eventually emerge in the standard calibration framework.

6.2.2.3 Model inadequacy/model errors

Considering the approximate nature of force fields, model inadequacy has to be expected as a typical feature of the calibration problem [42]. For instance, force field approximations make molecular simulation unable to fit a property over a large range of physical conditions [16,17]. This can be somewhat overcome by explicitly modeling the dependence of the parameters on the control variable(s) (for instance, by using temperature-dependent LJ parameters [43–45]). This kind of approach, i.e., force field *improvement*, is in fact a change of model F . Similarly, for LJ-type potentials, a unique set of parameters is typically unable to fit several observables (e.g., the liquid and vapor densities of Argon [35]), which would call for

observable-dependent force field parameters, and the loss of parameter transferability for the prediction of new properties.

Using the standard calibration scheme (Eq. 6.3) in presence of model inadequacy leads to statistical inconsistencies. Within this setup, parameter uncertainty is decreasing when the number of calibration data is increased, which means that prediction uncertainty of the calibrated model is also decreasing [46,47]. On the contrary, model errors are rather expected to increase—at best to stay constant—when new data are added to the calibration set. Therefore, parameter uncertainty as provided by the standard calibration scheme is intrinsically inadequate to account for model errors. It is thus necessary to devise alternative calibration schemes. There has been recently a marked interest in statistical solutions enabling to integrate model errors into parameter uncertainty [42,47–52]. These solutions, based on Bayesian inference, are treated in the next section.

6.2.3 Advanced Bayesian schemes

One has shown above that there are several causes, notably model inadequacy, to reject the standard force field calibration model. Alternative schemes which have been proposed in the literature to deal with these shortcomings are presented in this section.

6.2.3.1 Additive model correction

We consider here a solution which improves model predictions without involving a change of force field model. Model inadequacy can be solved with an additive term to the original model:

$$d_i = F_i(\boldsymbol{\vartheta}) + \delta F_i(\boldsymbol{\vartheta}_{\delta F}) + \varepsilon_i, \quad (6.17)$$

where the discrepancy function δF has its own set of parameters, $\boldsymbol{\vartheta}_{\delta F}$.

The representation of δF by a Gaussian process (GP) has been popularized by Kennedy and O’Hagan [53]. It has many advantages over, for instance, polynomial-based functions, but, by construction, δF can correct any error due to a misspecification of F , which weakens considerably the constraints of $\mathbf{D}$ on $\boldsymbol{\vartheta}$. The GP approach might therefore be subject to severe identification problems, if the parameters of F and δF are optimized simultaneously without strong prior information [46,50,54,55].

A two-staged solution, proposed by Pernot and Cailliez [30], is to constrain $\boldsymbol{\vartheta}$ with the posterior PDF resulting from an independent calibration of F . In this case, δF is designed to fit the residuals of $F(x; \boldsymbol{\vartheta})$ by a GP of mean 0 and covariance matrix $\boldsymbol{\Sigma}_{\delta F}$, with elements $\Sigma_{\delta F,ij} = k(x_i, x_j)$, based on a Gaussian kernel $k(u, v) = \alpha^2 \exp(-\beta^2(u - v)^2)$. The kernel’s parameters $\boldsymbol{\vartheta}_{\delta F} = \{\alpha, \beta\}$ have to be estimated in addition to $\boldsymbol{\vartheta}$.

The predictive posterior PDF has a closed form expression [56]

$$p(\tilde{d}|\tilde{x}, \mathbf{D}, \mathbf{X}, M) = \mathcal{N}(\tilde{d} | \boldsymbol{\Omega}^T \boldsymbol{\Sigma}_R^{-1} \mathbf{D}, \alpha^2 - \boldsymbol{\Omega}^T \boldsymbol{\Sigma}_R^{-1} \boldsymbol{\Omega}), \quad (6.18)$$

where $\Omega = \Omega(X)$ and $\Omega_i = k(x_i, \tilde{x})$.

The GP correction method is very efficient [30], but suffers from a major drawback, inherent to all additive correction methods: the discrepancy function δF is not transferable to other observables than the one it was calibrated with, nor can the GP correction be used for extrapolation out of the range of the calibration control variables.

6.2.3.2 Hierarchical models

There is a wealth of heterogeneity when considering the data used for calibrating potentials of molecular simulations. As discussed in Section 6.2.2.2, it is often the case that different experimental groups provide different values for quantities of interest, for example, diffusion constants, even when the experiments are performed in the same thermodynamic conditions. Even more, calibration of molecular systems may often require matching different experimental data ranging from structural properties like radial distribution functions (RDFs) to transport properties like diffusivity. Uncertainties due to different measurement techniques, facilities, and experimental conditions are often reflected in the values of such data.

When model inadequacy arises from the use of a unique parameter set for different observables or experimental conditions, hierarchical models may enable to derive more robust parameter sets [57,58].

In a hierarchical model, the data are being gathered into N_H groups, each containing N_i data, $\mathbf{D} = \{\mathbf{d}_i\}_{i=1}^{N_H}$ and $\mathbf{d}_i = \{d_{i,j}\}_{j=1}^{N_i}$. For each group, a different parameter set $\boldsymbol{\vartheta}_i$ is considered, and all the parameters are controlled by hyperparameters $\boldsymbol{\kappa}$. The structure of this relation is given in Fig. 6.2 in plate notation. The likelihood is now written as

$$p(\mathbf{D}|\boldsymbol{\kappa}, X, M) = \prod_{i=1}^{N_H} \int d\boldsymbol{\vartheta}_i p(\mathbf{D}_i|\boldsymbol{\vartheta}_i, M) p(\boldsymbol{\vartheta}_i|\boldsymbol{\kappa}, M). \quad (6.19)$$

For example, a specific choice for the prior PDF on the $\boldsymbol{\vartheta}_i$ is the normal distribution

$$p(\boldsymbol{\vartheta}_i|\boldsymbol{\kappa}, M) = \mathcal{N}(\boldsymbol{\vartheta}_i; \boldsymbol{\mu}_\vartheta, \boldsymbol{\Sigma}_\vartheta), \quad (6.20)$$

where $\boldsymbol{\kappa} = \{\boldsymbol{\mu}_\vartheta, \boldsymbol{\Sigma}_\vartheta\}$ are the parameters of an *overall* normal distribution, which have to be inferred along with the local values of $\boldsymbol{\vartheta}_i$.

Hierarchical models enable the robust inference of multiple parameter sets with global constraints (prior PDF on the hyperparameters). However, the uncertainty on the hyperparameters $\boldsymbol{\kappa}$ of the overall distribution is conditioned by the number of subsets in the calibration data N_H . When this number is small, strong prior information on the hyperparameters should be provided to help their identification [30,57].

This scheme has been recently applied to the calibration of LJ parameters from various sets of experimental data obtained in different thermodynamic conditions. In Ref. [52], the dataset is split into subsets corresponding to different control temperatures and pressures. A hierarchical model is used for the inference of the

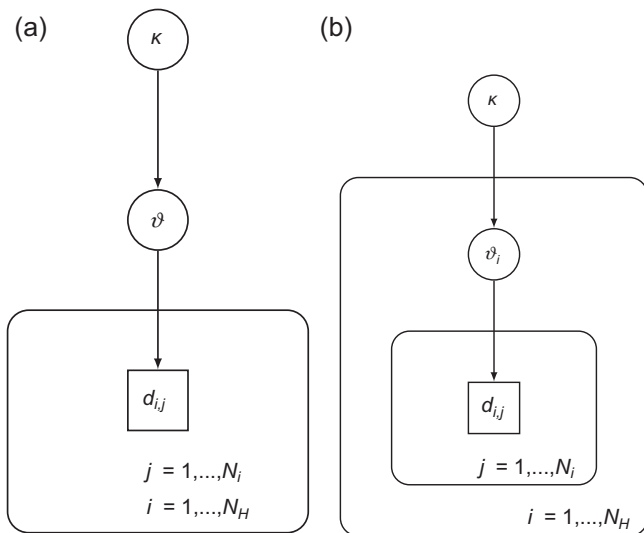


Figure 6.2 Two approaches of grouping the data in a Bayesian inference problem. (a) For the left graph, one parameter ϑ will be inferred using all the available data. (b) In the right graph, the data are gathered into N_H groups each containing N_i data. Each group has a different parameter ϑ_i . All the parameters are being linked through the hyperparameter κ .

hyperparameters describing the LJ potentials (model $\mathcal{M}_{H2}$ in Ref. [52]). Using a different data partition, the same authors used a parameter hierarchy to solve data inconsistency (model $\mathcal{M}_{H1}$ in Ref. [52]). Hierarchical models have also been used to accommodate heterogeneous datasets [59]. Pernot and Cailliez [30] introduced a hierarchical model on data shifts to solve data inconsistency.

Depending on the data partition scheme, predictions are made either from the locally adapted parameters ϑ_i or from their overall distribution [57,58]. For instance, when the data partition has been made along the control variables X or according to the nature of data, local parameters can be addressed unambiguously for prediction in any of the identified subset conditions. However, if the partition has been made to separate inconsistent data series, or if one wishes to predict a new property, the local sets cannot be addressed, and the overall distribution has to be used. In general, hierarchical Bayesian inference tries to accommodate information across distinct datasets and, as such, results in much larger prediction uncertainty than what can be inferred by using distinct local parameters sets. In some cases, the prediction uncertainty resulting from the overall distribution is too large for the prediction to be useful [30,59].

6.2.3.3 Stochastic Embedding models

A recent addition to the methods dealing with model inadequacy is based on the idea of replacing the parameters of the model by stochastic variables. This provides an additional variability source to the model's predictions which may be tuned to compensate for model inadequacy. It is important to note, as underlined by Pernot and Cailliez

[30], that this approach, mostly based on the tweaking of the parameters covariance matrix, cannot reduce the gap between model predictions and reference data. Its impact is on *marginal*, or individual, model prediction uncertainties, which can be enlarged sufficiently to cover the difference with the corresponding calibration data.

In the stochastic embedded (SEm) models approach [60,61], the model's parameters, ϑ , are defined as stochastic variables, with a PDF conditioned by a set of hyperparameters κ , typically their mean value vector μ_ϑ and a covariance matrix Σ_ϑ , defining a multivariate (normal) distribution $p(\vartheta|\mu_\vartheta, \Sigma_\vartheta, M)$.

Such stochastic parameters can be handled in the Bayesian framework either at the model or at the likelihood level, defining two classes of methods. Both suffer from degeneracy problems, because of the strong covariance of model predictions over the control variable range [42,51].

Model averaging. Statistical summaries (μ_F , Σ_F) of predictions of the model with stochastic parameters are first estimated and inserted into the likelihood:

$$p(D|\mu_\vartheta, \Sigma_\vartheta, M) \propto |\Sigma_T|^{-1/2} \exp\left(-\frac{1}{2} \mathbf{R}^T \Sigma_T^{-1} \mathbf{R}\right), \quad (6.21)$$

where $R_i = d_i - \mu_F(x_i)$ and $\Sigma_T = \Sigma_D + \Sigma_F$, and the mean values $\mu_F(x_i)$ and covariance matrix Σ_F have to be estimated by forward uncertainty propagation (UP), such as linear UP (or combination of variances) [4], or polynomial chaos UP (see below).

When the number of parameters is smaller than the number of data points, Σ_F is singular (non-positive definite), causing the likelihood to be degenerate, and the calibration to be intractable [51]. In presence of model inadequacy, the data covariance matrix (and the model measurement uncertainties for stochastic models) are too small to alleviate the degeneracy problem. As a remedy, it has been proposed to replace the multivariate problem by a set of univariate problems (marginal likelihoods [51]), i.e., to ignore the covariance structure of model predictions

$$\Sigma_{T,ij} = \Sigma_{D,ij} + \Sigma_{F,ij} \delta_{ij}. \quad (6.22)$$

It is then possible to modulate the shape of the prediction uncertainty bands by designing the Σ_ϑ matrix [42], notably through a judicious choice of prior PDFs for the hyperparameters.

Likelihood averaging. Integration of the initial likelihood over the model's stochastic parameters provides a new likelihood, conditioned on the hyperparameters κ [47,51].

$$p(D|\kappa, X, M) = \int d\vartheta p(D|\vartheta, X, M) p(\vartheta|\kappa, X, M). \quad (6.23)$$

The integrated likelihood is in general degenerate, and it has been proposed to replace it by a tractable expression involving summary statistics of the model

predictions, to be compared to similar statistics of the data [51]. This approach, called approximate Bayesian computation (ABC), is presented in the next section.

6.2.3.4 Approximate Bayesian Computation

The definition of the likelihood is a centerpiece of Bayesian inference. In certain cases, the analytical statistical models that have been examined above are not suitable for describing such likelihoods. One such example is computational models that generate outputs over several iterations or employ complex simulations. In such cases, ABC [62] has been introduced that bypass the calculation of the likelihood by using a metric to compare the output of the model and the observations. ABC methodologies have received significant attention in fields such as genetics [63], epidemiology [64], and psychology [65]. The ABC approach is often referred to as a *likelihood-free* approach.

The ABC algorithm [66] aims at sampling the joint posterior distribution $p(\vartheta, Y|D, X, M)$, where Y follows $p(\cdot|\vartheta, M)$, i.e., Y is a sample from the forward model. Applying Bayes' theorem to the joint distribution we get,

$$p(\vartheta, Y|D, X, M) \propto p(D|\vartheta, Y, X, M) p(Y|\vartheta, X, M) p(\vartheta|M). \quad (6.24)$$

The function $p(D|Y, \vartheta, X, M)$ gives higher values when Y is close to D and small values in the opposite case. The idea of the ABC algorithm is to sample ϑ from the prior $p(\vartheta|M)$, then sample Y from the forward model $p(Y|\vartheta, X, M)$, and finally accept the pair (ϑ, Y) when $Y = D$.

Since the space that Y lies in is usually uncountable, the event $Y = D$ has zero probability. The basic form of the ABC algorithm introduces a metric ρ and a tolerance parameter δ and accepts (ϑ, Y) when $\rho(Y, D) < \delta$ and rejects it otherwise. In another variant of the algorithm, a summary statistic S is used to compare Y and D through a different metric ρ . In this case, the pair is accepted when $\rho(S(Y), S(D)) < \delta$. Note that the ABC algorithm approximates the true posterior $p(\vartheta|D, X, M)$ with the density

$$p_\delta(\vartheta|D, X, M) \propto I_{A_\delta(D)}(Y)p(Y|\vartheta, X, M)p(\vartheta|M), \quad (6.25)$$

where $A_\delta(D) := \{y : \rho(S(y), S(D)) < \delta\}$ and the indicator function $I_{A_\delta(D)}(Y) = 1$ when $Y \in A_\delta(D)$ and zero otherwise.

Then, the approximation to the target marginal posterior is given by

$$p_\delta(\vartheta|D, X, M) = \int_{A_\delta(D)} dY p(Y|\vartheta, X, M) p(\vartheta|M). \quad (6.26)$$

Notice that the integration over $A_\delta(D)$ needs not to be done explicitly since only the ϑ component is kept from the pair (ϑ, Y) .

The parameter δ controls the amount of computational effort that needs to be spent for the generation of ϑ samples. For large values of δ , a large error is introduced in the

approximation, but less computational effort is needed to accept a sample ϑ . On the other hand, small δ leads to a better approximation but the event $Y \in A_\delta(\mathbf{D})$ becomes a rare event and most of the Y samples will be rejected.

Various algorithms have been proposed for the acceleration of the original plain ABC algorithm. In Ref. [66], the ABC-MCMC algorithm has been proposed where the rejection step has been replaced by a Markov chain Monte Carlo (MCMC) step leading to an increase of the acceptance ratio. In Ref. [67], the ABC-SubSim algorithm has been proposed, where the subset simulation, an algorithm for sampling rare events, has been combined with ABC. In Ref. [68], more accurate estimates of the posterior distribution are obtained by incorporating the error in the ABC approximation.

Recently, the ABC-SubSim [69] has been used in force field identification of molecular dynamics simulations. In Ref. [70], ABC has been used to approximate the likelihood in the force field calibration of a water model. In Refs. [30,47,51], the ABC algorithm has been used in order to approximate the intractable likelihood in SEM models discussed in Section 6.2.3.3.

6.3 Computational aspects

The implementation of Bayesian calibration for molecular simulations presents challenging aspects due to the necessity to generate a large representative sample of the posterior PDF for the estimation of parameters statistics that is incompatible with the high computational cost of molecular simulations.

6.3.1 Sampling from the posterior PDF

Except for simple toy models, there is no direct method to sample from the posterior PDF. The sampling is usually done by a random walk in parameters space based on the Metropolis algorithm [71] as generalized by Hastings [72]. This is the basis for a family of algorithms named MCMC. There are many flavors of MCMC, and the reader is referred to reference textbooks for more information [73–75].

For the calibration of force fields and model selection, Angelikopoulos et al. developed a version of transitional MCMC (TMCMC), which is well adapted to HPC [32,34,76]. If the evaluation of the model is not computationally heavy or model selection is not required, non-HPC versions of MCMC can be used. For instance, Pernot and Cailliez [17,30,77] used out-of-the-box functions available in the R [78] and `stan` [79] programming languages.

Whichever the type of MCMC algorithm, the comprehensive exploration of parameters space by a Markov chain requires many thousands to millions of evaluations of the model. One cannot envision to perform as many molecular simulations with limited resources, and it is mandatory to use alternative strategies involving computationally cheap emulators of the simulation model, also known as *surrogate models* or *metamodels*. Before treating metamodels, we give a brief presentation of the TMCMC algorithm.

Transitional Markov chain Monte Carlo (TMCMC). TMCMC is a sequential MCMC type algorithm for sampling the posterior distribution. It is based on a sequence of intermediate distributions controlled by an annealing scheme:

$$p_j(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, M) \propto p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, M)^{\gamma_j} p(\boldsymbol{\vartheta}|M), \quad (6.27)$$

for $j = 1, \dots, m$ and $0 = \gamma_1 < \dots < \gamma_m = 1$, that leads to the posterior distribution when $\gamma_m = 1$.

The algorithm first draws N_1 samples from the prior distribution and at the $j+1$ stage uses N_j samples from the distribution p_j to obtain N_{j+1} samples from the distribution p_{j+1} . Let $\Theta_j = \{\boldsymbol{\vartheta}_{j,k}\}_{k=1}^{N_j}$ be the samples obtained at the j -th step from p_j . The following procedure gives samples from p_{j+1} :

1. Draw N_{j+1} samples from the set Θ_j with probability of $\boldsymbol{\vartheta}_{j,k}$ equal to

$$\hat{w}_{j,k} = \frac{w_{j,k}}{\sum_{k=1}^{N_j} w_{j,k}}, \quad (6.28)$$

where $w_{j,k} = p(\mathbf{D}|\boldsymbol{\vartheta}_{j,k})^{\gamma_{j+1}-\gamma_j}$. Put the new samples in the set $\tilde{\Theta}_{j+1}$ and set

$$S_j = \frac{1}{N_j} \sum_{k=1}^{N_j} w_{j,k}. \quad (6.29)$$

2. For each sample in $\tilde{\Theta}_{j+1}$ perform TMCMC with Gaussian proposal distribution and covariance matrix $\beta^2 \Sigma_s^{(j)}$. Here, β is a scaling parameter and $\Sigma_s^{(j)}$ is the sample covariance at the j -th stage given by,

$$\Sigma_s^{(j)} = \sum_{k=1}^{N_j} \hat{w}_{j,k} \left(\boldsymbol{\vartheta}_{j,k} - \bar{\boldsymbol{\vartheta}}_j \right) \left(\boldsymbol{\vartheta}_{j,k} - \bar{\boldsymbol{\vartheta}}_j \right)^\top, \quad (6.30)$$

where $\bar{\boldsymbol{\vartheta}}_j = \sum_{k=1}^{N_j} \hat{w}_{j,k} \boldsymbol{\vartheta}_{j,k}$. Set the chain length equal to a predefined parameter $\ell_{\max}$.

In [Algorithm 6.1](#), the pseudocode of a reduced bias variant of TMCMC, namely the BASIS algorithm [52], is presented.

A key advantage of TMCMC is that it can be efficiently parallelized since the likelihood evaluation is independent for each sample. An additional computational benefit introduced by the BASIS algorithm is that all MCMC chains have equal length and thus the work load can be balanced among the processors. Moreover, an important by-product of the algorithm is that the evidence of the data is estimated by Ref. [37]

$$p(\mathbf{D}|M) \approx \prod_{j=1}^{m-1} S_j. \quad (6.31)$$

Algorithm 6.1. BASIS (TMCMC)

- 1 Input:** Likelihood function $p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M})$, prior distribution $p(\boldsymbol{\vartheta}|\mathbf{M})$
 N_j, N_{max} —number of samples per stage, maximum number of stages
 γ, β —threshold parameter, scale parameter
- 2 Output:** Θ_{final} —a set of samples from $p(\boldsymbol{\vartheta}|\mathbf{D}, \mathbf{X}, \mathbf{M})$
 S —estimation for the evidence $p(\mathbf{D}|\mathbf{M})$
- 3** Draw initial sample set $\Theta_1 = \{\boldsymbol{\vartheta}_{1,k}\}_{k=1}^{N_1}$ from prior
- 4** Initialize $j \leftarrow 1, \gamma_1 \leftarrow 0, S \leftarrow 1$
- 5 repeat**
- 6** Choose γ_{j+1} such that the coefficient of variation of $w_{j,k} < \gamma$ and $\gamma_{j+1} \leq 1$
- 7** Calculate $w_{j,k}$ with the chosen γ_{j+1}
- 8** $S \leftarrow S \cdot \frac{1}{N_j} \sum_{k=1}^{N_j} w_{j,k}$
- 9** Obtain $\tilde{\Theta}_{j+1}$ by drawing N_{j+1} samples from the set Θ_j with probabilities $\propto w_{j,k}$
- 10** Set Σ the weighted covariance given by Eq. (6.30)
- 11 for** each sample in $\tilde{\Theta}_{j+1}$ **do**
- 12** Perform MCMC with length equal to ℓ_{max} and proposal distribution $q(\cdot|\boldsymbol{\vartheta}) = \mathcal{N}(\cdot|\boldsymbol{\vartheta}, \beta^2 \Sigma)$
- 13** Add resulting samples in Θ_{j+1}
- 14 end for**
- 15** $j \leftarrow j + 1$
- 16 until** $\gamma_j = 1$ or $j > N_{max}$
- 17** $\Theta_{final} \leftarrow \Theta_j$

6.3.2 Metamodels

Metamodels are essential to reduce the computational cost of Bayesian inference. When employed as surrogates of the actual computationally expensive models, the accuracy of the Bayesian inference hinges on the accuracy of the metamodels. Metamodels are a familiar entity to human decision making and handling of uncertainty. Scarcely, we take a step or swim with complete knowledge of the mechanics associated with these processes. Humans are well capable of creating effective models of their environment and at the same time operate under uncertainty implied by these models. The use of metamodels is inherent to modeling procedures and a key element in Bayesian inference.

Over the last years, computational frameworks using metamodels have been devised to overcome the cost of simulations required by Bayesian calibration of force fields [32,34,76,77].

Metamodels can be built either from the physical laws of the system under study or as pure mathematical expressions capturing the dependence/behavior of the original model's outputs as a function of the input variables (force field parameters and control variables). Recently, Messerly et al. [80] proposed a third option, configuration sampling—based surrogate models.

Van Westen et al. [81] used PC-SAFT equations as physics-based models to fit simulation results for the calibration of LJ parameters for n-alkanes. A similar approach has been used recently to parameterize Mie force fields [82,83]. Such physics-based models are unfortunately confined to a restricted set of applications, and behavior-based models have been devised for a more general scope.

In the force field calibration literature, GPs, also called kriging [32,34,35,69,77], and polynomial chaos expansions (PCEs) [84] have been used to build metamodels replacing molecular simulations.

6.3.2.1 Kriging

We describe here shortly the principle of kriging metamodels. More details will be found in Refs. [85–87]. Let $\mathbf{Y} = \{y^{(i)}\}_{i=1}^N$ be a set of N values of a QoI at force field parameters $\boldsymbol{\Theta} = (\boldsymbol{\vartheta}^{(1)}, \dots, \boldsymbol{\vartheta}^{(N)})$, where $y^{(i)} = F(x; \boldsymbol{\vartheta}^{(i)}) \pm u_F^{(i)}(x)$. In the *universal kriging* framework, $\mathbf{Y}$ is assumed to be of the form

$$y(\boldsymbol{\vartheta}) = \sum_{i=1}^p b_i f_i(\boldsymbol{\vartheta}) + Z(\boldsymbol{\vartheta}), \quad (6.32)$$

where the f_i are known basis functions and Z is a GP of mean zero with a covariance kernel $k(\boldsymbol{\vartheta}, \boldsymbol{\vartheta}') = \alpha^2 r(\boldsymbol{\vartheta}, \boldsymbol{\vartheta}'; \boldsymbol{\beta})$, based on a correlation function r with parameters $\boldsymbol{\beta}$. This setup is more general than the one considered in Section 6.2.3.1.

The kriging best predictor and covariance at any point in parameter space are given by

$$\hat{y}(\boldsymbol{\vartheta}) = \mathbf{f}(\boldsymbol{\vartheta})^t \hat{\mathbf{b}} + \mathbf{k}(\boldsymbol{\vartheta})^t \mathbf{K}^{-1} (\mathbf{Y} - \mathbf{F} \hat{\mathbf{b}}), \quad (6.33)$$

$$\begin{aligned} c_y(\boldsymbol{\vartheta}, \boldsymbol{\vartheta}') &= k(\boldsymbol{\vartheta}, \boldsymbol{\vartheta}') - \mathbf{k}(\boldsymbol{\vartheta})^t \mathbf{K}^{-1} \mathbf{k}(\boldsymbol{\vartheta}') \\ &\quad + (\mathbf{f}(\boldsymbol{\vartheta})^t - \mathbf{k}(\boldsymbol{\vartheta})^t \mathbf{K}^{-1} \mathbf{F})^t (\mathbf{F}^t \mathbf{K}^{-1} \mathbf{F})^{-1} (\mathbf{f}(\boldsymbol{\vartheta}')^t - \mathbf{k}(\boldsymbol{\vartheta}')^t \mathbf{K}^{-1} \mathbf{F}), \end{aligned} \quad (6.34)$$

where $\mathbf{k}(\boldsymbol{\vartheta}) = [\mathbf{k}(\boldsymbol{\vartheta}^{(1)}, \boldsymbol{\vartheta}), \dots, \mathbf{k}(\boldsymbol{\vartheta}^{(N)}, \boldsymbol{\vartheta})]$, $\mathbf{K}$ is the GP's variance–covariance matrix with elements $K_{ij} = k(\boldsymbol{\vartheta}^{(i)}, \boldsymbol{\vartheta}^{(j)})$, $\mathbf{f}(\boldsymbol{\vartheta}) = (\mathbf{f}_1(\boldsymbol{\vartheta}), \dots, \mathbf{f}_p(\boldsymbol{\vartheta}))$ is a vector of basis functions, $\mathbf{F} = [\mathbf{f}(\boldsymbol{\vartheta}^{(1)})^t, \dots, \mathbf{f}(\boldsymbol{\vartheta}^{(N)})^t]^t$, and $\hat{\mathbf{b}} = (\mathbf{F}^t \mathbf{K}^{-1} \mathbf{F})^{-1} \mathbf{F}^t \mathbf{K}^{-1} \mathbf{Y}$ is the best linear unbiased estimate of $\mathbf{b}$. The kriging prediction uncertainty is $u_y(\boldsymbol{\vartheta}) = c_y(\boldsymbol{\vartheta}, \boldsymbol{\vartheta})^{1/2}$.

$\mathbf{K}$, $\mathbf{k}$, and $\hat{\mathbf{b}}$ depend implicitly on the parameters $\{\alpha, \boldsymbol{\beta}\}$ of the covariance kernel, which have to be calibrated on $\mathbf{Y}$, by maximum likelihood or Bayesian inference.

Different covariance structures are possible [85,87]. A common choice is the exponential family

$$k(\boldsymbol{\vartheta}, \boldsymbol{\vartheta}') = \alpha^2 \prod_{j=1}^{N_\theta} \exp\left(-\beta_j |\boldsymbol{\vartheta}_j - \boldsymbol{\vartheta}'_j|^\gamma\right), \quad (6.35)$$

with parameters $\alpha > 0$, $\beta_j \geq 0 \forall j$, and $0 < \gamma \leq 2$. The γ parameter can be optimized or fixed, for instance, at $\gamma = 2$ (Gaussian kernel), providing an interpolator with interesting smoothness properties.

In the Bayesian calibration of force fields, the computationally limiting step is the estimation of the likelihood, and kriging metamodels have been used to provide efficient interpolation functions, either at the likelihood level or at the property level. To account for the uncertainty of molecular simulation results, one has to add the simulation variances on the diagonal of the variance–covariance matrix, which becomes $K_{ij} = k(\boldsymbol{\vartheta}^{(i)}, \boldsymbol{\vartheta}^{(j)}) + \mathbf{u}_F^{(i)2} \delta_{ij}$ [87].

6.3.2.2 Adaptive learning of kriging metamodels

The construction of a kriging metamodel requires an ensemble of simulations for a set of parameter values Θ , which is to be kept as small as possible to reduce computational charge. The most economical scheme is to start with a small number of simulations, and run new ones at strategically chosen values of the parameters, usually in a sequential manner. This is called adaptive learning or infilling. In force field calibration, two approaches have been used to build metamodels of the likelihood function, either directly during the Bayesian inference algorithm (on-the-fly/synchronous learning) [32,34] or as a preliminary stage (asynchronous learning) [77].

Synchronous learning. In synchronous learning, the surrogate model is built in parallel with the sampling algorithm. The first samples of the sampling algorithm are produced by running the original model. After enough samples have been generated, a surrogate model is constructed. The sampling proceeds by using the surrogate or the exact model according to some criterion.

In Ref. [34], the synchronous learning approach was combined with the TMCMC sampling algorithm [37]. The algorithm is named K-TMCMC and the surrogate model used is kriging. In order to control the size of the error introduced by the approximation of the likelihood, the following rules have been used:

1. The training set consists only of points that have been accepted using the exact and not the surrogate model.
2. Given a point $\boldsymbol{\vartheta}_c$, the training set for the construction of the surrogate consists on the closest (in a chosen metric) n_{neigh} points. Moreover, $\boldsymbol{\vartheta}_c$ must be contained in the convex hull of those points. The parameter n_{neigh} is user-defined and its minimum value depends on the dimension of the sample space.

3. The estimate is checked to verify whether its value is within the lower 95% quantile of all posterior values of the points accounted so far with full model simulations.
4. The relative error $\sqrt{c_y(\boldsymbol{\vartheta}_c, \boldsymbol{\vartheta}_c) / \hat{y}(\boldsymbol{\vartheta}_c)}$ should be less than a user-defined tolerance ε , see Eqs. (6.33) and (6.34).

The algorithm has been applied on a structural dynamics problem.

Asynchronous learning. It is also possible to build a metamodel of the likelihood before performing Bayesian inference. In this case, one starts with a small design, typically based on a Latin hypercube sample [88], and add new points while searching for the maximum of the likelihood function, or equivalently, for the minimum of $-\log p(\mathbf{D}|\boldsymbol{\vartheta}, \mathbf{X}, \mathbf{M})$ [77].

It has been shown that optimizing directly a metamodel $\hat{y}$ is not very efficient [89], the risk being of getting trapped in minima of $\hat{y}$ resulting from its approximate nature. More reliable strategies have been defined for metamodel-based optimization: the *Efficient Global Optimization* (EGO) algorithm [89,90] and its variants [91–94]. The advantage of EGO is to provide an optimal infilling scheme, starting from sparse initial designs. In this context, metamodels such as low-order polynomials are too rigid to enable the discovery of new minima, and higher-order polynomial would require too large designs for their calibration. In contrast, kriging metamodels handle easily this issue and are generally associated with EGO [85,95,96].

EGO is initialized by computing the function y to be minimized for a sample of inputs $\boldsymbol{\Theta} = (\boldsymbol{\vartheta}^{(I)}, \dots, \boldsymbol{\vartheta}^{(N)})$. A first GP $\hat{y}$ is built that reproduces the value of Y for the design points. Outside of the design points, $\hat{y}(\boldsymbol{\vartheta})$ is a prediction of $y(\boldsymbol{\vartheta})$, with an uncertainty $u_y(\boldsymbol{\vartheta})$. As $\hat{y}$ is only an approximation of y , its optima do not necessarily coincide with those of y . The metamodel is thus improved by performing a new evaluation of y for a new parameter set $\boldsymbol{\vartheta}^{(N+I)}$ that maximizes a utility function $\Gamma(\boldsymbol{\vartheta})$. This utility function measures the improvement of the metamodel expected upon the inclusion of $\boldsymbol{\vartheta}^{(N+I)}$ into the sampling design. The process is iterated until $\max[\Gamma(\boldsymbol{\vartheta})]$ is below a user-defined threshold. At the end of the EGO, $\hat{y}$ can be used as a good estimator of y , especially in the neighborhood of its minima.

In the original version of EGO [90], dedicated to the optimization of deterministic functions, $\Gamma(\boldsymbol{\vartheta})$ is the expected improvement (EI) defined as

$$EI(\boldsymbol{\vartheta}) = \mathbb{E} \left[\max \left(y(\boldsymbol{\vartheta}^*) - \hat{y}(\boldsymbol{\vartheta}), 0 \right) \right], \quad (6.36)$$

where $\boldsymbol{\vartheta}^*$ is the point of the sampling design for which y is minimum. When $\hat{y}$ is a kriging metamodel, EI can be computed analytically which makes the search for $\boldsymbol{\vartheta}^{(N+I)}$ very efficient. When dealing with the minimization of a noisy function (which is the case when y is computed from molecular simulation data), the relevance of EI as defined above is questionable [92]. Many adaptations of EGO have been proposed, that differ by the definition of the utility function $\Gamma(\cdot)$, which consists of a trade-off

between minimizing $\hat{y}(\vartheta)$ and reducing its prediction uncertainty $u_y(\vartheta)$. For a recent review of the EGO variants adapted to noisy functions and their relative merits, the reader is referred to Ref. [93].

6.3.2.3 Polynomial Chaos expansions

A PCE is a spectral representation of a random variable [97–99]. Any real-valued random variable Y with finite variance can be expanded in terms of a PCE representation of the form

$$Y = \sum_{|I|=0}^{\infty} Y_I \Psi_I(\xi_1, \xi_2, \dots), \quad (6.37)$$

where $\{\xi_i\}_{i=1}^{\infty}$ are i.i.d. standard random variables, Y_I are the coefficients, $I = (I_1, I_2, \dots) \forall I_j \in \mathbb{N}_0$ is an infinite-dimensional multi-index, $|I| = I_1 + I_2 + \dots$ is the ℓ_1 norm, and Ψ_I are multivariate normalized orthogonal polynomials. The PCE in Eq. (6.37) converges to the true random variable Y in the mean-square sense [99,100]. The basis functions can be written as products of univariate orthonormal polynomials as

$$\Psi_I(\xi_1, \xi_2, \dots) = \prod_{j=1}^{\infty} \psi_{I_j}(\xi_j). \quad (6.38)$$

The univariate functions ψ_{I_j} are I_j -th order polynomials in the independent variable ξ_j orthonormal with respect to the probability density $p(\xi_j)$, i.e., they satisfy

$$\int \psi_{I_j}(\xi) \psi_{I_k}(\xi) dp(\xi) = \delta_{jk}. \quad (6.39)$$

For instance, if the germ ξ_j is a standard Gaussian random variable, then the PCE is built using Hermite polynomials. Different choices of ξ_j and ψ_m are available via the generalized Askey family [100]. For computational purposes, the infinite dimensional expansion (Eq. 6.37) must be truncated

$$Y = \sum_{I \in \mathcal{J}} Y_I \Psi_I(\xi_1, \xi_2, \dots, \xi_{n_s}), \quad (6.40)$$

where $\mathcal{J}$ is some index set, and n_s is some finite stochastic dimension that typically corresponds to the number of stochastic degrees of freedom in the system. For example, one possible choice for $\mathcal{J}$ is the total-order expansion of degree p , where $\mathcal{J} = \{I : |I| \leq p\}$.

To understand the applicability of a PCE to predictive modeling and simulation, assume that we have a target model of interest, $F(\vartheta)$, where ϑ is a single parameter.

The model yields a prediction for the quantity of interest $Q = F(\vartheta)$. If we expand the input ϑ like in (40), the PCE for a generic observable Q can then be written in a similar form

$$Q(\xi) = F(\vartheta(\xi)) = \sum_{I \in \mathcal{I}} c_I \Psi_I(\xi_1, \xi_2, \dots, \xi_{n_s}). \quad (6.41)$$

To compute the PC coefficients c_I with $I \in \mathcal{I}$, we can identify two classes of methods, namely intrusive and nonintrusive [99]. The former involves substituting the expansions into the governing equations and applying orthogonal projection to the resulting equations, resulting in a larger system for the PCE coefficients. This approach is applicable when one has access to the full forward model and can thus modify the governing equations. The nonintrusive approach is more generally applicable, because it involves finding an approximation in the subspace spanned by the basis functions by evaluating the original model many times. This nonintrusive approach basically treats the simulator for the forward model as a black-box, and it does not require any modification of the governing equations or the simulator itself.

One example of nonintrusive methods relies on orthogonal projection of the solution

$$c_I = \mathbb{E}[F(\vartheta)\Psi_I] = \int_{\Xi} F(\vartheta(\xi))\Psi_I(\xi)p(\xi)d\xi. \quad (6.42)$$

and is known as nonintrusive spectral projection (NISP). In general, this integral must be estimated numerically, using Monte Carlo or quadrature techniques [98,99]. Monte Carlo methods are insensitive to dimensionality, but it is well known that their convergence is slow with respect to the number of samples. For a sufficiently smooth integrand, quadrature methods converge faster, but they are affected by the curse of dimensionality. The number of dimensions that define the threshold for when the problem becomes unaffordable cannot be set a priori, and it is obviously problem dependent. However, one can guess that most physical problems of interest, due to their high computational cost, become intractable even for a small number of dimensions. Sparse grids can mitigate the curse of dimensionality, but they can lead to issues due to negative weights.

An alternative nonintrusive method is regression, which involves solving the linear system:

$$\underbrace{\begin{bmatrix} \Psi_{I^1}(\xi^{(1)}) & \dots & \Psi_{I^K}(\xi^{(1)}) \\ \vdots & & \vdots \\ \Psi_{I^1}(\xi^{(K)}) & \dots & \Psi_{I^K}(\xi^{(K)}) \end{bmatrix}}_A \underbrace{\begin{bmatrix} c_{I^1} \\ \vdots \\ c_{I^K} \end{bmatrix}}_c = \underbrace{\begin{bmatrix} F(\vartheta(\xi^{(1)})) \\ \vdots \\ F(\vartheta(\xi^{(K)})) \end{bmatrix}}_F, \quad (6.43)$$

where Ψ_{I^n} is the n -th basis function, c_{I^n} is the coefficient corresponding to that basis, and $\xi^{(m)}$ is the m -th regression point. In the regression matrix A , each column corresponds to a basis element and each row corresponds to a regression point from the training set.

The NISP or a fully tensorized regression approach is suitable when the data being modeled are not noisy. In the presence of noisy data, a straightforward regression or NISP would yield a deterministic answer, thus losing any information about the noise. A suitable approach to tackle these problems is Bayesian inference to infer the coefficients, which allows one to capture the uncertainty in the data in a consistent fashion [101]. This approach is convenient also because it allows a certain flexibility in the sampling method of the stochastic space, since no specific rule is required a priori. An obvious constraint, however, is that the number of sampling points should be adequate to the target order of the expansion to infer. The result of the Bayesian approach is an *uncertain* PC representation of a target observable, i.e., the vector of PC coefficients is not a deterministic vector, but it is a random vector defined by a joint probability density containing the full noise information. The Bayesian method to infer the PC coefficients consists of three main steps: collecting a set of the observations of the QoIs, formulating the Bayesian probabilistic model, and, finally, sampling the posterior distribution.

When collecting the observations, one should choose wisely the sampling points over the space. A possible option would be to use the same sampling points one would use for the NISP approach, but this would constrain how to choose the points. One possibility that would help with the curse of dimensionality is to use nested grids, which would benefit approaches like adaptive refinement. One example of this class of points is Fejér nodes [102]. Leveraging the nested nature of these grids, one can explore an adaptive sampling technique to build the target set of observations of the QoIs. Further details of this approach will be discussed below in Section 6.4.2.1.

Once a set of observations $\mathbf{F}$ is obtained, one needs to formulate the likelihood for the coefficients c_I with $I \in \mathcal{I}$. Using a standard Gaussian additive model to capture the discrepancy between each data point, f_i , and the corresponding model prediction yields the well-known Gaussian likelihood and the following the joint posterior distribution, of the PC coefficients and noise variance as

$$p(c_I | \mathbf{F}, M) \propto p(\mathbf{F} | c_I, M) p(c_I),$$

with $I \in \mathcal{I}$, and $p(c_I)$ denoting the prior on the PC coefficients. Once a proper prior distribution is chosen, sampling from this high-dimensional posterior can be performed using, e.g., MCMC methods.

6.3.3 Approximation of intractable posterior PDFs

The Laplace method. This is a technique for the approximation of integrals of the form

$$\int_{\Theta} e^{Nf(\vartheta)} d\vartheta.$$

The technique is based on approximating the integrand with a Taylor expansion around the unique maximum of the function f . The approximation is valid for large values of N .

The same idea can be applied for the approximation of intractable posterior distributions. We expand the logarithm of the posterior distribution, denoted by $\mathcal{L}(\boldsymbol{\vartheta})$, around the MAP estimate of [Eq. \(6.8\)](#), $\hat{\boldsymbol{\vartheta}}$,

$$\mathcal{L}(\boldsymbol{\vartheta}) \approx \mathcal{L}(\hat{\boldsymbol{\vartheta}}) + \frac{1}{2}(\boldsymbol{\vartheta} - \hat{\boldsymbol{\vartheta}})^\top \nabla \nabla^\top \mathcal{L}(\hat{\boldsymbol{\vartheta}}) (\boldsymbol{\vartheta} - \hat{\boldsymbol{\vartheta}}). \quad (6.44)$$

The posterior distribution is then approximated by

$$p(\boldsymbol{\vartheta} | \mathbf{D}, M) \approx c(\hat{\boldsymbol{\vartheta}}) \mathcal{N}(\boldsymbol{\vartheta} | \hat{\boldsymbol{\vartheta}}, \Sigma(\hat{\boldsymbol{\vartheta}})), \quad (6.45)$$

where

$$c(\hat{\boldsymbol{\vartheta}}) = \left((2\pi)^N |\Sigma(\hat{\boldsymbol{\vartheta}})| \right)^{-\frac{1}{2}} p(\hat{\boldsymbol{\vartheta}} | M) \quad (6.46)$$

is the normalization constant and

$$\Sigma(\hat{\boldsymbol{\vartheta}}) = \left(\nabla \nabla^\top \mathcal{L}(\hat{\boldsymbol{\vartheta}}) \right)^{-1} \quad (6.47)$$

is the inverse of the Hessian of $\mathcal{L}$ at $\hat{\boldsymbol{\vartheta}}$. The methodology has been applied in Ref. [103] for the approximation of the posterior distribution in a hierarchical Bayesian model (see [Section 6.2.3.2](#)).

Variational inference. This is another method for the approximation of intractable posterior distributions. We define a family $\mathcal{S}$ of densities over the space Θ of parameters, e.g., exponential functions, GPs, neural networks. From this family, we choose the member that is closest to the posterior distribution based on the Kullback–Leibler (or relative entropy) divergence,

$$\hat{q} = \operatorname{argmax}_{q \in \mathcal{S}} D_{KL}(q(\cdot) \parallel p(\cdot | \mathbf{D}, M)), \quad (6.48)$$

D_{KL} where the KL divergence is defined by

$$D_{KL}(q(\cdot) \parallel p(\cdot | \mathbf{D}, M)) = \int_{\Theta} \log \frac{q(\boldsymbol{\vartheta})}{p(\boldsymbol{\vartheta} | \mathbf{D}, M)} q(\boldsymbol{\vartheta}) d\boldsymbol{\vartheta}, \quad (6.49)$$

which can be also written as

$$D_{KL}(q(\cdot) \parallel p(\cdot | \mathbf{D}, M)) = -(\mathbb{E}_q[\log(p(\mathbf{D} | \boldsymbol{\vartheta}, M)p(\boldsymbol{\vartheta} | M)) - \mathbb{E}_q[\log(q(\boldsymbol{\vartheta}))]) + \log p(\mathbf{D} | M). \quad (6.50)$$

The last term, $\log p(\mathbf{D} | M)$, is intractable but does not depend on q and thus can be ignored in the optimization process. An usual assumption on the family $\mathcal{D}$ is that it contains product functions,

$$q(\boldsymbol{\vartheta}) = \prod_{i=1}^{N_\vartheta} q_i(\boldsymbol{\vartheta}_i). \quad (6.51)$$

This special case is called *mean-field* inference. One way to solve the optimization problem in this case is by coordinate ascent. At the k -th step of the iteration, we solve the problems

$$\hat{q}_j^{k+1} = \operatorname{argmax}_{q_j^{k+1} \in \mathcal{D}_i} D_{KL}\left(q_1^{k+1}, \dots, q_{j-1}^k, q_j^{k+1}, q_{j+1}^k, \dots, q_{N_\vartheta}^{k+1} \parallel p(\cdot | \mathbf{D}, M)\right), \quad (6.52)$$

for $j = 1, \dots, N_\vartheta$.

In Ref. [104], the variational approach has been applied for the inference of the forcing parameters and the system noise in diffusion processes. In Ref. [105], the authors applied this approach in the path-space measure of molecular dynamics simulations, in order to obtain optimized coarse-grained molecular models for both equilibrium and nonequilibrium simulations.

6.3.4 High-performance computing for Bayesian inference

Bayesian inference can be computationally costly, in particular when MCMC methods are used to sample the posterior distribution. This cost is further exacerbated when the model evaluations are expensive, which is often the case with large-scale molecular simulations. Performing such high throughput simulations in massively parallel HPC architectures may offer a remedy for the computational cost. However, this implementation introduces new challenges as MD simulations performed with different sets of parameters, each distributed on different nodes, may exhibit very different execution times. In such cases, the sampling of the posterior PDF will result in load imbalance as nodes who have completed their tasks would be idling, thus reducing the parallel efficiency of the process. One remedy in this situation is the introduction of task-based parallelism.

A number of frameworks have been proposed to address this situation. PSUADE [106], developed in Lawrence Livermore National Laboratory, is an HPC software

written in C++ for UQ and sensitivity analysis. VECMA [107] is a multipartner project under development that aims at running UQ problems on exascale environments. Another relevant software is SPUX [108], developed in EAWAG, Switzerland, aimed for UQ in water research written in Python. The CSE Laboratory at ETHZ has developed *Korali*, a framework for nonintrusive Bayesian UQ of complex and computationally demanding physical models on HPC architectures.¹ *Korali* builds on the framework $\Pi 4U$ [76] where Bayesian tools were expressed as engines upon the layer of the TORC [109] tasking library. TORC works by defining a set of workers, each spanning multiple processor cores, distributed throughout a computing cluster and assigning them a fixed set of model evaluations as guided by the stochastic method. However, TORC has two drawbacks: (i) its design is very strongly coupled with each UQ method that requires a problem-specific interface and (ii) its fixed work distribution strategy can cause load imbalance between the worker teams, causing cores to idle. In turn, the parallel implementation of *Korali* follows a producer–consumer paradigm to distribute the execution of many model evaluations across a computer cluster.

Upon initialization, the *Korali* runtime system instantiates multiple workers, each comprising one or more processor cores. During execution, *Korali* keeps workers busy by sending them a new batch of model evaluations to compute. In turn, as soon a worker finishes an evaluation, it returns its partial results to *Korali*'s runtime system. *Korali* prevents the detrimental effects of load imbalance, where a worker may finish before others and thus remaining idle, by distributing small work batches at a time. Communication between *Korali* and its worker tasks is entirely asynchronous. That is, each worker will communicate partial results to the runtime system without a reciprocal receive request from the latter. *Korali*'s runtime system employs remote procedure calls (RPCs) to handle worker requests opportunistically, eliminating the need for barriers or other synchronization mechanisms. *Korali* uses the UPC++ communication library [110] as its back-end for RPC execution.

Finally, *Korali* allows users to use their own code to simulate the computational model (e.g., a computational fluid dynamics simulation) to perform model evaluations by providing a simple C/C++/Python function call interface. The user code can embrace inter and intranode parallelism expressed with MPI communication, OpenMP directives, or GPUs (e.g., via CUDA).

6.4 Applications

Applications of Bayesian methods to force fields calibration are still few, and mostly focused on problems with a small number of parameters (typically less than 10): simple potentials (LJ, Mie) and coarse-grained potentials [111–113].

In this section, we present several applications at various levels of complexity in order to display the extent of successes and difficulties arising in this area.

¹ <https://cselab.github.io/korali/>.

6.4.1 Introductory example: two-parameter Lennard-Jones fluids

6.4.1.1 The Lennard-Jones potential

LJ fluids are one of the simplest systems studied in molecular simulation. They are considered a good model (qualitatively and for some applications quantitatively) for rare gases (Ar, Kr) or small “spherical” molecules (CH_4 , N_2 , etc.). In LJ fluids, two particles, separated by a distance r , interact according to the LJ potential:

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (6.53)$$

The LJ potential is the sum of two terms: a r^{-12} term repulsive at short distance and a r^{-6} attractive term. The two parameters, σ and ϵ , that control this interaction have a physical understanding: σ is related to the size of the particle (its “radius”), whereas ϵ controls the energetic strength of the interaction. The use of the LJ potential is not limited to the study of monoparticulate systems and is indeed one of the most commonly encountered term in common force fields to represent non-Coulombic interactions between two atoms in molecular systems. Note that the LJ potential is sometimes used in the framework of dimensionless units for the sake of generality. However, when one needs to study real fluids, one has to manipulate dimensioned properties in order to compare to experimental data.

The LJ potential has been the major target for force field calibration within the Bayesian framework [17,30,32,42,52,69,114]. This is due to its simplicity, with only two parameters to be calibrated, and to the fact that some experimental properties for LJ fluids (second virial coefficient, diffusion coefficient, etc.) can be obtained using analytical formulae. This enables (a) to get the likelihood “for free” and thus to perform a thorough exploration of the parameter space without the need to use advanced methodologies and (b) to get rid of the effects of simulation parameters, such as the cut-off radius [32], and of simulation numerical/measurement uncertainty in the calibration process ($u_{F_i} = 0$ in Eq. 6.4).

6.4.1.2 Bayesian calibration

As an illustration of the theoretical points presented in the previous sections, we calibrated the LJ potential for Ar over three different phase equilibrium properties (saturated liquid and vapor densities ρ_{liq} and ρ_{vap} , and saturated vapor pressure P_{sat}) at 12 temperatures ranging from 90 to 145 K. Calibration data were recovered from the NIST website [40], and property computation is made through the use of Eqs. (6.9)–(6.11) of Werth et al. [83], with $n = 12$. The NIST website reports upper limits on uncertainty for densities of 0.02% and 0.03% for pressures. The exact meaning of these uncertainties on equations-of-state results has been discussed earlier in this chapter. However, they are much smaller than the modeling errors expected from an LJ model, so that we do not need to be concerned by possible correlations. In all the following calibrations, uniform priors have been used for the LJ parameters σ and ϵ .

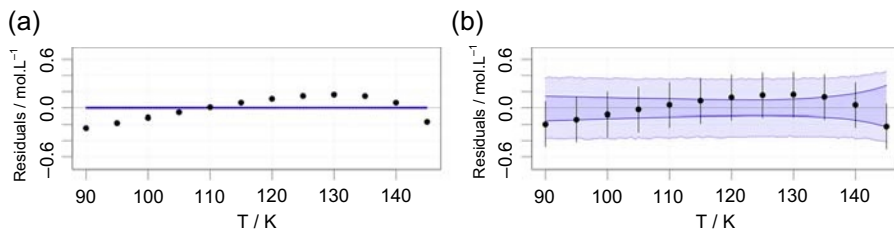


Figure 6.3 Calibration of LJ parameters for Ar over ρ_{liq} by the standard Bayesian scheme: (a) using fixed reference uncertainties or (b) calibrating uncertainty τ along with σ and ϵ to deal with model inadequacy. The points show the residuals at the MAP with the error bars representing 2τ (in (a), the error bars are smaller than the point size). The shaded areas represent posterior confidence (dark) and prediction (light) 95% probability intervals.

Fig. 6.3(a) shows the residuals of the fit at the MAP for calibration over ρ_{liq} , with a likelihood based on Eq. (6.7), where Σ_R is a diagonal matrix with elements $\Sigma_{R,ij} = u_{d_i}^2 \delta_{ij}$, with reference data uncertainties u_{d_i} set to the NIST recommended values. The calibration is clearly unsuccessful. Although the residuals are “small” (roughly 1% of the QoI values), they fall outside of the 95% prediction probability intervals and are clearly correlated. These two observations are symptomatic of model inadequacy: the physics contained in the LJ potential is not sufficient to enable accurate estimation of Ar-saturated liquid density over this range of temperature.

We will discuss here a simple way to overcome this limitation which is to consider $\Sigma_{R,ij} = \tau^2 \delta_{ij}$, where τ is a parameter to be calibrated along with σ and ϵ , in order to ensure a Birge ratio at the MAP close to 1 (Eq. 6.13). Note that τ is given a half-normal prior PDF with a large standard deviation of 0.5, in order to ensure its positivity and to disfavor unsuitably large values. The residuals of the calibration are displayed in Fig. 6.3(b). The values of parametric uncertainties (given in Table 6.1) are now consistent with the magnitude of the residuals.

Note that the residuals are still correlated due to model inadequacy, so that the calibration should not in principle be considered successful. However, for pedagogical

Table 6.1 Results of the calibration of an LJ force field for Argon.

Calibration data	σ (Å)	ϵ (K)	$\tau_{\rho_{liq}}$ (mol.L ⁻¹)	$\tau_{\rho_{vap}}$ (mol.L ⁻¹)	$\tau_{P_{sat}}$ (MPa)
ρ_{liq}	3.40(1)	115.3(3)	0.17(4)		
ρ_{vap}	3.73(4)	111.8(4)		0.09(2)	
P_{sat}	3.45(3)	115.7(6)			0.009(2)
Consensus	3.41(1)	116.5(1)	0.26(6)	0.24(6)	0.010(3)
Hierarchical	3.53(15)	114.2(2.1)	0.12(2)	0.07(2)	0.009(2)

The mean values of the parameters are given, as well as their marginal uncertainties in parenthesis notation.

purposes, we will ignore this issue for now and postpone discussion about advanced schemes to deal with model inadequacy to [Section 6.4.3](#).

Results of the calibration over ρ_{vap} or over P_{sat} are reported in [Table 6.1](#) and [Fig. 6.4](#). Values obtained for the parameters are quite different, both in terms of mean values and uncertainties (see [Table 6.1](#)). [Fig. 6.4](#) shows posterior PDF samples for σ and ϵ obtained from the three calibrations. The three PDFs do not overlap, the consequence being that it is not possible to reproduce quantitatively a property on which the parameters have not been calibrated, taking into account parameters uncertainties. This is true also when model errors are taken into account, as is done here through the calibration of τ values. This has already been shown in previous studies [[17,35,59](#)]. The very different values obtained in the calibration using ρ_{vap} or ρ_{liq} certainly originate from the fact that they deal with different states of matter: the two-body nature of the LJ potential is not appropriate to deal with condensed phase and its success relies on incorporation of many-body interactions into the LJ parameters, leading to values much different than those in gas phase. The choice of the reference data is thus of paramount importance when calibrating force field parameters, because their values will integrate, in an effective way, part of the physics not described in the mathematical expression of the force field.

[Fig. 6.4](#) also displays a sample of the posterior PDF of LJ parameters calibrated over the three observables together, using three different uncertainty parameters $\tau = \{\tau_{\rho_{liq}}, \tau_{\rho_{vap}}, \tau_{P_{sat}}\}$. This consensus situation leads to values of the parameters that are dominated by ρ_{liq} and P_{sat} , which is certainly due to the very high sensitivity of ρ_{liq} to σ . This can be acknowledged by the very small uncertainty on σ obtained from the calibration over ρ_{liq} .

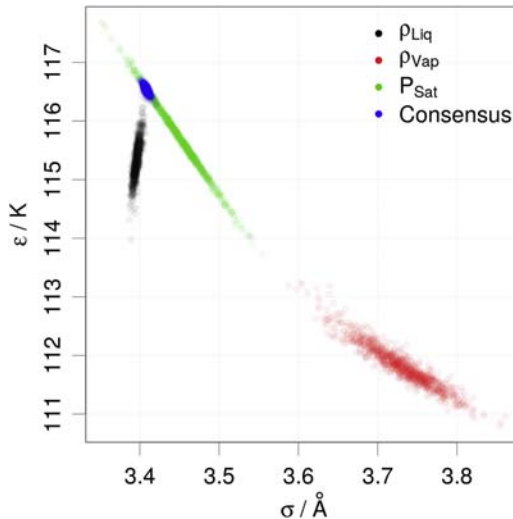


Figure 6.4 Samples of the posterior PDF of LJ parameters for Argon, calibrated on saturated liquid density (black), saturated vapor density (red), saturated vapor pressure (green), or using the three observables simultaneously as calibration data (blue).

It is interesting to note that the parameter uncertainties are greatly reduced in the “consensus” calibration, as can be seen in Fig. 6.4 and Table 6.1. This is balanced by an increase of $\tau_{\rho_{liq}}$ and $\tau_{\rho_{vap}}$, ensuring that the calibration remains statistically sound (when considering only the Birge ratio). As mentioned earlier, adding data to the reference set decreases the quality of the fit (larger residuals and values of τ_i), but simultaneously decreases the uncertainty on the parameters, and by consequence the uncertainty of model predictions. This unsuitable behavior justifies the development of more advanced statistical formulations to deal with model inadequacy.

Fig. 6.4 shows a strong correlation between σ and ϵ , whatever calibration data are used (although the correlation is not identical in all cases). Such information is crucial when one wants to perform UP. It is thus very important when reporting force field parameter uncertainties not only to limit to the sole marginal uncertainty on each parameter but also to include their correlation, or provide the full posterior PDF.

6.4.1.3 Hierarchical model

Calibration. A hierarchical model (see Section 6.2.3.2) was built to calibrate a unique set of LJ parameters on the three observables used above.

To define the overall PDF with a bivariate normal distribution, one has to calibrate five parameters (two for the center of the distribution, two for the uncertainties, and one for correlation) on six values (the coordinates of the three local LJ parameters). To formulate it differently, the question is “From which bivariate Gaussian distribution are these three points sampled?”. One has thus to expect a large statistical uncertainty on the overall distribution. To compensate for the sparse data, one introduces an exponential prior on the uncertainties to constrain them to be as small as possible. A few tests have shown that a too strong constraint affects the local LJ parameters, resulting in a bad fit of ρ_{vap} . The solution shown in Fig. 6.5(a) is the best compromise (i.e., the most compact overall distribution preserving reasonable local LJ parameters) we were able to achieve. The parameters are reported in Table 6.1 for comparison with the standard calibration. The correlation parameter is poorly identified $-0.56(37)$.

Prediction. The overall distribution was used to predict a new property, the second virial coefficient, using the analytical formula by Vargas et al. [115]. The 95% confidence interval is represented in Fig. 6.5(b) in comparison to experimental data [116]. The mean prediction is in very good agreement with the reference data up to 350 K. However, the prediction uncertainty is much larger than the experimental ones. For instance, at 200 K, the prediction uncertainty is more than 10 times larger than the experimental one (0.0040 vs. 0.0003 L.mol⁻¹). Although statistically consistent, hierarchical calibration leads, in this case, to predictions that may not be precise enough to replace experiments.

6.4.1.4 Uncertainty propagation through molecular simulations

UP is typically done by drawing samples from the parameters posterior PDF and computing quantities of interest with the model for each parameter set value. Following this procedure for the LJ parameters for Argon (calibrated over second virial

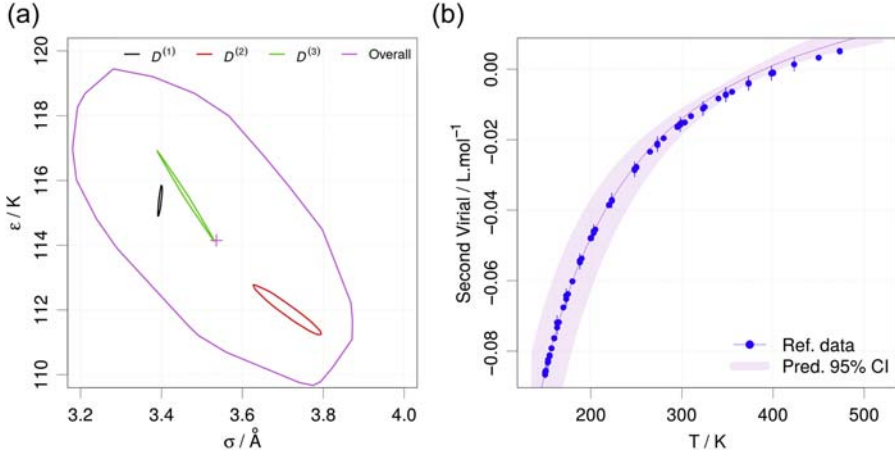


Figure 6.5 Calibration prediction with a hierarchical model: (a) 95% probability contour lines of the posterior PDF of LJ parameters for Ar: local parameters for saturated liquid density ($D^{(1)}$; black), saturated vapor density ($D^{(2)}$; red), saturated vapor pressure ($D^{(3)}$; green), and overall distribution (purple); (b) Comparison of the predicted second virial coefficients (purple) to experimental data (blue).

coefficient data), Cailliez and Pernot computed uncertainties obtained from MD and MC simulations [17]. They showed that molecular simulations amplify parametric uncertainties. Although relative uncertainties on σ and ϵ were around 0.1%, the output uncertainties were roughly 0.5%–2%, depending on the computed property. More importantly, when decomposing the uncertainties into their numerical (sum of computational and measurement uncertainties as defined in the Introduction) and parametric components, they observed that the latter was the most significant part of the total uncertainty budget. Similar observations have since been made in the literature in the case of other force fields [59,77]. This means that parametric uncertainties should not be overlooked anymore when reporting molecular simulation results.

6.4.1.5 Model improvement and model selection

As described earlier, the LJ potential is unable to reproduce various QoIs with a unique parameter set or even, in some cases, one quantity over a large range of physical conditions. One way to overcome this limitation is to improve the physical description of the interactions by modifying the form of the force field (model improvement). A “simple” improvement of the LJ potential is to add a new parameter to be calibrated. A straightforward choice is the repulsive exponent p (the value of 12 in the LJ potential has no physical grounds). The modified LJ potential (hereafter referred to as LJ_p) becomes

$$V_{LJ_p}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^p - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (6.54)$$

The LJ_p potential has been calibrated by the standard scheme for each of the three observables from the previous sections using the metamodel of Werth et al. [83]. Calibration summaries are presented in Table 6.2 and samples of the posterior PDFs are presented in Fig. 6.6. One sees that the situation is better for the densities, which are close to having an intersection but they do not overlap in the three parameter dimensions and there is no reconciliation with P_{sat} . The additional parameter is not sufficient to offer a complete data reconciliation.

Fit quality. The improvement of fit quality of the new potential can be assessed by comparing the optimized uncertainty parameters τ_i for each QoI in Tables 6.1 and 6.2. For ρ_{liq} the value has diminished from 0.17 to 0.10 mol L⁻¹, indicating a reduction of almost a factor two of the residuals amplitude. For ρ_{vap} the effect is even larger, from 0.09 to 0.02 mol L⁻¹, whereas the fit quality of P_{sat} has not been significantly affected.

Transferability. It also should be noted that the spread of the PDFs is sometimes much larger for σ and ϵ than for the LJ potential and ϵ has shifted to much larger values, which indicates that the LJ_p potential might be overparameterized for ρ_{Liq} . The additional parameter therefore improves the representation of the densities (through the metamodel used here) and helps to reconcile them. There remains, however, the impossibility to fit the three QoIs with a single set of these three parameters.

Fitting of LJ_p on the radial distribution functions. Kulakova et al. [35] calibrated LJ and LJ_p potentials in order to reproduce RDFs of argon in six different conditions: five liquid states at different temperatures and pressures (labeled L_1 to L_5) and one vapor state (labeled V). Some of the results from Ref. [35] are reproduced in Table 6.3.

As seen previously, adding one degree of freedom in the potential enables better representation of experimental data: the calibration of the LJ_p potential succeeded for two experimental conditions (L_1 and L_2) in which the LJ potential failed. Here again, the best values of the LJ parameters are modified when p is optimized. This is due to the fact that the best value for p is in all cases very different from 12 (between 6.15 and 9.84). This is especially true for ϵ , due to a strong anticorrelation between parameters ϵ and p observed in this study as well as in the previous example and in Ref. [83].

The added value of the force field improvement can be measured using the model selection criterion described in Section 6.2.1.3. Using equal a priori probabilities for models LJ and LJ_p , the preferred model is the one exhibiting the largest evidence. These are reported in Table 6.3. In all liquid conditions, the LJ_p model is shown to be a valuable improvement over the LJ potential. However, in vapor conditions, the result was opposite. In such conditions the LJ_p potential is overparameterized.

Although both examples considered above reach similar conclusions on the study of the LJ_p potential, one can see in the details that the model used (metamodel vs. simulation) and the choice of calibration QoIs have a strong impact on the numerical values of the parameters. For the metamodel of Werth calibrated on ρ_{liq} , ρ_{vap} , and P_{sat} , the optimal values of p lie between 19 and 27, while for simulations calibrated on RDF these lie between 6.15 and 9.84. Another study on Ar, with different model and data, reached the conclusion that the best value for p was close to 12 [117].

Table 6.2 Results of the calibration of an LJ_p force field for Argon.

Calibration data	σ (Å)	ϵ (K)	p	$\tau_{\rho_{liq}}$ (mol.L ⁻¹)	$\tau_{\rho_{vap}}$ (mol.L ⁻¹)	$\tau_{P_{sat}}$ (MPa)
ρ_{liq}	3.51(3)	162.1(9.1)	26.4(4.5)	0.10(3)	0.02(1)	0.007(2)
ρ_{vap}	3.48(2)	145.0(1.3)	19.5(4)			
P_{sat}	4.08(19)	136.6(5.3)	21.7(3.4)			

The mean values of the parameters are given, as well as their marginal uncertainties in parenthetic notation.

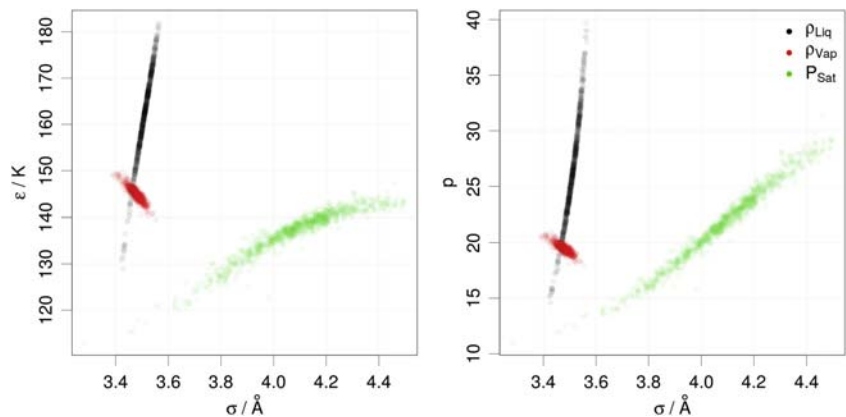


Figure 6.6 Projections of samples of the posterior PDF of the three-parameter LJ_p model, calibrated on saturated liquid density (in black), saturated vapor density (in red), and saturated vapor pressure (in green).

Table 6.3 Results of the calibration of LJ and LJ_p force field for Argon on radial distribution function.

Experimental data	Force field model	$q(\sigma)(\text{\AA})$	$q(\epsilon)(\text{K})$	$q(p)$	log(evidence)
L_2	LJ	—	—	[6.29, 8.31]	—
	LJ_p	[3.32, 3.43]	[358.3, 2222.2]		−14.8
L_3	LJ	[3.25, 3.33]	[142.9, 133.9]	[6.33, 7.07]	−9.72
	LJ_p	[3.30, 3.40]	[459.9, 1358.7]		2.81
L_4	LJ	[3.30, 3.36]	[127.8, 133.9]	[6.90, 9.84]	5.10
	LJ_p	[3.33, 3.40]	[162.0, 533.4]		5.18
V	LJ	[3.03, 3.21]	[41.8, 92.6]	[6.15, 6.92]	−3.83
	LJ_p	[3.04, 3.12]	[314.5, 1817.1]		−4.94

For each force field parameter, the 5%–95% quantiles are given in brackets. Values are taken from L. Kulakova, G. Arampatzis, P. Angelikopoulos, P. Hadjidoukas, C. Papadimitriou, P. Koumoutsakos, Data driven inference for the repulsive exponent of the Lennard-Jones potential in molecular dynamics simulations, Sci. Rep. 7 (2017) 16576. <https://doi.org/10.1038/s41598-017-16314-4>.

6.4.1.6 Summary

Exploration of the calibration of an LJ potential for Argon, one of the simplest problems in the field, has revealed several difficulties. Mainly the excessive simplicity of this popular potential function leads to model inadequacy, notably for condensed phase conditions. The Bayesian approach provides an unambiguous diagnostic for such problems, that would be difficult to assess with calibration methods ignoring parametric uncertainty. Bayesian inference also offers advanced methods (e.g., hierarchical modeling (HM)) to treat model inadequacy; however, we have seen that the solutions might be of a limited practical interest due to very large prediction uncertainties. The reduction of model inadequacy by improvement of the interaction potential is clearly a necessary step if one wishes to establish predictive models for multiple QoIs. Apparently, the LJ_p model, although a notable improvement over LJ, is not able to solve all the inadequacy problems.

6.4.2 Use of surrogate models for force field calibration

For most force fields and properties, no analytical formulae are available, and one has to resort to molecular simulations in order to compute properties to calibrate the force field parameters. For extensive exploration of parameter space, metamodels are needed to overcome the prohibitive cost of simulations. This section presents examples of PCE- and GP-based metamodels.

6.4.2.1 Polynomial Chaos expansions

An example of using PCE as surrogate models for calibrating force field parameters can be found in Refs. [84,118]. The work focuses on isothermal, isobaric MD simulations of water at ambient conditions, i.e., $T = 298\text{K}$ and $P = 1\text{ atm}$. In the first part, Rizzi et al. describe the forward problem, i.e., how to build a PC surrogate for target macroscale quantities of interest comparing a NISP against a Bayesian approach. The latter, as discussed, is more suited for noisy data because it yields an expansion capturing both the parametric uncertainty stemming from the force field parameters as well as the sampling noise inherent to MD computations. In the second part, Rizzi et al. show how to use these PC expansions as a surrogate model to infer small-scale, atomistic parameters, based on data from macroscale observables.

MD system and uncertain parameters. In this example, the computational domain is a cubic box of side length equal to $37.2\text{ \AA}$ with periodic boundary conditions along each axis, containing 1728 water molecules. The water molecule is modeled using the TIP4P representation [119]. The potential is a combination of an LJ component modeling dispersion forces, and Coulomb's law to model electrostatic interactions. The complete force field is defined by seven parameters: three defining the geometry of the water molecule, two for the charges of the hydrogen (H) and oxygen (O) atoms, and, finally, the two parameters for the LJ parameters defining the dispersion forces between molecules. Data for three target observables, namely density (ρ), self-diffusivity (ϕ), and enthalpy (H), are collected during the

steady-state part of each run via time averaging. The goal is to characterize how intrinsic sampling noise and uncertainty affecting a subset of the input parameters influence the MD predictions for the selected observables.

The study is based on a stochastic parametrization of the LJ characteristic energy, ϵ , and distance, σ , as well as the distance, d , from the oxygen to the massless point where the negative charge is placed in the TIP4P model as

$$\begin{aligned}\epsilon(\xi_1) &= 0.147 + 0.043\xi_1, \quad \text{kcal/mol}, \\ \sigma(\xi_2) &= 3.15061 + 0.021\xi_2, \quad \text{\AA}, \\ d(\xi_3) &= 0.14 + 0.035\xi_3, \quad \text{\AA},\end{aligned}\tag{6.55}$$

where $\{\xi_i\}_{i=1}^3$ are independent and identically distributed (i.i.d.) standard random variables (RVs) uniformly distributed in the interval $(-1, 1)$. This reformulation reflects an “uncertain” state of knowledge about these parameters and is based on means and standard deviations extracted from the following sources: [119–123]. All the remaining parameters are set to their values commonly used for computational applications of TIP4P water, see, e.g., Refs. [119, 120].

Collection of observations. Given N points $\{\xi^i\}_{i=1, \dots, N}$ in the parameter space $(-1, 1)^3$, and considering four realizations of the MD system at each sampling point, the three sets of $N \times 4$ observations (one for each observable ρ, ϕ, H) can be written as

$$D_k = \left\{ d_k^{i,j} \right\}_{i=1, \dots, N}^{j=1, \dots, 4}, \quad k = 1, 2, 3,\tag{6.56}$$

where $\left\{ d_k^{i,j} \right\}_{j=1, \dots, 4}$ represents the four values obtained for the k -th observable at the i -th sampling point $\xi^i = (\xi_1^i, \xi_2^i, \xi_3^i)$. The authors demonstrate how to leverage nested Fejér grids [102] to sample the stochastic space. In one dimension, each grid level, l' , is characterized by $n_{l'} = 2^{l'} - 1$ points in the interval $(-1, 1)$, corresponding to the abscissae of the maxima of Chebyshev polynomials of different orders. Extensions to higher-dimensional spaces can be readily obtained by tensorization. Leveraging the nested nature of these grids, an adaptive technique is used to build a set of observations of the quantities of interest for the Bayesian inference. More specifically, at a given level l'' , the density of sampling points is increased only in the regions of the domain where the “convergence” of the PC expansions inferred at levels $l' < l''$ is slower. Compared to fully tensored grids, this yields a considerable reduction in the computational cost without penalizing the accuracy.

The likelihood for the PC coefficients of the observables of interest is formulated by expressing the discrepancy between each data point, $d_k^{i,j}$, and the corresponding model prediction, $F_k(\xi^i)$, as

$$d_k^{i,j} = F_k(\xi^i) + \gamma_k^{i,j}, \quad k = 1, 2, 3, i = 1, \dots, N, j = 1, \dots, 4,\tag{6.57}$$

where $d_k^{i,j}$ represents the j -th data point obtained for the k -th observable at the i -th sampling point, ξ^i , $F_k(\xi^i)$ denotes the value of the PC representation of the k -th observable evaluated at ξ^i , and $\gamma_k^{i,j}$ is a random variable capturing their discrepancy. Based on central limit arguments one can argue that, in the present setting, as the number of atoms in the system and the number of time-averaged samples become large, the distribution of $\mathbf{D}_k$, $k = 1, 2, 3$, around the true mean tends to a Gaussian. A suitable and convenient choice is to assume each $\gamma_k^{i,j}$ to be *i.i.d.* normal RVs with mean zero and variance $\tilde{\sigma}_k^2$, i.e., $\gamma_k^{i,j} \sim \mathcal{N}(0, \tilde{\sigma}_k^2)$, $k = 1, 2, 3$, $i = 1, \dots, N$, $j = 1, \dots, 4$. The variances $\{\tilde{\sigma}_k^2\}_{k=1}^3$ are treated as hyperparameters, i.e., they are not fixed but become part of the unknowns.

These considerations yield the likelihood function:

$$p\left(D_k \left| \left\{c_l^{(k)}\right\}_{l=0}^P, \tilde{\sigma}_k^2, F_k\right.\right) = \prod_{i=1}^N \prod_{j=1}^4 \frac{1}{\sqrt{2\pi\tilde{\sigma}_k^2}} \exp\left(-\frac{\left[d_k^{i,j} - F_k(\xi^i)\right]^2}{2\tilde{\sigma}_k^2}\right),$$

$$k = 1, 2, 3,$$
(6.58)

where $d_k^{i,j}$ is the j -th observation obtained at the i -th sampling point ξ^i for the k -th observable, while $F_k(\xi^i)$ denotes the value of the PC representation of the k -th observable evaluated at the i -th sampling point ξ^i , and $\left\{c_l^{(k)}\right\}_{l=0}^P$ is the set of PC coefficients for the k -th observable. The set has $P+1$ terms, based on total order, where $P+1 = (3+p)!/3!/p!$, where p is the target order of the expansion. For instance, $p = 1$ for a linear expansion, $p = 2$ for a quadratic, etc.

Using Bayes' theorem, the joint posterior distribution of the PC coefficients and noise variance for the k -th observable can be expressed as

$$p\left(\left\{c_l^{(k)}\right\}_{l=0}^P, \tilde{\sigma}_k^2 \left| D_k, F_k\right.\right) \propto p\left(D_k \left| \left\{c_l^{(k)}\right\}_{l=0}^P, \tilde{\sigma}_k^2, F_k\right.\right) p(\tilde{\sigma}_k^2) \prod_{l=0}^P \hat{p}_k\left(c_l^{(k)}\right),$$

$$k = 1, 2, 3,$$
(6.59)

where $p(\tilde{\sigma}_k^2)$ and $\hat{p}_k(c_l^{(k)})$ denote the presumed independent priors of the noise variance and the l -th PC coefficient, respectively. Uniform priors are assumed on the coefficients, and a posterior sampling algorithm based on MCMC is employed.

Results. We illustrate a strategy based on adaptive selection of sampling points by analyzing, for a given observable, the convergence of the associated PC expansions at successive approximation levels. The idea behind this method can be summarized in two steps. Firstly, we infer, for each observable, the corresponding PC expansion at

the resolution levels $l' = 1$ and $l' = 2$ using the *full* grids of Fejér points. Secondly, rather than using the full grid also at level $l' = 3$, we select only a subset of nodes by identifying the regions of the domain where the differences between the expansions obtained at levels $l' = 1$ and 2 exceed a target threshold. This approach can be extended to higher-order levels $l' > 3$.

Specifically, we rely on the difference

$$Z_k^{(l'=1,2)}(\xi) = \left| F_k^{(l'=1,p=0)}(\xi) - F_k^{(l'=2,p=2)}(\xi) \right|, \quad k = 1, 2, 3, \quad (6.60)$$

where $F_k^{(l'=1,p=0)}$ represents the zeroth-order ($p = 0$) expansion of the k -th observable inferred at level 1 (level 1 includes, in fact, a single sampling point, so one can only build a zero-order PC representation), while $F_k^{(l'=2,p=2)}$ represents the second-order ($p = 2$) expansion of the k -th observable inferred at level 2 (quadratic is the maximum order for a well-posed problem at level 2). Also, rather than developing the analysis using the full joint posterior of the coefficients, we simplify the approach and rely on the MAP estimates of their marginalized posteriors which, as discussed in Ref. [118], can be justified here.

Fig. 6.7(a) shows the contours of $Z_k^{(l'=1,2)}(\xi)$ obtained for density. The minima of $Z_k^{(l'=1,2)}$ identify the central region of the space as the region where there is close agreement between the representations inferred at levels 1 and 2, while the maxima of $Z_k^{(l'=1,2)}$ localize near the corners $(-1, -1, -1)$ and $(1, 1, 1)$. The results for self-diffusivity and enthalpy are similar and are omitted here for brevity [118].

By analyzing the distribution of $Z_k^{(l'=1,2)}$, $k = 1, 2, 3$, we can identify which points of the full grid at $l' = 3$ are characterized by the highest values of $Z_k^{(l'=1,2)}$. Fig. 6.7(b)

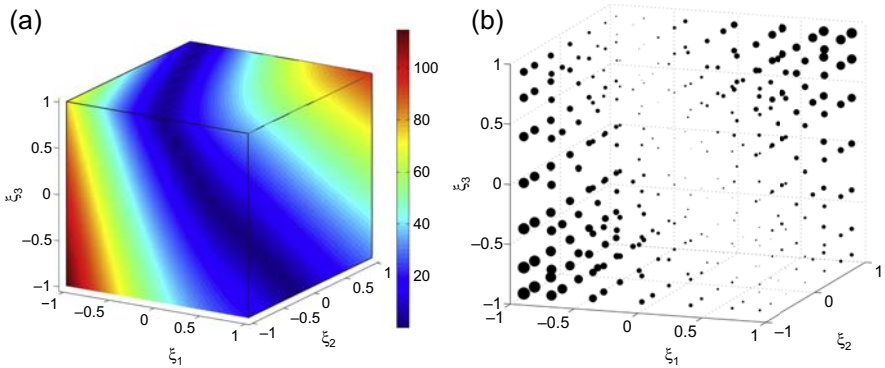


Figure 6.7 (a) Contours of $Z_k^{(l'=1,2)}$ obtained for density. (b) Distributions of Fejér grid points $\{\xi_i\}_{i=1}^{316}$ at level 3 (omitting the subset shared with levels 1 and 2), obtained for density, with each point ξ_i represented by a marker whose size is scaled according the corresponding value of $Z_k^{(l'=1,2)}(\xi_i)$.

This figure is reproduced from [118] with permission.

shows the grid of 316 points exclusively belonging to the third approximation level $l' = 3$ (i.e., we omit those shared with levels $l' = 1$ and $l' = 2$), depicted such that the size of the marker associated with the i -th node ξ^i is scaled according to the local value of $Z_k^{(l'=1,2)}(\xi^i)$. These plots give a first visual intuition of which subset will be selected and which will be neglected.

To define a quantitative metric to select subset of points, we first nondimensionalize the “error” $Z_k^{(l'=1,2)}(\xi)$ for each observable as

$$\widehat{Z}_k(\xi) = \frac{Z_k^{(l'=1,2)}(\xi)}{\max_{\Omega} \left(Z_k^{(l'=1,2)} \right)}, \quad k = 1, 2, 3, \quad (6.61)$$

where the normalization factor corresponds to the maximum value of $Z_k^{(l'=1,2)}$ in the parameter domain $\Omega = (-1, 1)^3$. Using a tolerance λ ($0 \leq \lambda \leq 1$), we define $A_k^{(\lambda)}$ to be the set of *new* sampling nodes for the k -th observable at level 3 according to

$$A_k^{(\lambda)} = \left\{ \xi^1, \dots, \xi^{N_k^{(\lambda)}} \right\} \doteq \left\{ \xi^i : \widehat{Z}_k(\xi^i) \geq \lambda, \quad i = 1, \dots, 316 \right\}, \quad k = 1, 2, 3, \quad (6.62)$$

where $N_k^{(\lambda)}$ represents the number of points in the resulting reduced grid, which depends on the type of observable and on the value of λ , while the index i enumerates the 316 points that belong exclusively to the full grid at $l' = 3$. Evidently, for any given λ , we must have $N_k^{(\lambda)} \leq 316$, and $N_k^{(\lambda)} = 316$ when $\lambda = 0$.

We explore the following values of the tolerance: $\lambda = 0, 0.25$, and 0.4 . The sets of observations at level $l' = 3$ for different values of λ , i.e., $\lambda = 0, 0.25$, and 0.40 , can be in turn exploited within the Bayesian inference framework as discussed before. We focus our attention on inferring for each observable a third-order PC expansion and investigate the dependence of the MAP estimates of the coefficients on λ . Fig. 6.8 shows the normalized difference $\left| c_l^{(k)} - c_{l,\lambda}^{(k)} \right| / \left| c_0^{(k)} \right|$, $l = 0, \dots, 19$, where $c_l^{(k)}$ represents the MAP estimate of the l -th PC coefficient for the k -th observable inferred at $l' = 3$ using the full grid, i.e., $\lambda = 0$, whereas $c_{l,\lambda}^{(k)}$ is the MAP estimate of the corresponding coefficient inferred at $l' = 3$ using $\lambda = 0.25$ or $\lambda = 0.40$. The figure shows that for density the differences are minimal, of the order $\sim O(10^{-4})$. Another interesting observation is that for density the discrepancy does not substantially vary with the order of the coefficients.

We stop at the third level for this test, but the grid adaptation process described above can be further extended to higher levels if necessary. A possible measure to monitor the impact of refinement can be based on the normalized relative error

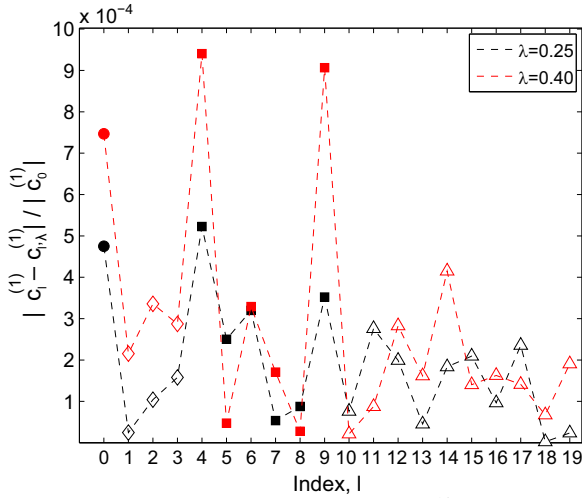


Figure 6.8 Normalized “discrepancy” $\left\{ \left| c_l^{(k)} - c_{l,\lambda}^{(k)} \right| / \left| c_0^{(k)} \right| \right\}_{l=0}^{19}$, for ρ , where $c_{l,\lambda}^{(k)}$ is the MAP estimate of the l -th PC coefficient inferred at $l' = 3$ using the set of observations derived for $\lambda = 0.25$ or $\lambda = 0.40$, while $\left| c_l^{(k)} \right|$ is the absolute value of the MAP estimate of the corresponding coefficient obtained using $\lambda = 0$. Subsequent orders are identified by the following markers: zeroth- ($\bullet$), first- ($\blacklozenge$), second- ($\blacksquare$), and third-order coefficients ($\blacktriangle$). This figure is reproduced from F. Rizzi, H.N. Najm, B.J. Debusschere, K. Sargsyan, M. Salloum, H. Adalsteinsson, O.M. Knio, Uncertainty quantification in MD simulations. Part I: forward propagation, Multiscale Model. Sim. 10 (2012) 1428–1459. <https://doi.org/10.1137/110853169>. with permission.

$$\frac{\left| Z_{k,\lambda}^{(l',l'+1)} \right|}{\left| c_0^{(k)} \right|}, \quad k = 1, 2, 3, \quad (6.63)$$

where $\left| c_0^{(k)} \right|$ is the leading term of the expansion at level l' , and the numerator is a global measure of the error defined as

$$\left\| Z_k^{(l'=1,2)} \right\|_2 = \left(\int_{\Omega} \left| F_k^{(l'=1,p=0)}(\xi) - F_k^{(l'=2,p=2)}(\xi) \right|^2 \frac{1}{8} d\xi \right)^{1/2}, \quad k = 1, 2, 3. \quad (6.64)$$

Exploiting the fact that the integrand is a fourth-order polynomial, the above integrals can be computed exactly using the cubature.

6.4.2.1.1 Calibration using an uncertain PC surrogate model

The inverse problem discussed in Ref. [84] involves the inference of force field parameters for TIP4P water model given a set of observations of one or more macroscale

observables of water. We focus on a synthetic problem where fixed values of the TIP4P force field parameters are used to run isothermal, isobaric MD simulations at ambient conditions, $T = 298\text{K}$ and $P = 1\text{ atm}$ and collect a set of noisy data of selected macroscale observables. The MD computational setting is the one earlier in this section. These data are then exploited in a Bayesian setting to recover the “true” set of driving parameters. Attention is focused on inferring the same three parameters, ε , σ , and d , for which we built the PC surrogate above.

The analysis can be regarded as a three-stage process: first, three values of the parameters of interest $\hat{\varepsilon} = 0.17\text{ (kcal/mol)}$, $\hat{\sigma} = 3.15\text{ (\AA)}$, and $\hat{d} = 0.14\text{ (\AA)}$ are chosen and regarded as the “true” parameters (the “hat” will be used to denote the “true” values); secondly, these “true” values are used to run $N = 10$ replica MD simulations and obtain N realizations of density (ρ), self-diffusion (ϕ), and enthalpy (H); finally, these observations are used within a Bayesian inference framework to recover the original (or “true”) subset of driving parameters. Our goal is to investigate the performance of the Bayesian approach in terms of the accuracy with which we recover the “true” parameters and characterize the main factors affecting the inference.

Formulation for a deterministic surrogate model. When using a *deterministic* PC expansion for each observable, the formulation yields the following posterior [118]

$$p(\xi, \tilde{\sigma}^2 | \{D_l\}_{l=1}^3) \propto \prod_{k=1}^3 \prod_{l=1}^N \frac{\exp\left(-\frac{[d_k^l - F_k(\xi)]^2}{2\tilde{\sigma}_k^2}\right)}{\sqrt{2\pi\tilde{\sigma}_k^2}} \tilde{p}(\tilde{\sigma}_k^2) p(\xi), \quad (6.65)$$

where D_l , $l = 1, 2, 3$, represents that data for the l -th observable, $\tilde{p}(\tilde{\sigma}_k^2)$ is the prior of the noise variance, $\tilde{\sigma}_k^2$, and $p(\xi)$ represents the probability in the ξ -space corresponding to the prior on the parameter vector $\boldsymbol{\vartheta} = \{\varepsilon, \sigma, d\}$. We have used a tilde to distinguish between the variance, $\tilde{\sigma}_k^2$, associated with the k -th observable, and the force field parameter, σ .

Formulation for a nondeterministic surrogate model. When using *nondeterministic* PC expansions for all three observables, the formulation is more complex. In this case, each PC coefficients vector $c^{(k)} = \{c_l^{(k)}\}_{l=0}^P$, $k = 1, 2, 3$, is a random vector defined by a $(P+1)$ -dimensional joint probability density. We can define a suitable likelihood function for this case as follows.

For a given sample $\xi^{(j)} = \{\xi_1^{(j)}, \xi_2^{(j)}, \xi_3^{(j)}\}$, we can construct the following constant column vector

$$a = \left\{ \Psi_0(\xi^{(j)}), \dots, \Psi_P(\xi^{(j)}) \right\}^T, \quad (6.66)$$

i.e., by substituting $\xi^{(j)}$ into the truncated PC basis. Hence, we can interpret each *nondeterministic* PC representation, $F_k(\xi)$, as a *linear combination* of the random vector $c^{(k)}$, according to

$$F_k = a^T c^{(k)}, \quad k = 1, 2, 3. \quad (6.67)$$

For this chapter, as shown in Ref. [118], the probability density describing the uncertain PC expansion of each observable closely resembles a Gaussian. We thus approximate the $(P+1)$ -dimensional distribution describing the random vector $c^{(k)} = \{c_0^{(k)}, \dots, c_P^{(k)}\}^T$, $k = 1, 2, 3$, with a $(P+1)$ -variate Gaussian with mean $\mu^{(k)}$ and covariance matrix $Z^{(k)}$, $k = 1, 2, 3$. Consequently, the linear combination

$$a^T c^{(k)} = \Psi_0(\xi^{(j)})c_0^{(k)} + \dots + \Psi_P(\xi^{(j)})c_P^{(k)}, \quad k = 1, 2, 3, \quad (6.68)$$

is distributed according to a *univariate* Gaussian with mean $(a^T \mu^{(k)})$ and variance $(a^T Z^{(k)} a)$, namely as

$$a^T c^{(k)} \sim \mathcal{N}\left(a^T \mu^{(k)}, a^T Z^{(k)} a\right), \quad k = 1, 2, 3. \quad (6.69)$$

Note that the uncertainty in the PC coefficients appears only through the mean vector $\mu^{(k)}$ and the covariance $Z^{(k)}$, because the constant vector a is only ξ -dependent. Assuming an independent additive error model, the discrepancy between each observation, d_k^i , $k = 1, 2, 3$, $i = 1, \dots, N$, and the *nondeterministic* surrogate model prediction, $F_k(\xi) = a^T c^{(k)}$, $k = 1, 2, 3$, can be expressed as

$$\begin{aligned} d_k^i &= F_k(\xi) + \gamma_k^i \\ &= a^T c^{(k)} + \gamma_k^i, \end{aligned} \quad (6.70)$$

$$k = 1, 2, 3, i = 1, \dots, N,$$

where each set $\{\gamma_k^i\}_{i=1}^N$, $k = 1, 2, 3$, comprises *i.i.d.* random variables with density p_{γ_k} , $k = 1, 2, 3$. Assuming $\gamma_k^i \sim \mathcal{N}(0, \tilde{\sigma}_k^2)$, $i = 1, \dots, N$, $k = 1, 2, 3$, and considering, by construction, N -independent realizations for each observable, we obtain the following likelihood function

$$p(\{D_l\}_{l=1}^3 | \xi) = \prod_{k=1}^3 \prod_{i=1}^N \frac{1}{\sqrt{2\pi(a^T Z^{(k)} a + \tilde{\sigma}_k^2)}} \exp\left(-\frac{[d_k^i - (a^T \mu^{(k)})]^2}{2(a^T Z^{(k)} a + \tilde{\sigma}_k^2)}\right), \quad (6.71)$$

where the index k enumerates the observables, i enumerates the observations, $\mu^{(k)}$ and $Z^{(k)}$, respectively, denote the mean and covariance matrix of the $(P+1)$ -variate Gaussian representing the $(P+1)$ -dimensional distribution of the *nondeterministic* PC coefficients featuring in the expansion of the k -th observable, and the constant vector $\mathbf{a} = \{\Psi_0(\xi), \dots, \Psi_P(\xi)\}^T$ is computed by evaluating the PC basis for a given ξ . We treat the variances $\tilde{\sigma}^2 = \{\tilde{\sigma}_k^2\}_{k=1}^3$ as hyperparameters. We remark that this likelihood function combines both data noise and surrogate uncertainty in a self-consistent manner.

Results. Fig. 6.9 shows the contour plots corresponding to 30%, 60%, and 90% of the maximum probability of the joint posteriors $p(e, \sigma | \mathbf{D})$ (a), $p(e, d | \mathbf{D})$ (b), and $p(\sigma, d | \mathbf{D})$ (c). The plots reveal that the posteriors obtained from a nondeterministic surrogate are centered on the true values, whereas those obtained with a deterministic surrogate do not capture the true values with the same accuracy. The blue and black contours plotted in the left column reveal, in fact, a similar orientation and a comparable spread. The results allow us to conclude that, for the present problem, the inference based on nondeterministic surrogates provides a more robust framework to perform the inverse problem.

6.4.2.2 Gaussian processes and efficient global Optimization strategies

We consider now an example of adaptive learning by kriging metamodels, as exposed in Section 6.3.2.2.

Calibration of a TIP4P water force field. EGO has been used in the context of the Bayesian calibration of a water force field by Cailliez et al. [77]. The TIP4P force field, as described above, is chosen to model water molecules. In addition to the three parameters σ , ϵ , and d optimized by Rizzi et al. [84, 118], the partial charge q_H borne by each hydrogen atom was optimized (note that the partial charge of the oxygen atom is constrained by the neutrality of the molecule: $q_O + 2q_H = 0$). The target of the calibration is the experimental liquid density of water at five temperatures between 253 and 350K under a pressure of 1 bar. On the molecular simulation side, those quantities are computed with MD simulations, the length of which prevents from a direct exploration of the parameter space. Predictions of MD simulations are assigned a constant uncertainty at all temperatures and for any parameter set. Due to the very small experimental uncertainties of the calibration data, those are ignored ($u_{d_i} \ll u_{F_i}$ in Eq. 6.4).

The score function G to be minimized by EGO is $-\log(p(\boldsymbol{\vartheta} | \mathbf{D}, \mathbf{X}, \mathbf{M}))$. The meta-model for G is built from five GP processes, each aiming at reproducing the liquid density obtained from an MD simulation with the TIP4P model at a given temperature over the parameter space. As G is computed from noisy data, a variant of the EI has been used, adapted from Huang et al. [91]:

$$EI^*(\boldsymbol{\vartheta}) = \mathbb{E}[\max(\tilde{G}(\boldsymbol{\vartheta}^{**}) - \tilde{G}(\boldsymbol{\vartheta})), 0], \quad (6.72)$$

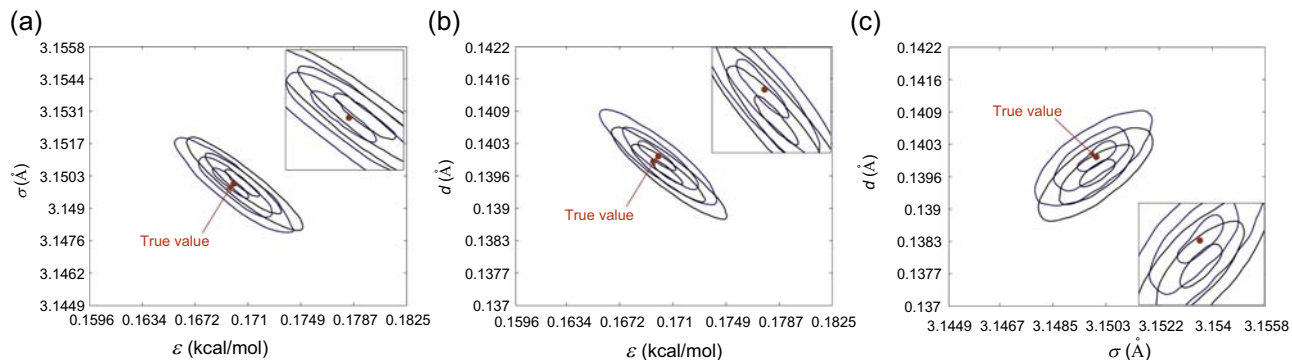


Figure 6.9 Contour plots corresponding to 30%, 60%, and 90% of the maximum probability of the marginalized joint posteriors $p(\epsilon, \sigma | \mathbf{D})$ (a), $p(\epsilon, d | \mathbf{D})$ (b), and $p(\sigma, d | \mathbf{D})$ (c). The black line represents the results obtained using a third-order *deterministic* surrogate model, whereas the blue line represents the results computed using a third-order *nondeterministic* PC surrogate with $\lambda = 0$. The results are based on considering all three observables (ρ, D, H) , with a total of 30 data points.

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where $\tilde{G}(\vartheta^{**})$ is the value of the metamodel at the point ϑ^{**} of the sampling design that minimizes $(\tilde{G}(\vartheta) - u_G(\vartheta))$, and $u_G(\vartheta)$ is an estimate of the standard deviation of $\tilde{G}(\vartheta)$.

The calibration procedure converged within five steps, which is due to the rather large initial sampling design (84 points, which corresponds to 21 points per dimension of the parameter space), leading to best parameter values consistent with the literature (see green point in Fig. 6.10). The results of the calibration reveal that there exists a

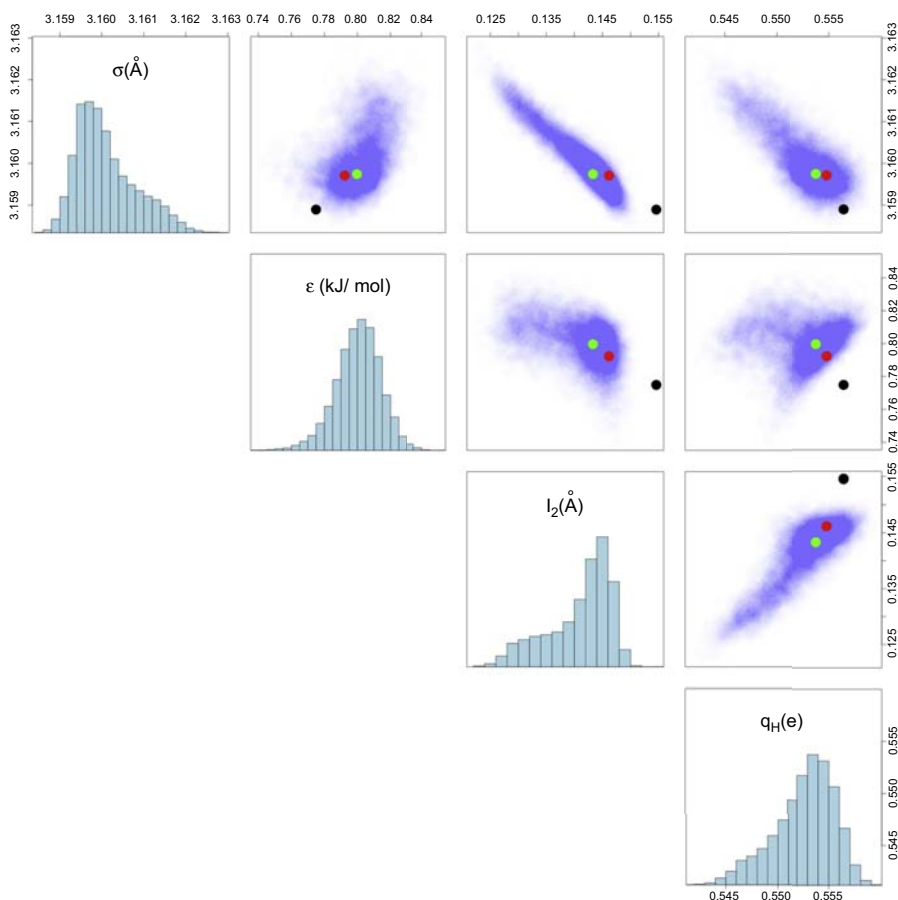


Figure 6.10 Markov chain over the PDF obtained after calibration of the TIP4P force field. Diagonal plots: marginal distribution of the parameters. Upper plots: 2D projections of the Markov chain (blue points). The black point corresponds to the TIP4P-2005 water model. The best values obtained after EGO calibration are displayed as green and red points. On this figure, variable d controlling the position of the oxygen point charge is named l_2 . This figure is reproduced from F. Cailliez, A. Bourasseau, P. Pernot, Calibration of forcefields for molecular simulation: sequential design of computer experiments for building cost-efficient kriging metamodels, J. Comput. Chem. 35 (2013) 130–149. <https://doi.org/10.1002/jcc.23475> with permission.

unique optimal region in parameter space for the TIP4P model that allows to reproduce the evolution of the water liquid density as a function of temperature, as shown in Fig. 6.10.

The advantage of this calibration strategy with respect to “standard” methods is that one also has access to an estimation of the PDF of the parameters around the MAP. This allows to perform parametric UP for the force field parameters. As already observed in the example of LJ fluids, the contribution of parametric uncertainties to the total uncertainty was found to be greater than that of the numerical uncertainties.

This application illustrates how metamodeling combined with efficient optimization strategies can be used in the context of statistical force field calibration. Before closing this topic, it is worth commenting on possible pitfalls of this kind of procedure:

- Metamodels are built on molecular simulation data, which may not always have reached convergence, due to sampling time smaller than the relaxation time of the system. This could be the case for the whole parameter space or in some regions of the parameter space with a global limited computational budget for molecular simulations. In Ref. [77], such a situation arose, due to some parameter sets leading to “glassy water” at low temperature. Removing those “incorrect” data (around a third of the initial design) in the process of metamodel building led to similar results (see the red point in Fig. 6.10) as when using the full design. This illustrates the stability of this calibration strategy.
- In order to reduce the computational burden, it is important to minimize the number of molecular simulations to be run. Cailliez and coworkers [77] estimated that reducing the size of the initial design to 32 points (8 points per dimension of the parameter space) should lead to a viable calibration. For smaller initial designs, the EI^* utility function used in Ref. [77] may not be successful, and the use of other variants of EGO would be required.

6.4.3 Model selection and model inadequacy

A number of recent works have addressed the issue of model inadequacy in capturing the properties of molecular systems by the classical LJ potentials [17,30,35,42,52,59].

Most studies have dealt with simple monoatomic gases, for which the simple LJ force field is expected to be adequate. The LJ potential (also noted as LJ 6–12) has been the main focus, with recent developments on an LJ 6- p potential. The shift to the 6- p model was motivated by the inability of the LJ potential to predict observables in different phases [35]. However, the introduction of variability on the p exponent of the repulsive term is not sufficient to compensate for all modeling adequacy issues of the LJ potential.

HM and SEm methods both aim at designing a PDF of the force field parameters which enables some form of compatibility between the model predictions and the calibration dataset.

HM attempts to reconcile heterogeneous observables and/or physical conditions: an overall distribution is designed to contain the different parameter sets best adapted to each subset [52,59]. As mentioned above, prediction of new data for a new observable or for new physical conditions should use the overall distribution. This typically leads to large prediction uncertainties, much larger than prediction uncertainties for new data

of observables contained in the calibration set (see Fig. 13 in Ref. [59] and the toy models in Ref. [30]).

As seen in Section 6.4.1.2, model inadequacy with LJ parameters might also be problematic when one considers a single observable.

Pernot and Cailliez [30] published a critical review of the available methods to manage this problem for the calibration of LJ parameters on viscosity data for Kr, among which additive correction by a GP, HM, or SEM was considered. We summarize the main results of that study here.

In the Kr example in Ref. [30] and the Ar case in Ref. [42], both SEM approaches described above (Sections 6.2.3.3–6.2.3.4) were evaluated, which lead to mitigated results. In both cases, it was possible to design a PDF for the LJ parameters which enabled prediction uncertainties to be large enough to compensate for model errors. Fig. 6.11 presents the residuals and 95% confidence and prediction bands for the LJ model calibrated on a dataset of five series of measurements of Ar viscosity [42]. The trend in the residuals is clearly visible at lower temperatures. As mentioned earlier,

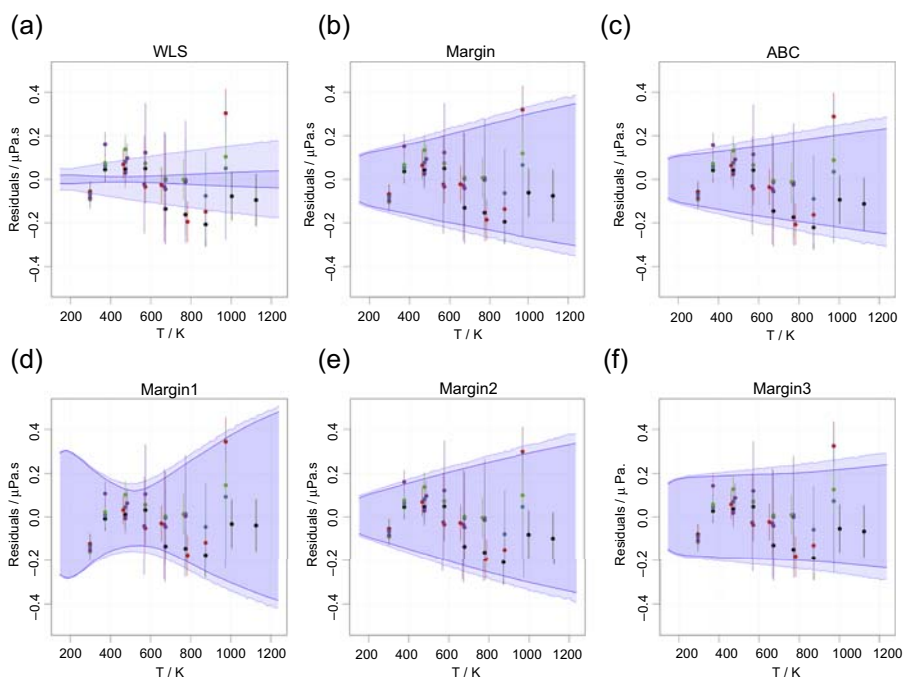


Figure 6.11 Calibration of LJ parameters for Ar over T-dependent viscosity data. Residuals and prediction uncertainty for the WLS (a), Margin (b), and ABC (c) methods and for the three degenerate solutions of the Margin method (d–f). The *dark blue bands* represent the model confidence 95% intervals, and the *light blue bands* the data prediction 95% intervals, corrected from the mean prediction.

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the basic calibration procedure using only data uncertainties (labeled WLS in Fig. 6.11) results in much too small prediction uncertainties, whereas both SEM approaches (labeled Margin and ABC) enable to successfully design prediction bands in agreement with the residuals. Note that the residuals are basically unchanged when compared to WLS: the fit of the data has not been improved.

Beyond this apparent success, the SEM strategies present a set of limitations, which might prevent its general applicability [30,42]:

- due to the geometry of the problem in data space [42,124], enlarging the uncertainty patch on the model manifold around the optimal parameters does not improve the statistical validity of an inadequate model (no improvement of the residuals);
- being constrained by the law of UP, the shape of the prediction uncertainty bands over the control variable(s) space does not necessarily conform to the shape of the model inadequacy errors [42];
- the elements of the covariance matrix of the stochastic parameters might have multimodal posterior distributions. This has been observed for the LJ potential calibration problem for both implementations of the SEM [30,42]. Samples of the posterior PDF for these methods reveal three modes, each one corresponding to the minimum value of one parameter of the covariance matrix. This diagnostic matches the observation that the estimates of covariance matrices in hierarchical models tend to be degenerate [125], i.e., with zero variance for some parameters or a perfect correlation among them. A major inconvenient of this degeneracy is that each mode corresponds to a different prediction uncertainty profile (see Fig. 6.11, bottom row). The posterior predictive uncertainty profile, being a weighted average of these modes, might consequently be very sensitive to the calibration dataset through mode flipping.

Considering these limitations, and notably the nonrobust shape of the prediction bands, it is still not clear whether the posterior PDFs estimated by SEM represent an improvement for the prediction of QoIs not in the calibration set. Further research is necessary to tackle the statistical treatment of model inadequacy.

In a recent work [36], HM was shown to be efficient in distinguishing between different models of coarse-grained molecular dynamics (CGMD) potentials. Such CGMD simulations are often calibrated on different experimental conditions, resulting in a plethora of models with little transferability. HM provides guidance on the model accuracy as well as on its trade-off with computational accuracy. In Fig. 6.12(a), the speed-up gained by using a CG model is plotted against its model evidence. Each model is characterized by the name of the model (1S, 2S, 2SF, 3S*, 3SF*) and the coarse-graining resolution (1, 3, 4, 5, 6), see Ref. [36] for a detailed description of the models. In Fig. 6.12(b), the evidences of three of the models of Fig. 6.12(a) are estimated at different temperatures. In order to combine all the evidences into one number, the HM approach is adopted.

6.5 Conclusion and perspectives

The increasing use of MD and MC in academia as well as in industry calls for a rigorous management of uncertainty in molecular simulations [126]. Among the

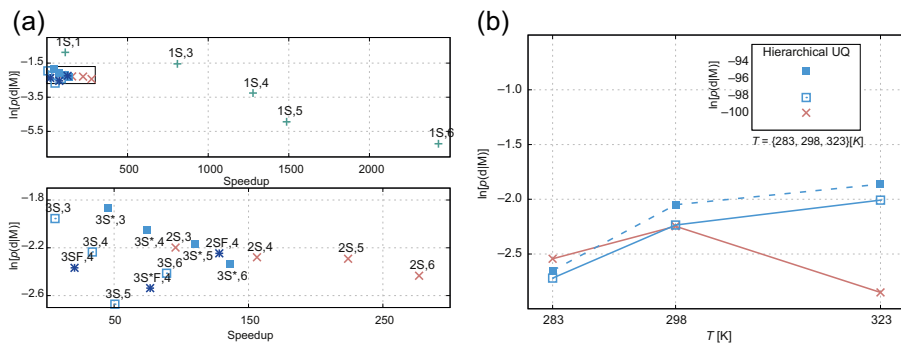


Figure 6.12 (a) Model evidences with respect to the speedup of the examined water models marked with the name and the mapping. The boxed section in the top plot is enlarged in the bottom plot. (b) Logarithm of the model evidences at different temperatures T for models $2SF$ ($\times$), $3S$ ($\square$), and $3S^*$ ($\blacksquare$). The inset shows the model evidences of the hierarchical UQ approach, where all three temperatures are considered concurrently.

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various sources of uncertainties in molecular simulations, this chapter focused on those originating from the values of the force field parameters. Bayesian approaches provide an operative and complete framework to deal with the determination of the parameter uncertainties and their propagation through molecular simulations. The computational cost of such methods has limited their use in the context of molecular simulations until the last decade. However, the increase in computational resources as well as the development of efficient numerical strategies currently enables the investigation of force fields parametric uncertainties.

In this chapter, we have reviewed recent approaches to address the issue of force field parameter calibration and outlined significant lessons that have been learned over the last 10 years. We have shown that uncertainty estimation for molecular simulation predictions can be more complex than the simulations themselves.

Section 6.4.1 has been designed to give a step-by-step pedagogical example of the application of Bayesian “standard” strategy to the calibration of an LJ force field for rare gases. Apart from giving an introduction to Bayesian methods, this application sheds light on the major issues arising during force field calibration. A large part of this chapter (Section 6.4.2) has been devoted to computational aspects, especially the use of metamodeling-based strategies, that are currently the only way to overcome the bottleneck of performing thousands, or more, of molecular simulations. However, the major challenge that emerged from the early studies on Bayesian calibration of force field parameters is that of model inadequacy. The physics contained in typical force fields is often too crude to enable a statistically valid calibration without employing advanced calibration schemes. Most of the time, the use of a more complex force field is computationally prohibitive, so one has to deal with inadequacy of

the current force fields. [Section 6.4.3](#) has been centered on the *pros* and *cons* of various strategies that have been used recently in the context of force field calibration with inadequate models.

Although significant advances have been made in recent years on the application of Bayesian methods to force field calibrations, the fully consistent characterization of the prediction uncertainty in molecular simulations is still an exciting research topic.

The need for reliable, reproducible, and portable molecular simulations is broadly recognized and has led, among other efforts, to the recent development of OpenKIM (openkim.org), a community-driven online framework. We suggest that frameworks such as OpenKIM could greatly benefit from adopting a systematic Bayesian inference approach to link experimental data with the results of MD simulations. Beyond being a formidable interdisciplinary scientific discovery framework, we believe that by proper integration of experimental data and simulations through Bayesian inference molecular simulation will become an effective virtual measurement tool.

Abbreviations and symbols

ABC	Approximate Bayesian computation
CGMD	Coarse-grained molecular dynamics
EGO	Efficient global optimization
GP	Gaussian process
LJ	Lennard-Jones
LUP	Linear uncertainty propagation
<i>M</i>	Full model, comprising the physical model and the statistical model
MAP	Maximum a posteriori
MC	Monte Carlo
MCMC	Markov chain Monte Carlo
MD	Molecular dynamics
PCE	Polynomial chaos expansion
PDF	Probability density function
PES	Potential energy surface
QoI	Quantity of interest
SEm	Stochastic embedding
TMCMC	Transitional MCMC
UP	Uncertainty propagation
δF	Discrepancy function for model <i>F</i>
ϵ	Interaction energy of the Lennard-Jones potential
κ	Hyperparameters of hierarchical model
μ_ϑ	Mean value of stochastic parameters
Ψ_{f_j}	Univariate orthogonal polynomial used in PCE
Ψ_I	Multivariate orthogonal polynomial used in PCE
σ	Radius parameter of the Lennard-Jones potential
σ_i^2	Variance of the errors at point x_i
Σ_D	Covariance matrix of the reference data <i>D</i>
Σ_F	Covariance matrix of the physical model errors
Σ_R	Covariance matrix of the residuals <i>R</i> (ϑ)
Σ_ϑ	Covariance matrix of stochastic parameters
τ_i	Parameter of the uncertainty model

ϑ	Parameter set of the physical model F
$\vartheta_{\delta F}$	Parameters of the discrepancy function δF
ε_i	Noise variable
ϑ_i	A parameter of the physical model F
$\mathbf{x}_i$	An auxiliary random variable for PCE
$\mathbf{D}$	Set of reference/calibration data
$\mathcal{L}(\vartheta)$	Logarithm of the posterior PDF
$\mathbf{R}(\vartheta)$	Vector of residuals
$\mathbf{X}$	Set of physical conditions for the reference data
d_i	A reference datum
D_{KL}	Kullback–Leibler divergence
$F(\mathbf{x}; \vartheta)$	Computational or physical model
$F_i(\vartheta)$	Value of the computational model at point x_i with parameters ϑ
N_τ	Number of parameters for the uncertainty model
N_ϑ	Number of parameters of the physical model F
N_D	Size of the reference dataset $\mathbf{D}$
$p(\mathbf{X} \mathbf{Y})$	Conditional PDF of $\mathbf{X}$ knowing $\mathbf{Y}$
r_B	Birge ratio
$u_{d_i}^2$	Variance of noise for datum d_i
$u_{F_i}^2$	Computational variance for model value $F_i(\vartheta)$
$\mathbf{x}_i$	Physical condition(s) for a reference datum
$\bar{\mathbf{x}}$	Mean value of parameters $\mathbf{x}$
$\hat{x}$	Optimal value of parameter x
$\tilde{x}$	Value of x out of the calibration dataset

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Reliable molecular dynamics simulations for intrusive uncertainty quantification using generalized interval analysis

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7.1 Introduction

Modeling and simulation tools are essential to accelerate the process of materials design. At the atomistic level, molecular dynamics (MD) is the most used tool to predict material properties from microstructures. Nevertheless, the accuracy and reliability of MD simulation predictions directly affect the effectiveness of the computational tool. To improve the credibility of simulation predictions, uncertainty associated with the simulation tool needs to be quantified.

Uncertainty in modeling and simulation comprises of two components: *aleatory* and *epistemic* uncertainties. Aleatory uncertainty is the inherent randomness of the system because of the fluctuation and perturbation. Epistemic uncertainty is due to the lack of knowledge about the system. In MD simulation, the aleatory uncertainty is the thermal fluctuation, whereas the epistemic uncertainty is mostly due to the imprecision of the interatomic potential. Typically, these interatomic potentials are derived from either first-principles calculations or experimental results. Both of these results contain systematic and random errors. The systematic errors in MD models, also known as model-form and parameter uncertainty, are embedded when certain analytical forms and number of parameters in the interatomic potential functions are chosen, or when parameters are calibrated. When first-principles calculations are used in calibration, the errors are inherited from different approximations and assumptions in quantum mechanics models, such as Born–Oppenheimer approximation, Hartree–Fock approximation, and the finite number of basis functions in functional approximations. Specifically, models with multiple level of fidelity have been involved in approximating the exchange–correlation energy in DFT, forming the rungs in a Jacob’s ladder, increasing in complexity from local spin-density approximation to generalized gradient approximation (GGA), meta-GGA, hyper-GGA, exact exchange and compatible correlation, and exact

exchange and exact partial correlation [1,2]. Furthermore, pseudopotentials have been regularly applied in DFT to reduce computational burden. In pseudopotential-based DFT calculations, the nuclear potential and core electrons of an atom are replaced by a significantly softer potential on the valence electrons, thus substantially reducing the number of basis functions used to approximate. As a result, the success of popular DFT codes which use plane-wave basis sets, including VASP, Quantum-ESPRESSO [3,4], and ABINIT [5–8], is dependent on the availability of good pseudopotentials [9]. Furthermore, the DFT calculation is also dependent on a good guess for the initial electron density. If the initial electron density is too wrong, the DFT calculation may not converge or converge to the wrong solution. Numerical treatments such as k-point sampling and orbital basis selection also introduce model-form uncertainty. On the other hand, the systematic errors can also be from experimental data where instrument error, human bias, and model-form uncertainty of sensor models are included. Approximations are also involved in the data fitting procedure. Therefore, the interatomic potentials are inherently imprecise. In addition, other sources of uncertainty in MD simulations include the cutoff distance in simulation for ease of computation, the imposed boundary conditions that may introduce artificial effects, small simulation domain size that is not representative, modeled microstructure that is deviated from the physical one, and short simulation time to estimate statistical ensembles over time. To overcome the time scale limitation of MD, simulation acceleration through larger time steps, modified interatomic potentials to simulate transitions, or the application of physically unrealistic high strain rates of mechanical or thermal load also introduce errors. Given the various sources of errors in MD simulations, it is important to provide users the level of confidence for the predictions of physical properties along with the predictions themselves.

Generally speaking, there are two main approaches for uncertainty quantification (UQ), nonintrusive and intrusive methods. Nonintrusive methods such as Monte Carlo simulation, global sensitivity analysis, surrogate model, polynomial chaos, and stochastic collocation treat simulation models as black boxes and rely on statistical techniques to characterize the correlation between the assumed probability density functions (PDFs) of the input parameters and the observable outputs. In contrast, intrusive methods such as local sensitivity analysis and interval-based approaches require the modification of the classical simulation tools so that uncertainty is represented internally.

UQ methods have been applied to multiscale simulation for materials. Comprehensive literature reviews are available in Refs. [10,11]. For MD simulation, Frederiksen et al. [12] utilized the Bayesian ensemble framework to quantify the uncertainty associated with elastic constants, gamma-surface energies, structural energies, and dislocation properties induced by different molybdenum interatomic potentials. Jacobson et al. [13] constructed response surfaces with Lagrange interpolation to study the sensitivity of macroscopic properties with respect to interatomic potential parameters. Cailliez and Pernot [14] as well as Rizzi et al. [15] applied Bayesian model calibration to calibrate interatomic potentials parameters. Angelikopoulos et al. [16] showed the applicability of Bayesian model calibration with water

molecule models. Rizzi et al. [17] applied polynomial chaos expansion to study the effect of input uncertainty in MD. Cailliez et al. [18] applied Gaussian process in water molecule MD model calibration. Wen et al. [19] studied the effect of different spline interpolations in tabulated interatomic potentials. Hunt et al. [20] presented a software package for nonintrusive propagation of uncertainties in input parameters, using surrogate models and adaptive sampling methods, such as Latin Hypercube and Smolyak sparse grids.

As an intrusive approach, we recently proposed an interval-based reliable MD (R-MD) mechanism [21–23] where generalized interval arithmetic [24] is used to assess input uncertainty effect. Generalized interval is a generalization and extension of classical interval [25] with more complete algebraic properties. Under the extended additive and multiplicative operations, generalized intervals form a group thus with simplified calculus. In contrast, the classical intervals only form a semigroup. The difference comes from the existence of inverse elements in the space of generalized intervals. Therefore, calculation in generalized interval arithmetic is simpler than that in classical interval. Most importantly, the overestimation of variation ranges in classical interval is significantly reduced. In R-MD, the input uncertainty associated with interatomic potentials is represented with interval functions. As a result of arithmetic, each atom's position and velocity are also intervals. Fig. 7.1 presents a schematic sketch of a simple 2D R-MD simulation cell, where the atomistic positions are interval-valued. In other words, the precise locations and velocities of atoms are unknown. As a generalization of previous work, here four R-MD uncertainty schemes are implemented in the framework of LAMMPS [26]. The details of how generalized interval arithmetic is applied in simulation including interval potential, interval force computation, and interval statistical ensemble are described here.

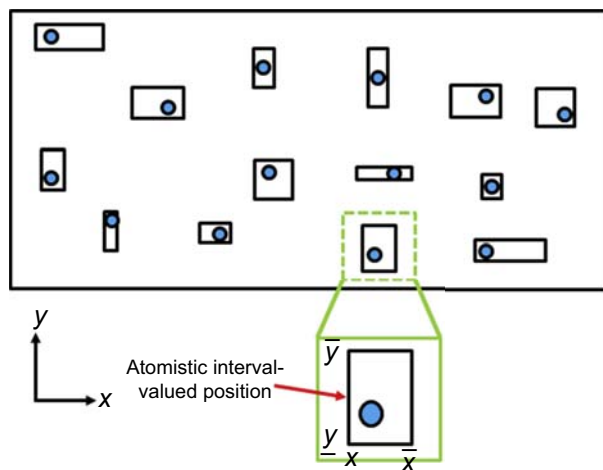


Figure 7.1 Schematic illustration of R-MD in 2D.

7.2 Generalized interval arithmetic

Traditionally an interval is defined as a set of real values between its lower and upper bounds. Therefore, the lower bound should be less than or equal to the upper bound. Different from the classical interval, a generalized interval is defined as a pair of numbers as $\mathbf{x} := [\underline{x}, \bar{x}]$, where the constraint of upper bound being greater than lower bound ($\underline{x} \leq \bar{x}$) is no longer necessary. Interval analysis emphasizes efficient range estimations, i.e., for any given $x \in [\underline{x}, \bar{x}]$, what is the possible variation range of $f(x)$ without Monte Carlo sampling or sampling in other nonintrusive UQ methods? As a simple example [27]: given $f(x) = x/(1-x)$ and $x \in [2, 3]$, interval function $f(\mathbf{x})$ can be quickly computed as $1/(1/[2, 3] - 1) = [-2, -3/2]$, which is the true variation range of $f(x)$. Because of its compact and efficient computational framework, interval analysis is well suited for intrusive UQ applications, as well as local sensitivity analysis.

The generalized interval space formed by generalized intervals is denoted as $\mathbb{KR}$, which is a collection of interval $\mathbf{x}$. The basic operation on $\mathbb{KR}$ is denoted with a circumscribed operator in order to distinguish from the classical interval arithmetic, defined as follows: addition $[\underline{x}, \bar{x}] \oplus [\underline{y}, \bar{y}] = [\underline{x} + \underline{y}, \bar{x} + \bar{y}]$, subtraction $[\underline{x}, \bar{x}] \ominus [\underline{y}, \bar{y}] = [\underline{x} - \underline{y}, \bar{x} - \bar{y}]$, multiplication $[\underline{x}, \bar{x}] \otimes [\underline{y}, \bar{y}]$ is defined in Table 7.1, and division $[\underline{x}, \bar{x}] \oslash [\underline{y}, \bar{y}] = [\underline{x}, \bar{x}] \otimes [1/\bar{y}, 1/\underline{y}]$. In Table 7.1, the generalized interval space $\mathbb{KR}$ is decomposed into four subspaces: $\rho := \{\mathbf{x} \in \mathbb{KR} \mid \underline{x} \geq 0, \bar{x} \geq 0\}$ contains positive intervals, $\mathcal{Z} := \{\mathbf{x} \in \mathbb{KR} \mid \underline{x} \leq 0 \leq \bar{x}\}$ contains intervals that include zero, $-\rho := \{\mathbf{x} \in \mathbb{KR} \mid -\mathbf{x} \in \rho\}$ contains negative intervals, and dual $\mathcal{Z} := \{\mathbf{x} \in \mathbb{KR} \mid \text{dual } \mathbf{x} \in \mathcal{Z}\}$ contains intervals that are included by zero, where $\text{dual}[\underline{x}, \bar{x}] := [\bar{x}, \underline{x}]$.

Let $x^+ = \max\{x, 0\}$, $x^- = \max\{-x, 0\}$, $x \vee y = \max\{x, y\}$, the multiplication table can be further simplified [28,29] as

$$[\underline{x}, \bar{x}] \otimes [\underline{y}, \bar{y}] = \left[\left((\underline{x}^+ \underline{y}^+) \vee (\bar{x}^- \bar{y}^-) - (\bar{x}^+ \underline{y}^-) \vee (\underline{x}^- \bar{y}^+) \right), \left((\bar{x}^+ \bar{y}^+) \vee (\underline{x}^- \underline{y}^-) - (\underline{x}^+ \bar{y}^-) \vee (\bar{x}^- \underline{y}^+) \right) \right] \quad (7.1)$$

The above definitions of the generalized interval arithmetic or Kaucher arithmetic significantly simplifies the algebraic structure of interval computation, compared to classical interval arithmetic. The four basic interval arithmetic operations are used for the calculation of interval-valued quantities such as position, momentum, and force in the R-MD mechanism. Based on the four basic ones, other operations such as derivative and integral can be defined in a form that is similar to tradition real analysis. In order to compare intervals, a norm on $\mathbb{KR}$ is defined as

$$\|\mathbf{x}\| := \max\{|\underline{x}|, |\bar{x}|\} \quad (7.2)$$

Table 7.1 Definition of Kaucher multiplication.

	$y \in \rho$	$y \in \mathcal{Z}$	$y \in -\rho$	$y \in \text{dual } \mathcal{Z}$
$x \in \rho$	$[\underline{x}y, \bar{x}\bar{y}]$	$[\bar{x}y, \bar{x}\bar{y}]$	$[\bar{x}y, \underline{x}\bar{y}]$	$[\underline{x}y, \underline{x}\bar{y}]$
$x \in \mathcal{Z}$	$[\underline{x}\bar{y}, \bar{x}\bar{y}]$	$[\min\{\underline{x}\bar{y}, \bar{x}\underline{y}\}, \max\{\underline{x}\bar{y}, \bar{x}\bar{y}\}]$	$[\bar{x}\underline{y}, \underline{x}\bar{y}]$	0
$x \in -\rho$	$[\underline{x}\bar{y}, \bar{x}\underline{y}]$	$[\underline{x}\bar{y}, \underline{x}\underline{y}]$	$[\bar{x}\bar{y}, \underline{x}\bar{y}]$	$[\bar{x}\bar{y}, \bar{x}\underline{y}]$
$x \in \text{dual } \mathcal{Z}$	$[\underline{x}\underline{y}, \bar{x}\bar{y}]$	0	$[\bar{x}\bar{y}, \underline{x}\bar{y}]$	$[\max\{\underline{x}\underline{y}, \bar{x}\bar{y}\}, \min\{\underline{x}\bar{y}, \bar{x}\underline{y}\}]$

with the following properties: $\|\mathbf{x}\| = 0$ if and only if $\mathbf{x} = 0$. $\|\mathbf{x} + \mathbf{y}\| \leq \|\mathbf{x}\| + \|\mathbf{y}\|$. $\|\alpha\mathbf{x}\| = |\alpha|\|\mathbf{x}\|$ with $\alpha \in \mathbb{R}$. $\|\mathbf{x} - \mathbf{y}\| \leq \|\mathbf{x}\| + \|\mathbf{y}\|$. The distance metric on $\mathbb{KR}$ is then defined as

$$d(\mathbf{x}, \mathbf{y}) := \max\left\{\left|\underline{x} - \underline{y}\right|, \left|\bar{x} - \bar{y}\right|\right\} \quad (7.3)$$

which is associated with the norm by $d(\mathbf{x}, 0) = \|\mathbf{x}\|$ and $d(\mathbf{x}, \mathbf{y}) = \|\mathbf{x} \ominus \mathbf{y}\|$

As shown in Ref. [24], $\mathbb{KR}$ is a complete metric space under the defined metrics.

Interval $\mathbf{x}$ is called *proper* if $\underline{x} \leq \bar{x}$, and called *improper* if $\underline{x} > \bar{x}$. If $\underline{x} = \bar{x}$, then $\mathbf{x}$ is a *degenerated*, *pointwise*, or *singleton* interval and has a precise value. An interval is called *sound* if it does not include inadmissible solutions; an interval solution is called *complete* if it includes all possible solutions. In general, a sound interval is a subset of the true solution set, whereas a complete interval is a superset. Classical interval arithmetic emphasizes completeness, therefore usually overestimates the interval range. Generalized interval on the other hand emphasizes more on soundness and significantly reduces the overestimation problem.

In summary, there are major advantages of the new definitions of arithmetic operations in generalized interval. First, they simplify the calculation because generalized intervals form a group with the new arithmetic operations. They are algebraically more intuitive. Second, the new arithmetic avoids the overestimation of interval bounds as in classical interval arithmetic. The dual operator plays an important role in generalized interval arithmetic, because its introduction forms a group in the generalized interval space $\mathbb{KR}$. That is, the similar inverse elements and inverse operations of addition and multiplication are available in generalized interval as in real arithmetic, as $\mathbf{x} + (-\text{dual}(\mathbf{x})) = 0$ and $\mathbf{x} \otimes 1/\text{dual}(\mathbf{x}) = 1$. In contrast, there are no inverse elements in classical interval arithmetic. Therefore, classical intervals only form a semigroup. For interested readers, the structures of generalized intervals, including metric structure, order structure, and algebraic structure, are available in literature [24,30–33].

Interval can be regarded as a more practical representation of uncertainty than probability distribution when the distribution is not precisely known or there is a lack of data. The quantity of interests is only known to be bounded between the interval bounds, whereas the information about the PDF is not available. The interval and PDF however are closely related. The interval can serve the same purpose of a confidence interval which is to measure the extent of uncertainty, or simply the lower and upper bounds of the support of the PDF to measure the variation range. Imprecise or interval probability is a combination of interval and probability, where epistemic uncertainty associated with probability is captured as intervals. The fusion of Bayesian framework and generalized intervals also exists in literature (e.g., Refs. [34–36]). The general notion of imprecise probability is when the cumulative distribution function is unknown, a lower and an upper cumulative distribution functions are applied to enclose the distribution as the basis for interval representation.

7.3 Reliable molecular dynamics mechanism

Based on generalized intervals, the model-form and parameter uncertainty in the interatomic potential is captured in the interval form of potential functions. That is, lower and upper functions are used to capture each interatomic potential, instead of one in original MD. As a result, interval-valued interatomic forces are calculated from the potential functions. The momenta and positions of atoms are recorded with intervals. The uncertainty and imprecision thus can be estimated on-the-fly at every time step of R-MD simulation. The total uncertainty of the interested physical quantities in the output is obtained directly using *only one run* without the repeated simulation runs as in the nonintrusive approaches, since within each run of R-MD, the lower and upper limits are calculated and updated simultaneously. Compared to the nonintrusive solutions, the computational load of the intrusive R-MD mechanism is in the same order of the time in regular MD. This on-the-fly intrusive approach significantly reduces the computational complexity to estimate the uncertainty of the MD output. As the number of atoms in the MD simulation is N , the number of pairs scales quadratically as $\mathcal{O}(N^2)$. In practice, the number of atoms varies from 10^3 to 10^9 . Thus, a small change in the interatomic potential may lead to a substantial change of the MD outputs.

The interval representation of uncertainty is limited in the sense that there is no more information of uncertainty other than the lower and upper bounds of the intervals. That is, the distribution within the interval bound is unknown. When this representation is applied in real-world problems, it is usually acceptable to assume a uniform distribution between the bounds based on the maximum entropy principle. Nevertheless, the interval representation is computationally efficient because it only takes two times of memory usage compared to the original real-valued scheme if using a low-upper bound scheme to store $\underline{x}$ and $\bar{x}$ for interval $\mathbf{x} = [\underline{x}, \bar{x}]$ or midradius scheme to store $\text{mid}(\mathbf{x}) = (\underline{x} + \bar{x})/2$ and $\text{rad}(\mathbf{x}) = (\bar{x} - \underline{x})/2$, or three times in a more general nominal–radius or midpoint–radius scheme to store nominal value x_0 , $\text{rad}_{\text{inner}}(\mathbf{x}) = \min(|\bar{x} - x_0|, |x_0 - \underline{x}|)$, $\text{rad}_{\text{outer}}(\mathbf{x}) = \max(|\bar{x} - x_0|, |x_0 - \underline{x}|)$. Theoretically it uses the same computational complexity $\mathcal{O}(1)$ to perform computation.

The interval representation is thus appealing to large-scale engineering problems where efficiency is of the major concern.

7.3.1 Interval interatomic potential

In R-MD, the uncertainty in interatomic potentials is modeled using generalized intervals. Any parameterized model for interatomic potentials can be further extended to perform intrusive UQ study on-the-fly through the R-MD mechanism, simply by replacing the parameters with generalized intervals. For example, for parametric Lennard-Jones potential, the uncertain well depth ε (the lowest negative potential value) and the location σ (at which the interatomic potential between two atoms is zero) can be represented with interval-valued parameters $[\underline{\varepsilon}, \bar{\varepsilon}]$ and $[\underline{\sigma}, \bar{\sigma}]$. For tabulated potentials such as embedded atomic method (EAM), some analytical error generating functions can be devised to represent the error bounds of potentials and the interpolation error of the potentials. With the interval potential functions, the calculated forces are also intervals. The update of positions and velocities is based on Kaucher arithmetic as described in Section 7.2. In this section, three interatomic potential examples, including Lennard-Jones, Morse, and EAM, are provided. More complex parameterized potential models, such as Tersoff, Born–Mayer–Huggins, Buckingham, Kolmogorov–Crespi, can be similarly extended to adopt the R-MD framework.

7.3.1.1 Interval potential: Lennard-Jones

The LJ model is widely used in the literature due to their mathematical simple form with two parameters (ε and σ) that approximate the interaction between a pair of a neutral atom or molecule. The 12-6 LJ potential is explicitly given by

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (7.4)$$

where ε is the depth of the potential well and σ is the distance at which the interatomic potential is zero, and r is the interatomic distance. Usually, in practice, the lower and upper bounds of ε and σ are unknown, but it is safe to assume their bounds. Using the interval potential concept, the 12-6 LJ potential is generalized to

$$[\underline{V}, \bar{V}](r) = 4[\underline{\varepsilon}, \bar{\varepsilon}] \left[\left(\frac{[\underline{\sigma}, \bar{\sigma}]}{[\underline{r}, \bar{r}]} \right)^{12} - \left(\frac{[\underline{\sigma}, \bar{\sigma}]}{[\underline{r}, \bar{r}]} \right)^6 \right] \quad (7.5)$$

The interval force calculation is straightforward in this case, as

$$[\underline{F}, \bar{F}](r) = -24[\underline{\varepsilon}, \bar{\varepsilon}] \left[\frac{2}{[\underline{r}, \bar{r}]} \left(\frac{[\underline{\sigma}, \bar{\sigma}]}{[\underline{r}, \bar{r}]} \right)^{12} - \frac{1}{[\underline{r}, \bar{r}]} \left(\frac{[\underline{\sigma}, \bar{\sigma}]}{[\underline{r}, \bar{r}]} \right)^6 \right] \quad (7.6)$$

7.3.1.2 Interval potential: Morse potential

$$V(r) = D \left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right), \quad (7.7)$$

where r is the pairwise distance between atoms, D is the dissociation energy, α is a constant with dimension of reciprocal distance, and r_0 is the equilibrium distance between two atoms [37]. The interval Morse potential can be rewritten as

$$[\underline{V}, \overline{V}](r) = [\underline{D}, \overline{D}] \left(e^{-2[\underline{\alpha}, \overline{\alpha}](r-r_0)} - 2e^{-[\underline{\alpha}, \overline{\alpha}](r-r_0)} \right). \quad (7.8)$$

The generalized interval arithmetic can be subsequently applied to compute the interatomic interval force as a derivative of the interval interatomic potential.

7.3.1.3 Interval potential: embedded atomic method potential

The EAM is a semiempirical and many-atom potential and is particularly well suited for metallic systems. Instead of solving the many-electron Schrödinger equation, the total energy of a solid at any atomic arrangement can be calculated based on the local-density approximation. This approximation views the energy of the metal as the energy obtained by embedding an atom into the local electron density provided by the remaining atoms of the system. In addition, there is an electrostatic interaction, which is the two-body term. The energy of the i^{th} atom is $E_i = B(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij})$

where B is the embedding energy function, which is the energy associated with placing an atom in the electron environment quantified by local electron density ρ_i , and $\phi(r_{ij})$ is the pairwise potential that describes the electrostatic contribution. The local electron density is further modeled as $\rho_i = \sum_{j \neq i} f_j(r_{ij})$ which is the sum

of electron density contributions from other neighboring atoms. The total energy of the system is $E_{\text{tot}} = \sum_i E_i$. The background density for each atom is determined by evaluating the superposition of atomic-density tails from the other atoms at its nucleus [38].

In the R-MD mechanism, the uncertainty associated with interatomic potential is characterized by two error generating functions, $e_1(r_{ij})$ and $e_2(\rho)$, which are associated with $\rho(r_{ij})$ or $\phi(r_{ij})$ and $B(\rho)$, respectively, depending on whether the function's domain is the electron density ρ or the interatomic distance r . We refer to $e_1(r)$ as type I error generating function which associates with r domain, and $e_2(\rho)$ as type II error generating function which associates with ρ domain. The interval electron density function is $[\underline{\rho}, \overline{\rho}](r_{ij}) = \rho(r_{ij}) \pm e_1^{(\rho)}(r_{ij})$, the interval pairwise potential is $[\underline{\phi}, \overline{\phi}](r_{ij}) = \phi(r_{ij}) \pm e_1^{(\phi)}(r_{ij})$, and the interval embedding energy function is $[\underline{B}, \overline{B}](\rho) = B(\rho) \pm e_2^{(B)}(\rho)$.

As the interatomic distance r_{ij} between two atom i and j approaches ∞ , their interaction becomes weaker and approach to 0 asymptotically. On the other hand, the electron density function $\rho(r_{ij})$ and the pairwise potential $\phi(r_{ij})$ of r_{ij} must remain bounded as $r_{ij} \rightarrow 0$. In addition, the inclusion properties of interval must be kept for both the original functions and their first derivatives. Consequently, the type I error generating function $e_1(r)$ is required to satisfy the following six conditions,

- $\lim_{r \rightarrow 0} e_1(r) < \infty$
- $\lim_{r \rightarrow \infty} e_1(r) = 0$
- $\lim_{r \rightarrow 0} \frac{\partial e_1(r)}{\partial r} < \infty$
- $\lim_{r \rightarrow \infty} \frac{\partial e_1(r)}{\partial r} = 0$
- $\forall r \in [0, \infty) : f(r) \in [f(r) \pm e_1(r)]$
- $\frac{\partial f(r)}{\partial r} \in \left[\frac{\partial \rho_0(r) \pm \partial e_1(r)}{\partial r} \right]$

where $f(r)$ denotes the function either $\rho(r_{ij})$ or $\phi(r_{ij})$. Based on the above six required conditions, two analytical and admissible forms are found. They are a rational function where the denominator is one degree higher than the numerator as

$$e_1(r) = \frac{a_1 r + a_0}{b_2 r^2 + b_1 r + b_0} \quad (7.9)$$

and an exponential function as

$$e_1(r) = a e^{-br} \quad \text{where } b > 0. \quad (7.10)$$

Similarly, the analytical choice of type II error generating function associated with $B(\rho)$ is limited by:

- negative finite slope at $\rho = 0$ for $B(\rho) \pm e_2(\rho)$
 - positive slope at large electron density for $B(\rho) \pm e_2(\rho)$
 - $e_2(0) = 0$ where atoms are far separated
 - nonnegative function $e_2(\rho) \geq 0, \forall \rho \in [0, \infty)$
 - local extrema (in this case, maxima) at $\rho = \rho_0$ because $B(\rho) \pm e_2(\rho)$ attains its minimum ρ_0
- as well, thus $\left. \frac{\partial [B(\rho) \pm e_2(\rho)]}{\partial \rho} \right|_{\rho=\rho_0} = 0$ means that $\left. \frac{\partial e_2(\rho)}{\partial \rho} \right|_{\rho=\rho_0} = 0$

The last condition corresponds to the so-called effective pair scheme, which requires the embedding function to attain its minimum at the density of equilibrium crystal [39]. One analytical choice of the error generating function of type II that satisfies all of these conditions is

$$e_2(\rho) = a \left(\frac{\rho}{\rho_0} \right)^{b\rho_0} e^{-b(\rho-\rho_0)}, \quad b > \frac{1}{\rho_0}, \quad b\rho_0 \notin \{0, 1\}. \quad (7.11)$$

Practically speaking, the limit $r_{ij} \rightarrow 0$ is almost never encountered, should the simulated time step be sufficiently small. However, for rigorous mathematical derivation, it is necessary to impose boundedness constraints at asymptotic limits. Otherwise, the R-MD framework is no longer robust.

In this work, we strictly follow the original derivation of the EAM potential, as in Daw and Baskes [40]. However, the requirement that the embedding energy function must attain its minimum at $\rho = \rho_0$ for EAM potentials may not be necessary or always employed in practice. Some authors impose this constraint in the fitting process to address an ambiguity in the definition of the potentials. Adding a linear term to the embedding energy function can always be exactly compensated by a modification of the pair potential, for example, in the work of Cai and Ye [41].

For EAM potential, the classical force for atom i th based on its neighborhood (j th atoms) is calculated as

$$\begin{aligned} \vec{F}_i = & - \sum_{j \neq i} \left[\left. \frac{\partial B_i(\rho)}{\partial \rho} \right|_{\rho=\rho_i} \cdot \left. \frac{\partial \rho_j(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial B_j(\rho)}{\partial \rho} \right|_{\rho=\rho_j} \cdot \left. \frac{\partial \rho_i(r)}{\partial r} \right|_{r=r_{ij}} \right. \\ & \left. + \left. \frac{\partial \phi_{ij}(r)}{\partial r} \right|_{r=r_{ij}} \right] \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}} \end{aligned} \quad (7.12)$$

where $\vec{F}$ is the vector force, $B(\rho)$ is the embedding energy, $\rho(r)$ is the local electron density function, and $\phi(r_{ij})$ is the pairwise potential. For interval EAM potential, the upper and lower bounds of the interval force are extended based on the classical force calculation and calculated separately as

$$\begin{aligned} \vec{F}_i = & - \sum_{j \neq i} \left[\left(\left. \frac{\partial B_i(\rho)}{\partial \rho} \right|_{\rho=\rho_i} - \left. \frac{\partial e_2^{(B)}(\rho)}{\partial \rho} \right|_{\rho=\rho_i} \right) \cdot \left(\left. \frac{\partial \rho_j(r)}{\partial r} \right|_{r=r_{ij}} - \left. \frac{\partial e_1^{(\rho)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \right. \\ & + \left(\left. \frac{\partial B_j(\rho)}{\partial \rho} \right|_{\rho=\rho_j} - \left. \frac{\partial e_2^{(B)}(\rho)}{\partial \rho} \right|_{\rho=\rho_j} \right) \cdot \left(\left. \frac{\partial \rho_i(r)}{\partial r} \right|_{r=r_{ij}} - \left. \frac{\partial e_1^{(\rho)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \\ & \left. + \left(\left. \frac{\partial \phi(r)}{\partial r} \right|_{r=r_{ij}} - \left. \frac{\partial e_1^{(\phi)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \right] \cdot \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}} \end{aligned} \quad (7.13)$$

$$\begin{aligned} \vec{F}_i = & - \sum_{j \neq i} \left[\left(\left. \frac{\partial B_i(\rho)}{\partial \rho} \right|_{\rho=\rho_i} + \left. \frac{\partial e_2^{(B)}(\rho)}{\partial \rho} \right|_{\rho=\rho_i} \right) \cdot \left(\left. \frac{\partial \rho_j(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial e_1^{(\rho)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \right. \\ & + \left(\left. \frac{\partial B_j(\rho)}{\partial \rho} \right|_{\rho=\rho_j} + \left. \frac{\partial e_2^{(B)}(\rho)}{\partial \rho} \right|_{\rho=\rho_j} \right) \cdot \left(\left. \frac{\partial \rho_i(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial e_1^{(\rho)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \\ & \left. + \left(\left. \frac{\partial \phi(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial e_1^{(\phi)}(r)}{\partial r} \right|_{r=r_{ij}} \right) \right] \cdot \frac{(\vec{r}_i - \vec{r}_j)}{r_{ij}} \end{aligned} \quad (7.14)$$

If the error generating functions are zeros almost everywhere, the interval force converges to the classical force. The atomic interactions between atom i and its neighbors are assumed to vary within some ranges and become slightly stronger or weaker based on the prescribed interval potential functions. Therefore, the total force acting on atom i at one time step can be captured by an upper bound and a lower bound, or an interval force vector. The upper bound and lower bound of the force interval can have different magnitudes, as well as different directions, as illustrated Fig. 7.4(b). Compared to our previous work [21,22], here the signum function is not included to allow more variations in the interval interatomic forces.

7.3.2 Interval-valued position, velocity, and force

An appropriate representation of atomistic values in interval form is a key step to efficiently perform an intrusive UQ study in MD. There are two ways to represent an interval. The first representation $\mathbf{x} = [\underline{x}, \bar{x}]$ is using upper bound $\bar{x}$ and lower bound $\underline{x}$. The second representation is midpoint $\text{mid}(\mathbf{x}) = \frac{1}{2}(\bar{x} + \underline{x})$ and radius $\text{rad}(\mathbf{x}) = \frac{1}{2}(\bar{x} - \underline{x})$. There are considerable differences in terms of computational efficiency between these two representations. The advantage of the lower–upper bound representation is the low computational time for interval arithmetic because most of the interval calculations in Section 7.2 are implemented under this representation. However, it would require to rewrite an MD package to incorporate the intervals into MD simulation. On the other hand, the midpoint–radius representation can be conveniently built as an extension based on the classical MD packages. The midpoint values of atoms’ interval positions, velocities, and forces intervals can be assigned as the nominal values in classical MD at every time step, and the radii can be computed based on the lower or upper bounds accordingly. With the radii of the interval positions, velocities, and forces, the uncertainty of the quantities of interest can be quantified accordingly. The drawback of this technique is that it is not computationally optimal because of the repetitive converting processes.

As shown in Fig. 7.2(a), because the nominal values from classical MD are not necessarily the exact midpoint, two radii need to be differentiated. One is inner radius, the other is outer radius. The inner radius is the smaller distance from midpoint to one of the interval bounds, whereas the outer radius is the larger distance. If the inner radius is chosen, the solution underestimates the true uncertainty, and the interval underestimation is called *sound*. If the outer radius is chosen, the solution overestimates the true uncertainty, and the interval is called *complete*. In the inner radius case, the soundness is chosen over the completeness. In the outer radius case, the completeness is chosen over the soundness. Based on the introduction of radius variable to represent intervals, Fig. 7.2(b) presents the possibility of decoupling radius variables from the interval variables for the atomistic positions, velocities, and forces. This is an advantage of the midpoint–radius representation because instead of building interval objects to handle, the decoupling allows for

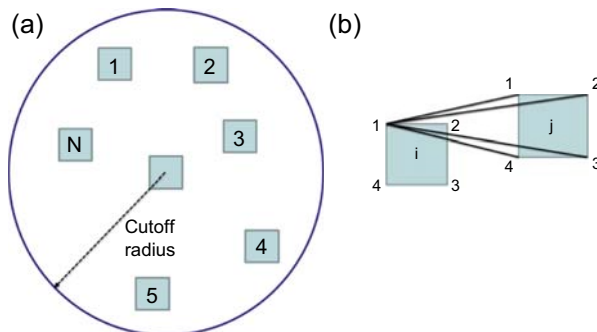


Figure 7.3 2D R-MD force simplification problem. (a) N atom in a neighboring list and (b) Interaction between one vertex with other vertices in another prism in R-MD.

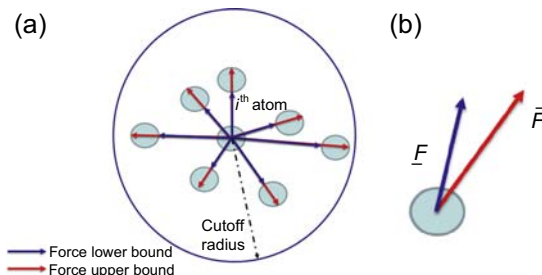


Figure 7.4 The process of computing the interval force acting on one atom at every time step. (a) Pairwise force between atom i and its neighbors: upper and lower bounds calculation and (b) total force acting on atom i at one time step.

7.3.3 Uncertainty propagation schemes in R-MD

Four computational schemes are developed to quantify and propagate the uncertainty. They are called *midpoint–radius*, *lower–upper bound*, *total uncertainty principle*, and *interval statistical ensemble* schemes.

7.3.3.1 Midpoint–radius or nominal–radius scheme

Following the midpoint–radius representation of an interval in [Section 7.2](#), the inner and outer radii of force intervals are calculated as

$$\begin{aligned}
 \text{rad}_{\text{inner}} \left[\underline{f}, \bar{f} \right] &= \begin{cases} \min \{ \bar{f} - f^*, f^* - \underline{f} \}, & \text{if } [\underline{f}, \bar{f}] \text{ is proper} \\ \max \{ \bar{f} - f^*, f^* - \underline{f} \}, & \text{if } [\underline{f}, \bar{f}] \text{ is improper} \end{cases} \\
 \text{rad}_{\text{outer}} \left[\underline{f}, \bar{f} \right] &= \begin{cases} \max \{ \bar{f} - f^*, f^* - \underline{f} \}, & \text{if } [\underline{f}, \bar{f}] \text{ is proper} \\ \min \{ \bar{f} - f^*, f^* - \underline{f} \}, & \text{if } [\underline{f}, \bar{f}] \text{ is improper} \end{cases}
 \end{aligned} \tag{7.15}$$

where f^* denotes the force calculated from traditional MD calculation. This is consistent with the fact that a proper interval has positive interval radius, and an improper interval has negative interval radius. The radii for atomistic interval positions and atomistic interval velocities are defined similarly. At each time step, the midpoint value of pairwise interval force is assigned as the usual pairwise force value in classical MD simulation, as shown in Fig. 7.2(a). Then, the radius of pairwise interval force is computed based on the choice of inner or outer radius. The radius of each pairwise interval force associated with atom i then can be added together to produce the radius of the total interval force at one time step. With the radius and midpoint of the total interval, one can reconstruct the total interval force acting on atom i at that time step. It is then straightforward to compute the interval-valued velocities and positions of atoms.

The advantage of the midpoint–radius scheme is that the number of operations can be reduced based on the fact that the midpoint of interval positions and interval velocities are the same as the classical MD values and the calculations of radii and midpoints can be decoupled, as described in Section 7.3.2. The decoupling process allows for shortening computational time by computing the radii of the atomistic intervals directly. The computational procedure is summarized in Algorithm 1.

One technical issue of the midpoint–radius representation is that the inner radii tend to underestimate the uncertainty of the forces, positions, and velocities, whereas the outer radii tend to overestimate the uncertainty. The ideal case is these two estimations are coincident. Yet in most cases, they have differences. Therefore, to have a better estimation of uncertainty, two runs of simulation are recommended, one with inner radii and the other with outer radii. Although the actual interval bounds are unknown, the results from these two simulation runs can give a better estimate of error bounds.

A caveat for this implementation scheme is that for isothermal ensemble, such as isothermal-isobaric (NPT) statistical ensemble, the uncertainty associated with temperature is pessimistically large even though the epistemic uncertainty associated with temperature should be small, because it mostly fluctuates around a constant. The temperature is computed based on its relation to the kinetic energy as

$$\sum_{k=1}^N \frac{mv_k^2}{2} = \frac{1}{2} dNk_B T \quad (7.16)$$

Algorithm 1 Implementation of midpoint–radius scheme.

```

1: for every time step do
2:   compute the total upper bound force  $\bar{f}$ 
3:   compute the total lower bound force  $\underline{f}$ 
4:   compute the total nominal force  $f^*$ 
5:   compute the pairwise force interval radius  $frad$  based on the choice of inner or outer radius
6:    $vrad \leftarrow vrad + frad/m$ 
7:    $xrad \leftarrow xrad + vrad \cdot \Delta t$ 
8:   quantifying uncertainty by interval radius of atomistic positions, velocities, and forces
9: end for

```

where N is the number of atoms, k_B is the Boltzmann constant, T is the temperature, and d is the dimensionality of the simulation. Because of the overestimation issue, the uncertainty associated with temperature is set as 0 in this scheme to preserve the isothermal properties of the statistical isothermal-isobaric ensemble, and hence only the uncertainties in atoms' positions and forces contribute to the pressure uncertainty. The output of this scheme is the radii values of the interval output.

7.3.3.2 Lower–upper bound scheme

The second approach to implement the interval-based simulation scheme is based on the lower and upper bounds directly to estimate the uncertainty of the system. In this approach, the upper and lower bound values of the atomistic positions, velocities, and forces, along with their nominal values are retained at every time step. The nominal values are updated based on the classical algorithm in MD, whereas the upper and lower bounds are updated from the nominal values and the interval force. For a standard velocity–Verlet integrator, this concept is described in [Algorithm 2](#). The output of this scheme is interval outputs, with lower and upper bound values.

7.3.3.3 Total uncertainty principle scheme

In the computational scheme of total uncertainty principle, the radii of atoms' interval velocities are assumed to be a fixed percentage of the magnitude of velocities, besides using the error generating function to quantify the uncertainty in the atomistic total force. This is conceptually equivalent to the temperature scaling process in isothermal-isobaric ensemble by coupling the simulation system to a thermostat. This is based on a so-called *total uncertainty principle*, which states that the total uncertainty level of the system during two consecutive observations remains the same. As a result, the uncertainty needs to be scaled back from time to time during simulation. The physical meaning of this process is that the temperature of the simulation cell is measured at every time step, so that the total uncertainty of the simulation

Algorithm 2 Implementation of lower–upper bound scheme.

```

1: for every time step do
2:  $\bar{v} \leftarrow v + \bar{f}/m$ 
3:  $\underline{v} \leftarrow v + \underline{f}/m$ 
4:  $v \leftarrow v + f/m$ 
5:  $\bar{x} \leftarrow x + \bar{v} \cdot \Delta t$ 
6:  $\underline{x} \leftarrow x + \underline{v} \cdot \Delta t$ 
7:  $x \leftarrow x + v \cdot \Delta t$ 
8: quantifying uncertainty by generalized interval arithmetic
9: end for

```

is roughly at the same scale throughout the system. This concept is expressed mathematically as

$$\text{rad}(\mathbf{v}) = \alpha\% \cdot v^* \quad (7.17)$$

$$\text{rad}(\mathbf{v}) = \alpha\% \cdot |\mathbf{v}^*| \quad (7.18)$$

where v^* denotes the classical MD values of the atoms' velocities. Eqs. (7.17) and (7.18) are associated with generalized intervals and classical intervals, respectively. The total uncertainty principle scheme is implemented according to Algorithm 3. The total uncertainty scheme with the strictly nonnegative radius of interval velocities, described by Eq. (7.18), is the total uncertainty scheme *with classical intervals*. The other uncertainty scheme, described by Eq. (7.17), is referred to as the total uncertainty scheme *with generalized intervals*. The total principle uncertainty scheme can be thought as an extension to the midpoint–radius scheme described in Section 7.3.3.1.

7.3.3.4 Interval statistical ensemble scheme: interval isothermal-isobaric (NPT) ensemble

As a result of incorporating the uncertainty into each atomistic position, velocity, and force, the system control variables also have their own uncertainty and should be consequently modeled as intervals. For example, in NPT ensemble, the pressure and temperature of the system are the control variables and could be represented as generalized intervals. Furthermore, if the simulation cell is coupled to a chain of thermostats and barostats, then the atomistic positions, velocities, and forces can be updated via generalized interval arithmetic. The advantage of this approach is that the scheme preserves the dynamics of the statistical ensemble, and therefore the uncertainty of the system can be quantified more rigorously. We refer to this scheme as the *interval statistical ensemble scheme*.

Algorithm 3 Implementation of total uncertainty principle scheme.

```

1: for every time step do
2: compute the total upper bound force  $\bar{f}$ 
3: compute the total lower bound force  $\underline{f}$ 
4: compute the total nominal force  $f^*$ 
5: compute the pairwise force interval radius  $frad$  based on the choice of inner or outer radius
6:  $vrad \leftarrow \alpha\% \cdot v^*$  or  $vrad \leftarrow \alpha\% \cdot |\mathbf{v}^*|$ 
7:  $vrad \leftarrow vrad + frad/m$ 
8:  $xrad \leftarrow vrad \cdot \Delta t$ 
9: quantifying uncertainty by interval radius of atomistic positions, velocities, and forces
10: end for

```

In the NPT statistical ensemble, the simulation cell is coupled to the Nosé–Hoover chain (NHC) of thermostats. The corresponding interval governing equations of motions [42] are extended to generalized intervals space $\mathbb{K}\mathbb{R}$ as

$$\begin{aligned}
 [\underline{\dot{\mathbf{r}}}_i, \overline{\dot{\mathbf{r}}}_i] &= \frac{[\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i]}{m_i} \oplus \frac{[\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g]}{W_g} \otimes [\underline{\mathbf{r}}_i, \overline{\mathbf{r}}_i], \\
 [\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i] &= [\underline{\mathbf{F}}_i, \overline{\mathbf{F}}_i] \ominus \frac{\mathbf{p}_g}{W_g} \otimes [\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i] \ominus \frac{1}{N_f} \frac{\text{Tr}[\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g]}{W_g} \otimes \mathbf{p}_i \ominus \frac{[\underline{p}_\xi, \overline{p}_\xi]}{Q} \otimes [\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i] \\
 [\underline{\dot{\mathbf{h}}}, \overline{\dot{\mathbf{h}}}] &= \frac{[\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g]}{W_g} \otimes [\underline{\mathbf{h}}, \overline{\mathbf{h}}], \\
 [\underline{\dot{\mathbf{p}}}_g, \overline{\dot{\mathbf{p}}}_g] &= V \left([\underline{\mathbf{P}}_{\text{int}}, \overline{\mathbf{P}}_{\text{int}}] \ominus I \mathbf{P}_{\text{ext}} \right) \ominus [\underline{\mathbf{h}}, \overline{\mathbf{h}}] \otimes [\underline{\Sigma}, \overline{\Sigma}] \otimes [\underline{\mathbf{h}}^T, \overline{\mathbf{h}}^T] \oplus \left(\frac{1}{N_f} \sum_{i=1}^N \frac{[\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i]^2}{m_i} \right) \mathbf{I} \ominus \frac{[\underline{p}_{\xi_1}, \overline{p}_{\xi_1}]}{Q_1} \\
 &\quad \otimes [\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g], [\underline{\dot{\xi}}_k, \overline{\dot{\xi}}_k] = \frac{[\underline{p}_{\xi_k}, \overline{p}_{\xi_k}]}{Q_k} \quad \text{for } k = 1, \dots, M, \\
 [\underline{\dot{p}}_{\xi_1}, \overline{\dot{p}}_{\xi_1}] &= \sum_{i=1}^N \frac{[\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i]^2}{m_i} \oplus \frac{1}{W_g} \text{Tr} \left[[\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g]^T \otimes [\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g] \right] \ominus (N_f + d^2) k T_{\text{ext}} \ominus [\underline{p}_{\xi_1}, \overline{p}_{\xi_1}] \otimes \frac{[\underline{p}_{\xi_2}, \overline{p}_{\xi_2}]}{Q_2}, \\
 [\underline{\dot{p}}_{\xi_k}, \overline{\dot{p}}_{\xi_k}] &= \left(\frac{[\underline{p}_{\xi_{k-1}}^2, \overline{p}_{\xi_{k-1}}^2]}{Q_{k-1}} \ominus k T_{\text{ext}} \right) \ominus [\underline{p}_{\xi_k}, \overline{p}_{\xi_k}] \otimes \frac{[\underline{p}_{\xi_{k+1}}, \overline{p}_{\xi_{k+1}}]}{Q_{k+1}} \quad \text{for } k = 2, \dots, M-1, \\
 [\underline{\dot{p}}_{\xi_M}, \overline{\dot{p}}_{\xi_M}] &= \left(\frac{[\underline{p}_{\xi_{M-1}}^2, \overline{p}_{\xi_{M-1}}^2]}{Q_{M-1}} \ominus k T_{\text{ext}} \right),
 \end{aligned} \tag{7.19}$$

where $[\underline{\mathbf{r}}_i, \overline{\mathbf{r}}_i]$ and $[\underline{\mathbf{p}}_i, \overline{\mathbf{p}}_i]$ are the interval positions and momentum of atom i , respectively, $[\underline{\mathbf{h}}, \overline{\mathbf{h}}]$ is the interval cell matrix, $[\underline{\mathbf{p}}_g, \overline{\mathbf{p}}_g]$ is the interval modularly

invariant form of the cell momenta, and $\left[\underline{\xi}_k, \overline{\xi}_k\right]$ and $\left[\underline{p}_{\xi_k}, \overline{p}_{\xi_k}\right]$ are, respectively, the thermostat interval variable and its conjugated interval momentum of the k th thermostat of the Nosé–Hoover chain of length M . The constants m_i , W_g , and Q_k are the mass of atom i , barostat, and k th thermostat, respectively. The masses of the thermostats and barostat are used to tune the frequency where those variables fluctuate. The tensor $\mathbf{I}$ is the identity matrix. The constant $N_f = 3N$ is the system degrees of freedom. T_{ext} and P_{ext} denote the external temperature and external hydrostatic pressure, respectively. The matrix $\mathbf{\Sigma}$ is defined by

$$\mathbf{\Sigma} = \mathbf{h}_0^{-1} (\mathbf{t} - \mathbf{I} P_{\text{ext}}) \mathbf{h}_0^{-T} \quad (7.20)$$

The extended interval time integration schemes are also implemented, following the time-reversible measure-preserving Verlet integrators derived by Tuckerman et al. [43].

7.4 An example of R-MD: uniaxial tensile loading of an aluminum single crystal oriented in $\langle 100 \rangle$ direction

The R-MD mechanism is implemented on Large-scale Atomic/Molecular Massively Parallel Simulator, also known as LAMMPS [26]. For each atom, the lower and upper bounds of positions, velocities, and forces are added and retained in the computer temporary memory for every time step. Based on the interval positions, velocities, and forces, we followed the virial formula to compute the interval or radius of the microscopic symmetric pressure tensor. The implementation of the interval statistical ensemble is based on the modified C-XSC libraries [44] to include generalized interval arithmetic.

In the rest of this section, the simulation setting of a case study of uniaxial tensile loading of an aluminum single crystal is introduced in Section 7.4.1. Section 7.4.2 introduces the interval EAM potential for aluminum based on the error generating functions described in Section 7.3.1.3. Section 7.4.3 presents the numerical results of the study. Section 7.4.4 compares the results of different uncertainty propagation schemes against each other. In Section 7.4.5, different schemes and their effectiveness are verified according to the soundness and completeness levels. In Section 7.4.6, the results are further verified by studying the finite size effects of four different schemes.

7.4.1 Simulation settings

An R-MD simulation of stress–strain relation for fcc aluminum single crystal loaded in $\langle 100 \rangle$ direction [45–47] is adopted. The simulation cell contains 10 lattice constants in x , y , and z direction, which has 4000 atoms. The used time step is 1 fs, and the boundary condition is periodic for all directions of the simulation cell.

The modified aluminum interatomic potential used here is developed based on Mishin et al. [39], which was originally derived from both experiments and ab initio calculations. The simulation cell is initially equilibrated for 20ps, and the lattice is allowed to expand at each simulation cell boundary to a temperature of 300K and a pressure of 0 bar. After the equilibration, all the uncertainties associated with the system control variables are reset to 0, and all the atomistic intervals are degenerated into singleton intervals. Next, the simulation cell is deformed in x direction at a strain rate of $\dot{\epsilon} = 10^{10}\text{s}^{-1}$ under the NPT ensemble. The symmetric microscopic pressure tensor is then computed as

$$P_{ij} = \frac{\sum_{k=1}^N m_k v_{ki} v_{kj}}{V} + \frac{\sum_{k=1}^N r_{ki} f_{kj}}{V} \quad (7.21)$$

where m is the mass of the atoms, and r , v , and f are the atoms' positions, velocities, and interatomic forces, respectively. The pressure tensor component P_{xx} is taken as the stress σ and engineering strain values ϵ are output into a separate file, which later is postprocessed in MATLAB. As a self-consistency check, we also ran another simulation with $40 \times 40 \times 40$ lattice constants with 1 fs time step, and another $10 \times 10 \times 10$ with 0.1 fs to compare with the simulation results. Our interested quantity is the stress, which is also one the outputs of the simulation, and is directly proportional to P_{xx} . Thus, the goal of this case study is to quantify the uncertainty associated with the element P_{xx} in the microscopic pressure tensor.

Fig. 7.5 presents the results of stress $\sigma = P_{xx}$ versus strain ϵ using aluminum EAM interatomic potentials from Winey et al. [48], Mishin et al. [39], Voter and Chen [49], Zhou et al. [50], Liu et al. [51], and Mendelev et al. [52]. Fig. 7.5 shows that the choice in potentials in MD simulation is indeed a major source of uncertainty and demonstrates the need for quantifying uncertainty in MD potentials.

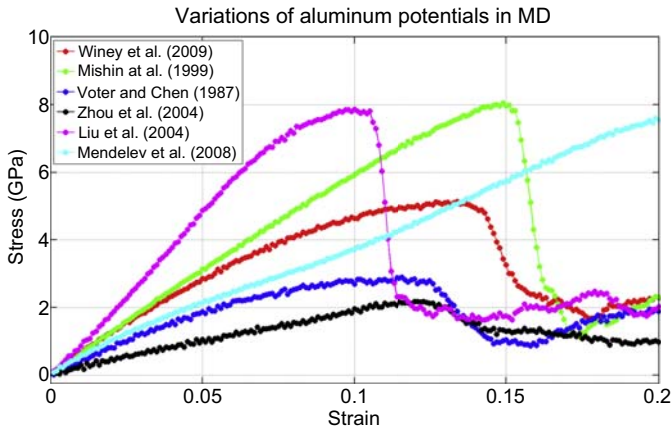


Figure 7.5 Uniaxial tensile deformation of aluminum simulation cell using various interatomic potential.

7.4.2 Interval EAM potential for aluminum based on Mishin's potential

One example of type I error generating function associated with $\rho(r)$ is shown in Fig. 7.6(a), where $e_1(r) = ae^{-br}$, along with the sensitivity analysis results in Fig. 7.6(b). Table 7.2 specifies the numerical parameters and the associated functional form to generate the uncertainty in the modified Mishin's aluminum potential [39]. An error generating function for $\rho(r)$ in the exponential form is shown in Fig. 7.7(a), and the sensitivity analysis result is shown in Fig. 7.7(b).

An example of type II error generating function is shown in Fig. 7.8(a), and the sensitivity of stress–strain relation because of the error is shown in Fig. 7.8(b). The result shows that the curve is much less sensitive with respect to type II errors than to type I errors.

7.4.3 Numerical results

In this section, we concentrate on Mishin et al. [39] EAM potential, where the cutoff radius is 6.28721 Å, and study three sets of parameters for error generating functions, as tabulated in Table 7.3. We also set $\rho_0 = 1.0$ for all the schemes and $\alpha = 0.001$ for the total uncertainty scheme.

Fig. 7.8 demonstrates a sensitivity analysis, where the parameters of error generating functions are listed in Table 7.2. The parameters are chosen in such a way that the uncertainty can be easily visualized. Because the number of atomic pairs is scaled as $\mathcal{O}(N^2)$ (where $N = 4000$ atoms in this example), the uncertainty associated with stress, which is the quantity of interest, is substantial. In practice, the uncertainty associated with the interatomic potentials is usually smaller, because they have been well calibrated. Thus, for subsequent UQ analyses, the parameters of error generating functions are reduced, as shown in Table 7.3 to be more realistic.

We compare and analyze the error qualitatively with tables and contrast the patterns of different schemes in Section 7.4.4. Fig. 7.9(a) shows the lower and upper bounds of pressure P_{yy} using the interval statistical ensemble during the equilibration phase, with the parameters described in Table 7.3. We show that the differences between the lower bound and upper bound with respect to the nominal value, which are $(\overline{P_{yy}} - P_{yy})$ and $(P_{yy} - \underline{P_{yy}})$, are not necessarily the same in Fig. 7.9(c). Furthermore, Fig. 7.9(c) also demonstrates that the uncertainty stabilizes toward the end of the equilibration phase.

Fig. 7.9(d) shows that the relative error,
$$0.5 \cdot \frac{(\overline{P_{yy}} + \underline{P_{yy}}) - P_{yy}}{\overline{P_{yy}} - \underline{P_{yy}}},$$
 which is computed as the

distance between interval midpoint and nominal values divided by the interval width, remains oscillating close to zero from the beginning to the end of the equilibration. The corresponding terms for P_{xx} and P_{zz} are similar to Fig. 7.9. Fig. 7.10(a) illustrates the concept of the R-MD framework, where the interval positions of atoms are plotted as prisms at the time $t = 12\text{ps}$ within the simulation cell. The midpoints of atoms'

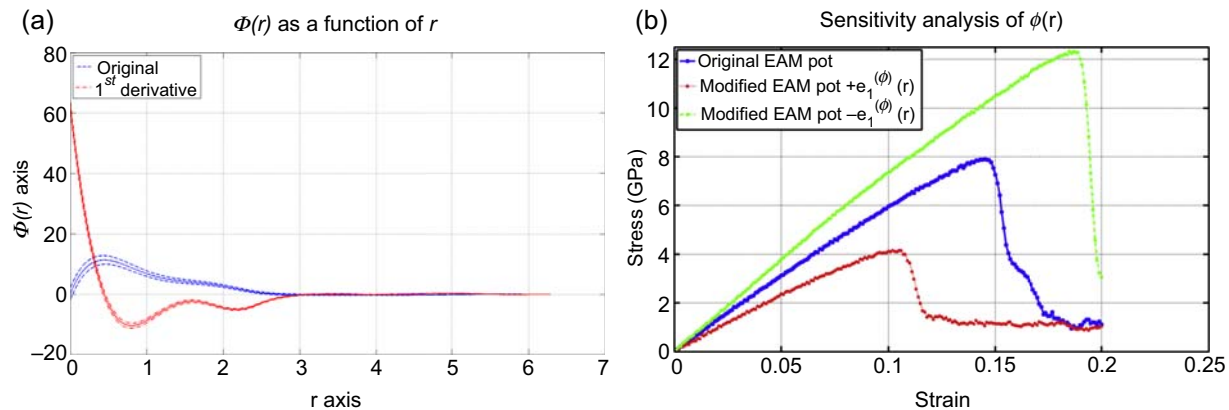


Figure 7.6 (a) Error generating function in $\rho(r)$ and (b) sensitivity analysis results. (a) Enclosed $\phi(r)$ and its first derivative by the error generating function $e_1^{(\phi)}(r_{ij})$ and (b) the sensitivity analysis results of $\phi(r)$ with respect to the error generating function $e_1^{(\phi)}(r_{ij})$.

Table 7.2 Error generating function parameters used in the simulation sensitivity analysis.

Function	Error type	Functional form	Parameters
Pairwise potential $\phi(r_{ij})$	Type I	$e_1(r) = ae^{-br}$	$a = 2.0000, b = 0.7675$
Electron density $\rho(r)$	Type I	$e_1(r) = ae^{-br}$	$a = 0.0139, b = 0.4993$
Embedding function $F(\rho)$	Type II	$e_2(\rho) = a\left(\frac{\rho}{\rho_0}\right)^{b\rho_0} e^{-b(\rho-\rho_0)}$	$a = 0.2700, b = 1.5000$

interval positions, which are the results from the traditional MD simulation, are computed from the Verlet integrals, using the parameters from Table 7.3. The periodic boundary is plotted as the box. Fig. 7.10(b) shows the histogram distribution of the radius variable $\text{rad}[\underline{x}, \bar{x}]$ described in Fig. 7.10(a) with the mean $\mu = 2.45064 \cdot 10^{-6} \approx 0$, implying that half of the interval positions are proper intervals, and the other half are improper intervals. This finding is consistent with the Newton's third law $[\underline{F}_{ij}, \bar{F}_{ij}] + [\underline{F}_{ji}, \bar{F}_{ji}] = 0$ or $\text{rad}(\underline{F}_{ij}) = -\text{rad}(\underline{F}_{ji})$ in generalized interval form, where half of the interval radii are positive, and the other half are negative. The range of the $\text{rad}[\underline{x}, \bar{x}]$ in Fig. 7.10(b) is $[-0.1037, 0.0835]$, and the histogram is fitted with a normal distribution where $(\mu, \sigma) = (2.45064 \cdot 10^{-6}, 0.0238857)$. The histogram of the atomic interval position in y and z directions are similar to Fig. 7.10(b).

7.4.4 Comparisons of numerical results for different schemes

To measure the deviation between the results from these four implementation schemes and those of the classical MD simulations and compare the errors between different schemes, the maximum deviation from the nominal values to the interval bounds,

$$A(\varepsilon) = \begin{cases} |\text{rad}[\underline{\sigma}(\varepsilon), \bar{\sigma}(\varepsilon)]|, & \text{for midpoint - radius} \\ \max\{|\bar{\sigma}(\varepsilon) - \sigma_0(\varepsilon)|, |\underline{\sigma}(\varepsilon) - \sigma_0(\varepsilon)|\}, & \text{for lower - upper bounds} \end{cases} \quad (7.22)$$

is used to describe the absolute error, where $\underline{\sigma}(\varepsilon)$ is the lower bound and $\bar{\sigma}$ is the upper bound of the stress, respectively, $\sigma_0(\varepsilon)$ is the result of the classical MD simulations for the same simulation cell size. The maximum deviation $A(\varepsilon)$ is equivalent to the l_∞ -norm of $[\underline{\sigma}, \bar{\sigma}] - \sigma_0$ in $\mathbb{R}^2$ for any ε of the simulation.

Fig. 7.11(a) presents the overall comparison graph among four implementation schemes, where the total uncertainty scheme is further split into two subschemes, one with classical intervals, and the other with generalized intervals. As indicated in Fig. 7.11(a), the total uncertainty scheme with classical intervals clearly covers all the possibilities of the solutions, whereas other schemes follow very closely with

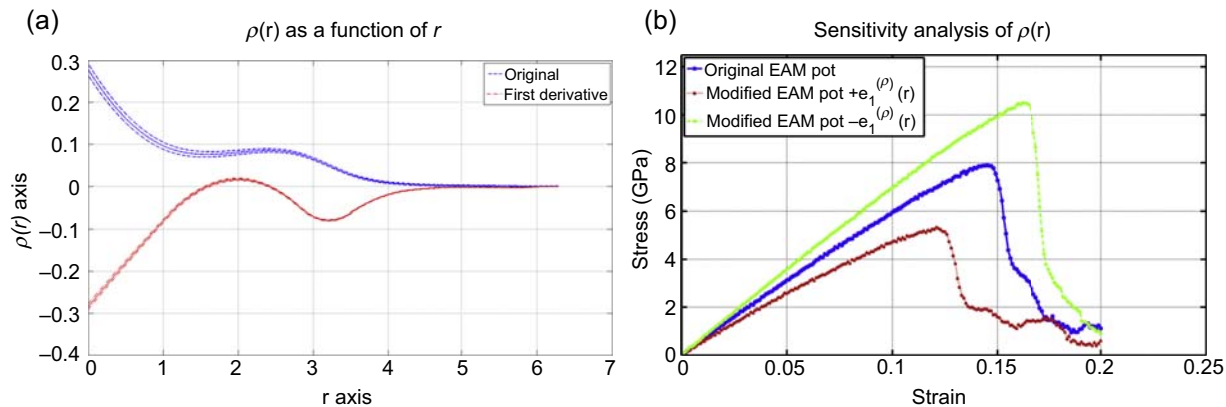


Figure 7.7 (a) Error generating function in $\rho(r)$ and (b) sensitivity analysis results. (a) Enclosed $\rho(r)$ and its first derivative by the error generating function $e_1^{(\rho)}(r_{ij})$ and (b) the sensitivity analysis results of $\rho(r)$ with respect to the error generating function $e_1^{(\rho)}(r_{ij})$.

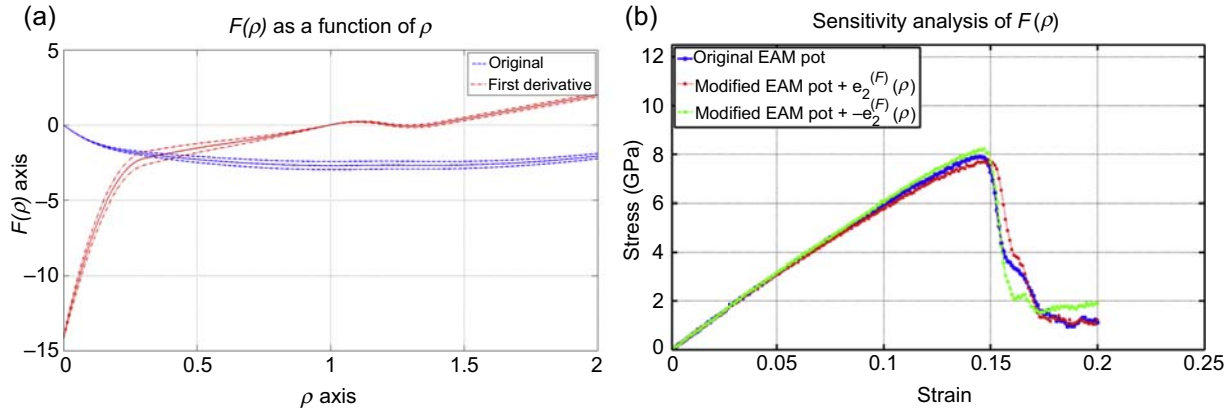


Figure 7.8 (a) Error generating function in $F(\rho)$ and (b) sensitivity analysis results. (a) Enclosed $F(\rho)$ and its first derivative by the error generating function $e_1^{(F)}(\rho)$ and (b) the sensitivity analysis results of $F(\rho)$ with respect to the error generating function $e_1^{(F)}(\rho)$.

Table 7.3 Error generating function parameters used in numerical study.

$e_1^{(\phi)}(r)$		$e_2^{(\rho)}(r)$		$e_2^{(F)}(\rho)$	
a	b	a	b	a	b
$1.2500 \cdot 10^{-2}$	$9.2103 \cdot 10^{-1}$	$1.3930 \cdot 10^{-4}$	$1.2668 \cdot 10^0$	$1.0800 \cdot 10^{-3}$	$1.5000 \cdot 10^0$

the classical MD simulation result. Fig. 7.11(b) provides a magnified view of Fig. 7.11(a), where the ranges of strain and stress are $0.0901 \leq \epsilon \leq 0.943$ and $5.4486 \leq \sigma \leq 5.6817$. We note that for all the schemes, the classical MD simulation result lies between the lower and upper bounds. More interestingly, for the total uncertainty scheme with generalized intervals, the lower and upper bounds sometimes swap the positions, but still capture the classical MD simulation solution in their ranges. This observation is contrast with the total uncertainty scheme with classical intervals, where an overestimated solution is expected, as presented in Fig. 7.11(a). After the plastic deformation, the result in interval statistical ensemble schemes does not follow the classical MD simulation result as closely as other nonpropagating schemes, such as the midpoint–radius scheme and the lower–upper bounds scheme, but the absolute errors are comparable in the elastic portion during the deformation process.

Fig. 7.12(a) compares the absolute value of outer radius $A(\epsilon)$ for the range $0 \leq \epsilon \leq 0.1$. Fig. 7.12(d) presents the same plot, but the total uncertainty with generalized intervals scheme is removed to further contrast the error between the other three schemes. All of them show that the uncertainty of the simulation slightly decreases during the elastic deformation. The uncertainty in the interval statistical ensemble decreases with a slower rate, compared to the midpoint–radius and lower–upper bounds scheme. There is a good agreement between the midpoint–radius and the lower–upper bounds scheme results, because in the midpoint–radius, the midpoint of interval stress is assigned as the classical MD value, and in the lower–upper bounds scheme, the upper and lower bounds are also calculated based on the classical MD value as well. It is then expected that the uncertainty estimated by these two methods are comparable. One common feature between the midpoint–radius scheme and the interval statistical ensemble scheme is that the uncertainty does not oscillate as heavily as in the total uncertainty ensemble scheme (Fig. 7.12(a)) and the lower–upper bounds scheme (Fig. 7.12(d)). This observation is explained by the hypothesis that compared to the nonpropagating implementation schemes, the schemes that propagate the uncertainty tend to produce smoother transition between time step. Last but not least, in three schemes excluding the total uncertainty scheme, the uncertainty of the stress is predicted to grow larger after the yield point, especially in the interval statistical ensemble scheme (Fig. 7.12(c)). However, the interval statistical ensemble scheme predicts much fluctuation of the stress before the yield point (Fig. 7.12(d)), which perhaps makes more physical intuition.

Table 7.4 compares the computational time and slow-down factor between the different schemes to the classical MD simulation. The computational time is obtained by running the simulation with different schemes on four processors with

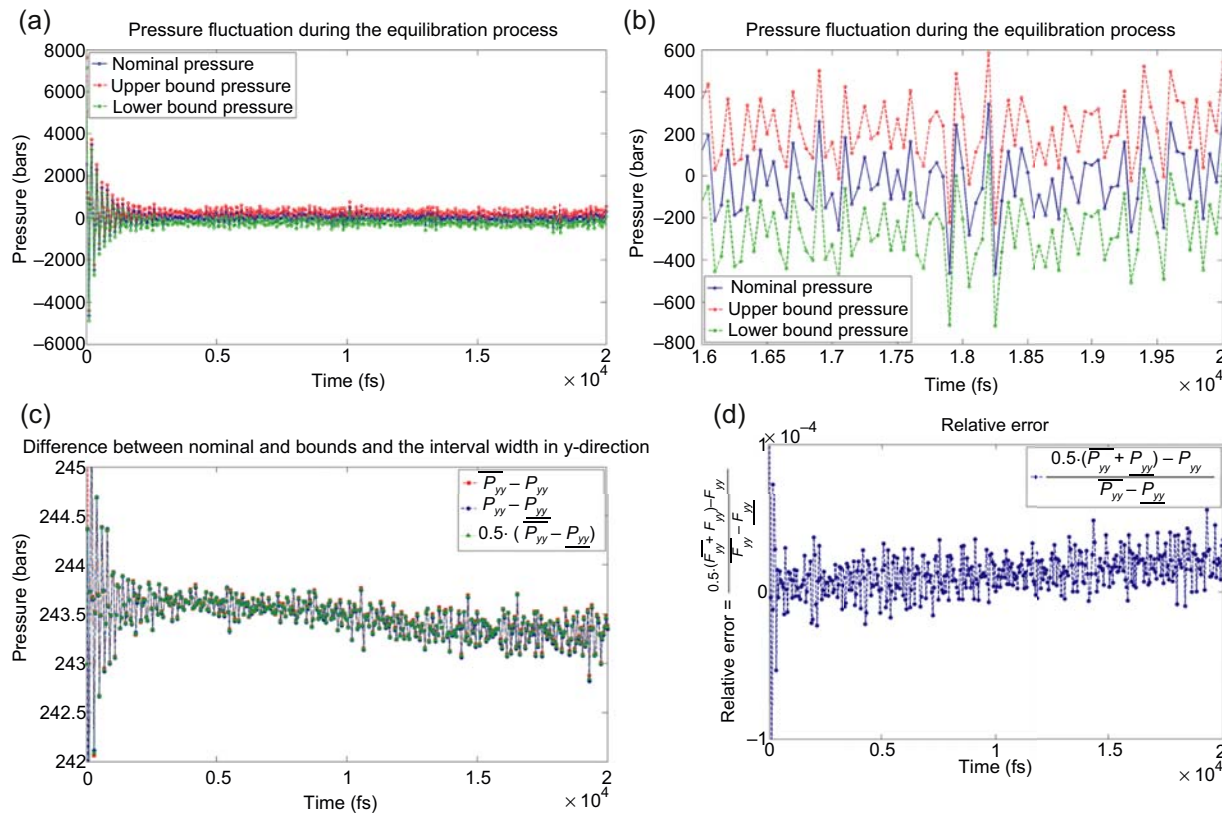
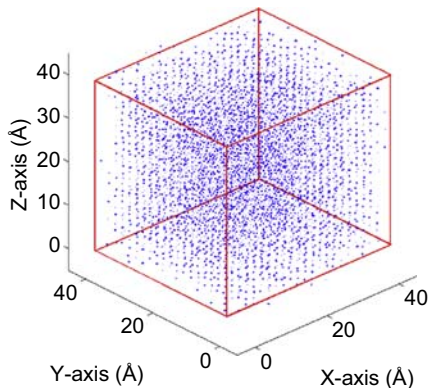


Figure 7.9 Relationship between the lower bound $\underline{P_{yy}}$, the upper bound $\overline{P_{yy}}$, and the nominal P_{yy} in the pressure tensor component of y direction. (a) Microscopic pressure P_{yy} fluctuation with nominal values, lower and upper bounds during equilibration phase; (b) magnified view for microscopic pressure P_{yy} in Fig. 7.9(a) between 16ps and 20ps during equilibration phase; (c) the difference between the bounds and nominal pressure and the interval width in y direction P_{yy} ; and (d) relative error computed as distance between midpoint and nominal values divided by interval width of the P_{yy} component.

(a) Atomistic box in reliable-MD simulation at step 12000



(b)

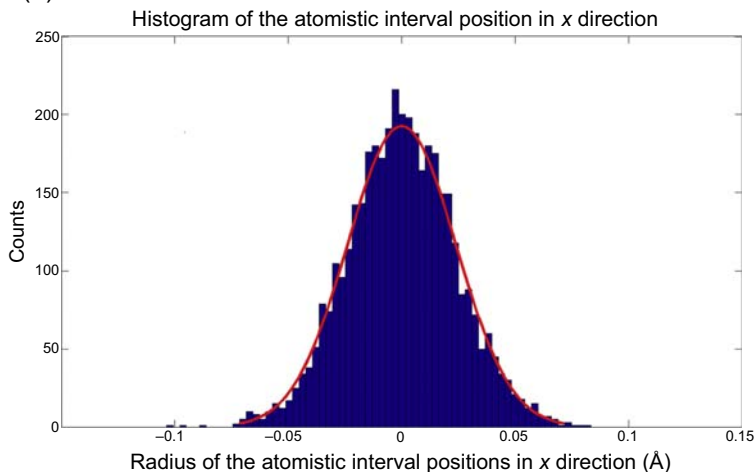


Figure 7.10 (a) Orthographic view of simulation cell in MATLAB where atoms are presented as prisms according to their interval centers and radii at time 12ps during the deformation process in the interval statistical ensemble scheme and (b) histogram of the radii of atomistic interval positions in x direction in Fig. 10(a) shows a mean very close to 0.

MPI support. The slow-down factor is calculated by the ratio of the computational time using R-MD to the classical MD simulations, showing a factor of between 4 and 5 times slower compared to the classical MD simulations. This result shows the advantage of the proposed intrusive UQ method. Nonintrusive UQ techniques, such as polynomial chaos expansion, stochastic collocation, etc., could have much more significant slow-down ratios. It demonstrates that the intrusive UQ techniques are much more computationally affordable to high-fidelity simulations, where the computational time can vary from days to months.

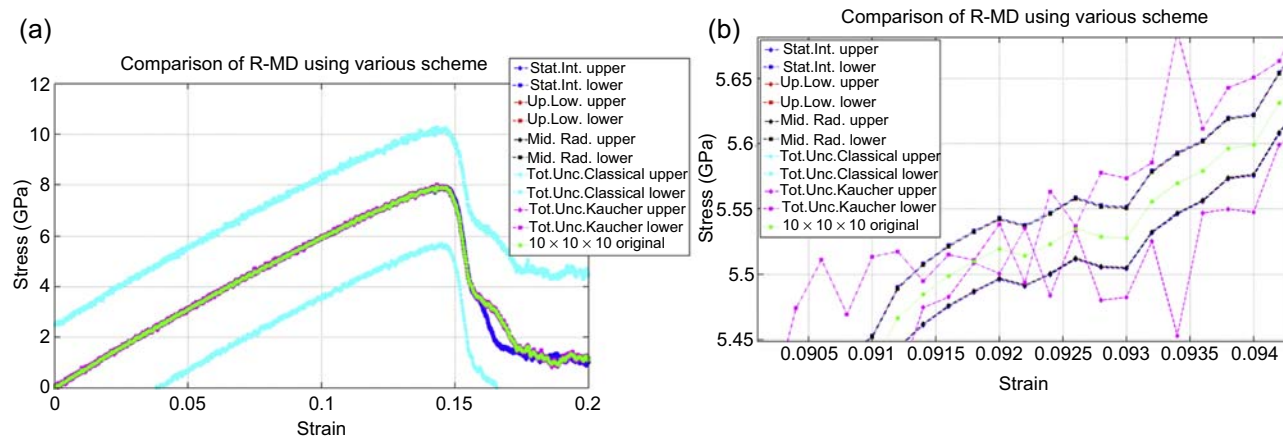


Figure 7.11 Comparisons of the stress outputs computed by four different schemes. The figures show that in all implementation schemes, the classical MD simulation result is contained in the range of the implementation results. (a) Overall comparison between the results of all schemes showing bands with different widths covering the classical MD simulation result and (b) magnified view of Fig. 11(a) where $0.0901 \leq \epsilon \leq 0.943$ and $5.4486 \leq \sigma \leq 5.6817$ show the total uncertainty scheme with generalized intervals swap bounds during the simulation.

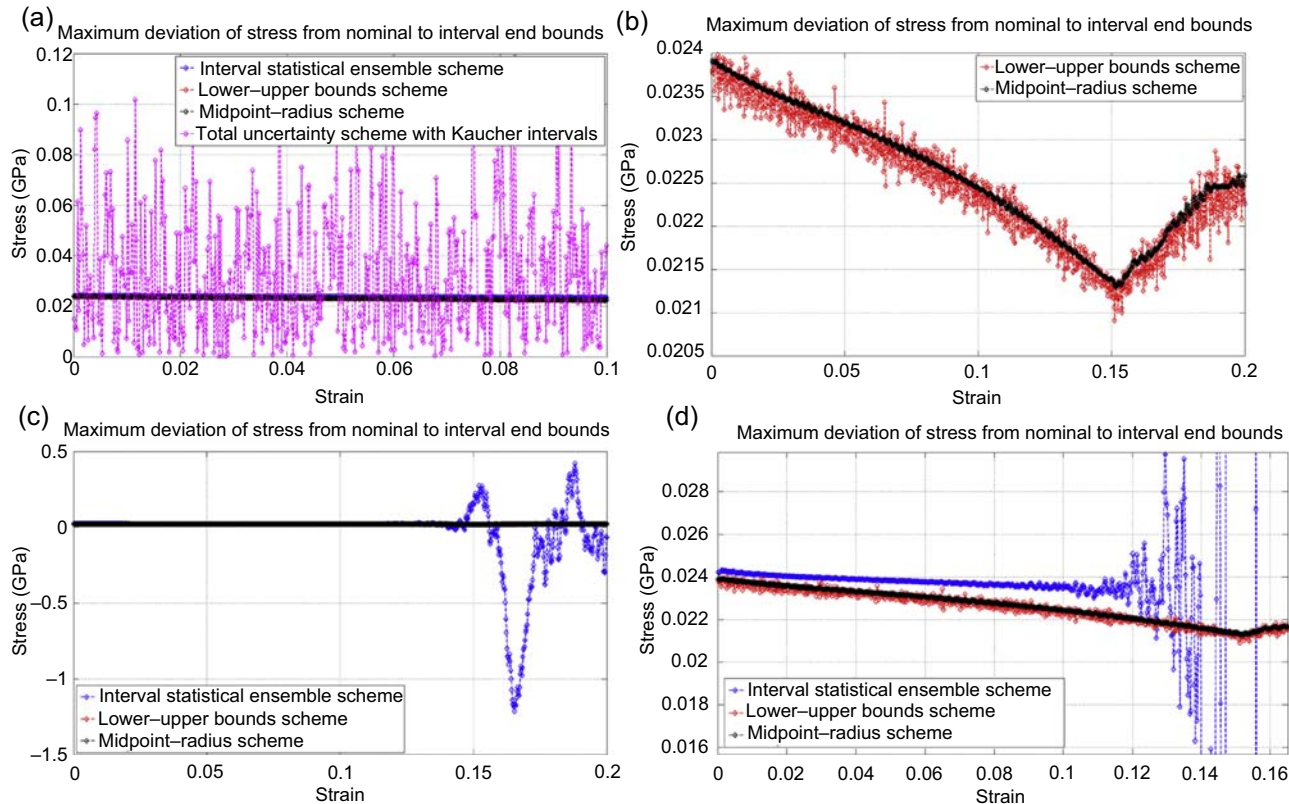


Figure 7.12 Plots of $A(\epsilon) = \max\{|\bar{\sigma} - \sigma_0|, |\underline{\sigma} - \sigma_0|\}$ in different schemes. (a) l_∞ -norm $A(\epsilon)$ in the four implementation schemes; (b) l_∞ -norm $A(\epsilon)$ in midpoint-radius and lower-upper bounds schemes for $0 \leq \epsilon \leq 0.2$ shows an increase in stress uncertainty after the yield point; (c) l_∞ -norm $A(\epsilon)$ for $0 \leq \epsilon \leq 0.2$ shows a prediction of large stress uncertainty in the interval statistical ensemble scheme compared to midpoint-radius and lower-upper bounds schemes after the yield point; and (d) l_∞ -norm $A(\epsilon)$ in three schemes (excluding the total uncertainty scheme) between $0 \leq \epsilon \leq 0.165$ indicates a considerable fluctuation of stress uncertainty in the interval statistical ensemble scheme before the yield point.

Table 7.4 Comparison of computational time for various schemes in R-MD.

	Classical MD	Midpoint–radius	Lower–upper	Total uncertainty	Interval ensemble
Computationaltime (seconds)	467.941	1989.812	1911.058	1932.983	2170.92
Slow-down factor	1	4.252	4.086	4.1308	4.639

7.4.5 Verification and validation

We repeat the sensitivity analysis as in Figs. 7.6, 7.7 and 7.8 in Section 7.3.1.3 with the error generating function parameters as tabulated in Table 7.3. Fig. 7.13 presents an overview of the four implementation results along with the sensitivity analysis results. The total uncertainty scheme with classical intervals provides not only a complete but also overestimated solution. However, it does capture the variations around the yield point and after the plastic deformation. The results of sensitivity analysis are compared with the results of different schemes. We follow the soundness and completeness concepts described in Section 7.2. Fig. 7.14(a) explains the relationship between the estimated, the sensitive, and the true range of uncertainty in UQ problem. The sensitive range, which is the solution of sensitivity analysis, is a subset of the true range. Theoretically, the true range can be obtained by Monte Carlo sampling methods. Practically, such methods are very computationally expensive and thus are not applicable. To evaluate the effectiveness of different schemes, the results obtained by R-MD are contrasted with the sensitivity analysis results using classical MD simulation with modified potentials by the error generating functions described in Section 7.3.1.3. A solution set is sound if it does not include an inadmissible or impossible solution; a solution set is called complete if it covers all possible solutions [35,53]. In Fig. 7.14(a), if the estimated range X_E is a subset of the true range X_T , that

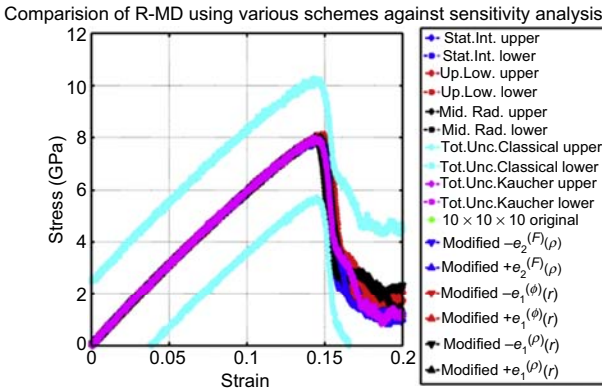


Figure 7.13 Plots of sensitivity analysis and all schemes results.

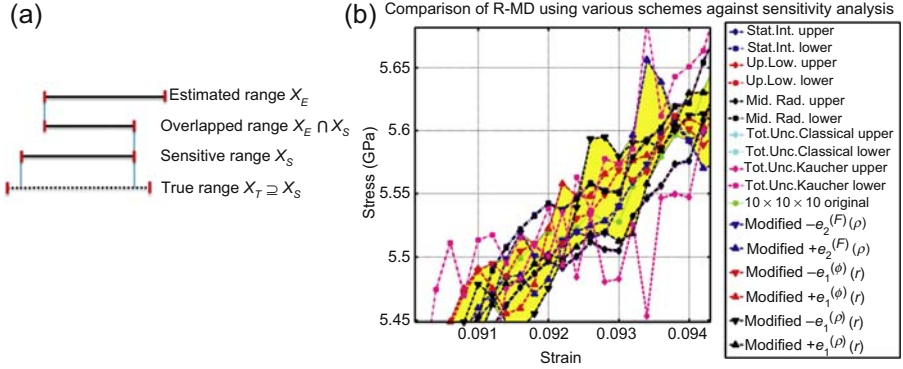


Figure 7.14 The schematic plot and actual plot of output uncertainty. In this simulation, the sensitive range is the min and max of classical MD simulation results with the original interatomic potential and the alternated potentials by adding or subtracting error generating functions to one of its three functions. (a) Schematic plot of estimated, sensitive, and true range of uncertainty. The sensitive range X_S obtained by parametric study or sensitivity analysis is always a subset of the true range X_T and (b) zoom-in plots of estimated stress uncertainties and sensitive stress uncertainties between $0.07 \leq \epsilon \leq 0.075$ and $4.25 \leq \sigma \leq 4.70$. The sensitive range is called as shaded area.

is $X_E \subseteq X_T$, then X_E is sound. If $X_T \subseteq X_E$, the solution set X_E is complete. As intervals can also be thought of as the sets of possible solutions, the term solution set is hereby used interchangeably with the interval or the range.

In measure theory, the Lebesgue measure μ is a standard way of assigning a measure to a subsets in $\mathbb{R}^n$. For 1D, 2D, and 3D, the physical meaning of Lebesgue measure is the length, the area, and the volume of the set. The soundness is assigned as the ratio of Lebesgue measure of the overlapped range $X_E \cap X_T$ and the Lebesgue measure of the estimated range. Similarly, the completeness is assigned as the ratio of Lebesgue measure of the overlapped range $X_E \cap X_T$ and the Lebesgue measure of the true range.

$$\text{Soundness index} = \frac{\mu(X_E \cap X_T)}{\mu(X_E)}, \quad \text{Completeness index} = \frac{\mu(X_E \cap X_T)}{\mu(X_T)} \quad (7.23)$$

The soundness and completeness indices are mathematically bounded between 0 and 1, as obviously $X_E \cap X_T$ is the subset of X_E and X_T . The soundness close to 1 means the estimated solution set not only contains nearly all possible solutions but also is likely to underestimate true solution set. Analogously, the completeness index close to 1 indicates a complete but overestimated solution sets. In this case, the true solution set X_T is approximated by the sensitive range X_S , which is defined as the smallest proper interval that contains seven classical MD simulation results. The equivalent mathematical expression is $X_T \approx X_S$. The sensitive range X_S includes one run with original interatomic potential and six other runs with modified interatomic potentials by the error generating functions, whose parameters are

tabulated in Table 7.3. Consequently, the soundness and completeness indices are approximated as

$$\text{Soundness index} \approx \frac{\mu(X_E \cap X_S)}{\mu(X_E)}, \quad \text{Completeness index} \approx \frac{\mu(X_E \cap X_S)}{\mu(X_S)} \quad (7.24)$$

Fig. 7.15(a,b) plot the soundness and completeness of the four schemes, respectively, with the total uncertainty scheme is further divided into classical and generalized intervals. Fig. 7.15(a,b) also indicate that the R-MD results overlap with the

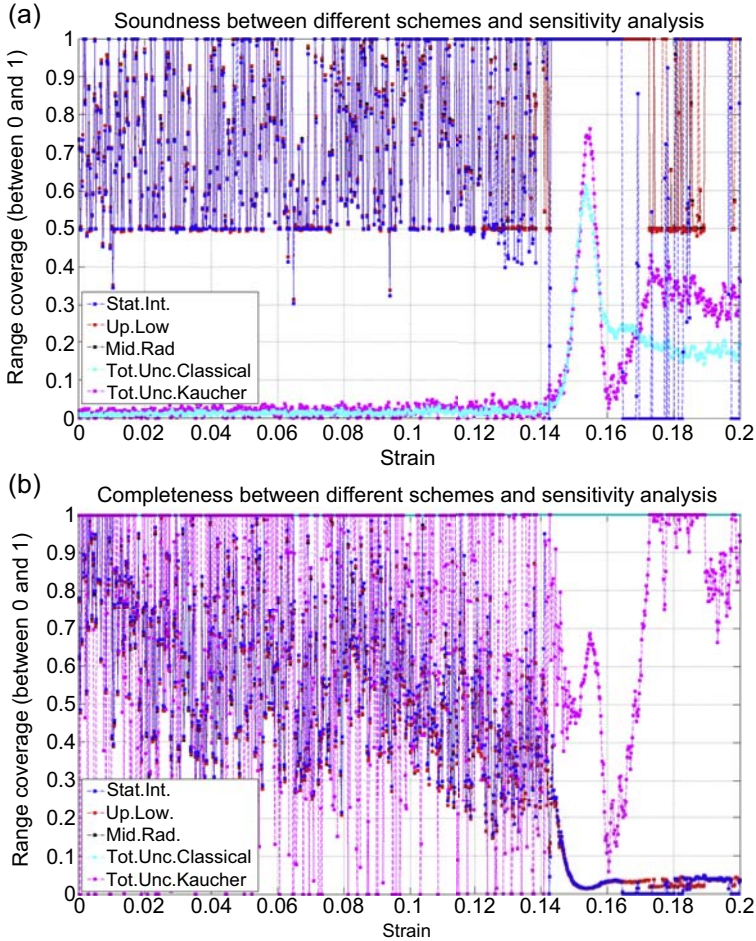


Figure 7.15 The schematic plot and actual plot of output uncertainty. In this simulation, the sensitive range is the min and max of classical MD simulation results with the original interatomic potential and the alternated potentials by adding or subtracting error generating functions to one of its three functions. (a) Soundness indices of different uncertainty schemes and (b) completeness indices of different uncertainty schemes.

sensitivity analysis. One of the differences with [Section 7.3.1.3](#) sensitivity analysis is that the original result no longer always lies in the middle of the $\pm e_2^{(F)}(\rho)$, $\pm e^{(\phi)}(r)$, $\pm e^{(\rho)}(r)$ as in [Section 7.3.1.3](#). Indeed, among 7 runs, the result of the classical simulation run with the original interatomic potential ends up with 10.40% getting the maximum value and 14.40% getting the minimum value in 7 values accounting for the sensitivity analysis results. The total uncertainty scheme with classical intervals achieves the completeness of 1 thoroughly during the simulation, implying that it always covers all of the true solution set. The soundness of the interval statistical ensemble scheme, along with midpoint–radius and lower–upper bounds schemes, is more consistent compared to the total uncertainty scheme. Their results represent mostly between 50% and 100% of the sensitive range. The completeness is, however, less consistent and fluctuates much, meaning they do not cover all the possibilities in the sensitive ranges, and thus will not cover all the possibilities in the true ranges as well. The total uncertainty scheme with generalized intervals captures the uncertainty most effectively after the deformation process, with high completeness (around 80%–90% in [Fig. 7.15\(b\)](#)) and reasonably high soundness (30%–40% in [Fig. 7.15\(a\)](#)).

Mathematically, the sensitive range is a subset of the true range, $X_S \subseteq X_T$, which also means $\mu(X_S) \leq \mu(X_T)$, [Eqs. \(7.23\) and \(7.24\)](#) can be manipulated further as

$$\frac{\mu(X_E \cap X_S)}{\mu(X_E)} \leq \frac{\mu(X_E \cap X_T)}{\mu(X_E)}, \quad (7.25)$$

and as

$$\frac{\mu(X_E \cap X_S)}{\mu(X_S)} = \frac{\mu(X_E \cap X_T) - \mu(X_E \cap (X_T/X_S))}{\mu(X_T) - \mu(X_T/X_S)} \quad (7.26)$$

because of the additivity properties of Lebesgue measure on disjoint sets $X_T = X_S \cup (X_T/X_S)$ and $X_S \cap (X_T/X_S) = \emptyset \Rightarrow \mu(X_T) = \mu(X_S) + \mu(X_T/X_S)$. Consequently, the actual soundness is expected to be higher than [Fig. 7.15\(a\)](#) if the true range X_T is known. However, there is not enough numerical evidence to draw a conclusive comment about the completeness in [Fig. 7.15\(b\)](#). The completeness could either increase or decrease depending on how $\frac{\mu(X_E \cap (X_T/X_S))}{\mu(X_T/X_S)}$ compares with $\frac{\mu(X_E \cap X_T)}{\mu(X_T)}$. Yet, one can be certain that if the output is not complete compared to the sensitivity analysis result, the output is also not complete compared to the true solution set.

7.4.6 Finite size effect

We performed finite size effect analysis for four implementation schemes with $10 \times 10 \times 10$ (4000 atoms), $12 \times 12 \times 12$ (6912 atoms), $14 \times 14 \times 14$ (10976 atoms), and $16 \times 16 \times 16$ (16384 atoms) lattice constants of the simulation cell with parameters as in [Table 7.3](#). The results of R-MD are then compared with the results of the classical MD simulations with the corresponding size of $10 \times 10 \times 10$, $12 \times 12 \times 12$, $14 \times 14 \times 14$, and $16 \times 16 \times 16$. [Fig. 7.16](#) presents magnified view of the finite size effect of the interval statistical

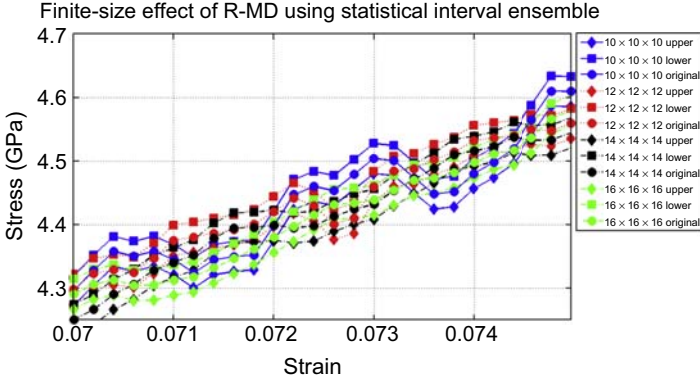


Figure 7.16 Finite size effect of R-MD and MD, where *solid lines* denote the $10 \times 10 \times 10$, *dotted lines* denote $12 \times 12 \times 12$, *dashdot lines* denote $14 \times 14 \times 14$, and *dashed lines* denote $16 \times 16 \times 16$.

ensemble between $0.07 \leq \varepsilon \leq 0.075$ and $4.25 \leq \sigma \leq 4.70$. The solid lines denote the $10 \times 10 \times 10$, the dotted lines denote $12 \times 12 \times 12$, dashdot lines denote $14 \times 14 \times 14$, and dashed lines denote $16 \times 16 \times 16$ simulation results. Also, on the same graph, the diamond markers denote the upper bound, the square markers denote the lower bound, and the circles denote the classical MD simulation results.

To measure the convergent of different UQ schemes, the strain-averaged absolute stress error between $0 \leq \varepsilon \leq 0.1$, denoted as A^* ,

$$A^* = \frac{1}{0.1} \int_0^{0.1} A(\varepsilon) d\varepsilon \quad (7.27)$$

where $A(\varepsilon)$ is the maximum deviation from the nominal to the interval end bounds in Eq. (7.22) because of the input uncertainty in the interatomic potential, is used to verify the finite size effect of different schemes. The reason that $\varepsilon = 0.1$ is picked as the upper bound of the integral is that after the simulation cell runs into plastic deformation, it is hard to quantify and predict the error exactly, and between the range $[0, 0.1]$ the stress σ versus strain ε curves are more consistent so that they can be compared qualitative against each other. Mathematically, A^* is proportional to the L_1 -norm of $A(\varepsilon)$ because $A(\varepsilon)$ measures how far the interval bounds are compared to the nominal values. Concisely, A^* is a compound $L_1 \circ l_\infty$ -norms to qualitatively describe the finite size effect of the simulation results. We expect other compound norms of the same kind, that is, $L_p \circ l_q$ -norms, to behave similarly, and thus, the quantity A^* can be justified as an arbitrary measure for the finite size effects. The value of A^* is obtained by integrating the $A(\varepsilon)$ numerically by trapezoidal rule.

Fig. 7.17 presents the integral strain-averaged absolute stress error A^* with respect to different sizes of the simulation cell, showing a convergent error with respect to the

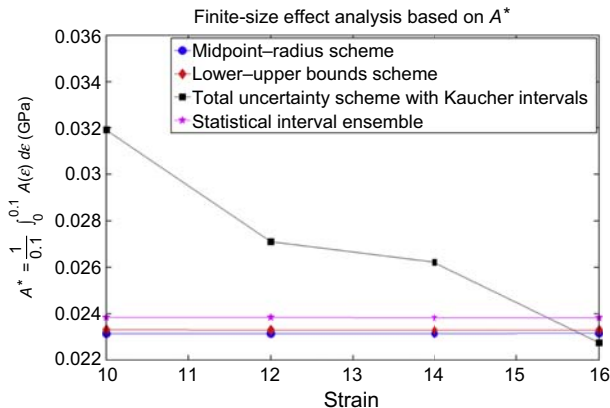


Figure 7.17 Error analysis of A^* for different schemes with respect to different sizes of the simulation cell.

size of simulation cells for all the schemes. The total uncertainty scheme with generalized intervals has one more parameter α to model the temperature measurement at every time step, thus it is not expected to exactly follow other schemes. However, the total uncertainty scheme with generalized interval still shows a convergent pattern with respect to the increased size in the simulation cell. We then conclude all four implementation schemes yield reliable results.

7.5 Discussion

One of the main challenges in intrusive UQ techniques is the comprehensive understanding of the underlying computational scheme and simulation settings. The advantage of this approach is that the uncertainty effect can be assessed on-the-fly as the simulation advances, with only one run of simulation. Compared to the traditional nonintrusive global sensitivity analysis or parametric expansion studies, the intrusive UQ techniques are very efficient, because this methodology does not require the simulation to repeat numerous times. In our experimental study, the computational time is only about 4 times slower than the classical MD simulations because of the additional computation time of interval values. This high efficiency is particularly important for MD simulations, since each MD run is computationally expensive. A UQ method that requires for many runs will not be cost-effective. For nonintrusive approaches, the number of simulation runs depends on the dimension of the problem. For the polynomial chaos expansion with full tensor grid, the number of runs is s^d , where s is the number of sampling points along one dimension, and d is the dimension of the problem. For the polynomial chaos expansion with sparse grid, the number of nodes sampled is approximately $(2^k/k!)d^k$, where k is the level of the sparse grid [54,55]. Both the tensor and sparse grid approaches are cursed with the high-dimensional problems. The intrusive interval approach only requires one or two runs. However, the drawback of the intrusive UQ solution is that it requires the

in-depth physical knowledge about the simulation settings. As the simulation changes, a new intrusive UQ solution needs to be developed and implemented to adapt with the changes in simulation. During this study, we have implemented a basic platform for intrusive UQ in MD, which can be extended to different thermodynamic ensembles. There is always a bargaining trade-off between the time invested to develop an intrusive UQ solution specifically for a simulation that can run efficiently and the time spent on running simulations repetitively with generic nonintrusive UQ techniques.

The criteria of evaluating a UQ solution are completeness and soundness by comparing the estimated uncertainties with the true ones. Overly pessimistic overestimations do not provide much valuable information. Overly optimistic underestimations provide false information. The classical interval arithmetic has been shown to be a conservative choice, in the sense that it almost always produces a complete but overestimated range. The interval could grow too wide to be meaningful, especially when it propagates through a dynamic simulation over many iterations. Generalized interval based on Kaucher arithmetic is used here because of its better algebraic properties for computation and its soundness of estimation. Generalized interval arithmetic yields a much smaller uncertainty compared to the classical interval arithmetic with the introduction of improper intervals. The interval estimation emphasizes the soundness instead of completeness; therefore, the overestimation problem in classical intervals is avoided. The epistemic uncertainty thus is estimated within some acceptable range.

Note that correlation exists between atoms in terms of their individual quantities for positions, velocities, and forces. That is, these quantities between atoms are dependent to each other. However, the number of atoms is usually large, ranging from 10^3 to 10^9 . Traditional statistical approaches to track the interatomic correlations are not feasible. If independence is assumed, the uncertainty associated with the predicted physical properties as statistical ensembles will be overly estimated, with either traditional statistical approach or the worst-case classical interval approach. The consideration of correlation reduces the overestimation. Generalized interval thus can be regarded as an approach with the indirect correlation consideration.

So far, we have considered the uncertainty of the force by computing the *total* lower and upper bounds of interval force separately. Another way to compute the force uncertainty is to consider its contribution from each *individual* pair. In generalized interval arithmetic, $[x, \bar{x}] \ominus [x, \bar{x}] = 0$. The Newton's third law characterizing the interaction between the atoms can then be generalized into $\mathbb{KR}$. As shown in Fig. 7.18, the lower and upper bound reaction forces between atoms i and j satisfy the constraint $[E_{ij}, \bar{F}_{ij}] = -[E_{ji}, \bar{F}_{ji}]$, which is Newton's third law in generalized interval form. This is mathematically equivalent to

$$\text{rad}(\mathbf{F}_{ij}) = -\text{rad}(\mathbf{F}_{ji}) \quad (7.28)$$

This scheme has also been attempted in the study, and the same issue for this implementation scheme is that the temperature uncertainty is very large, even compared to the total uncertainty scheme with classical intervals. The same treatment for temperature is also applied, that is, the uncertainty of pressure is only calculated by the interval

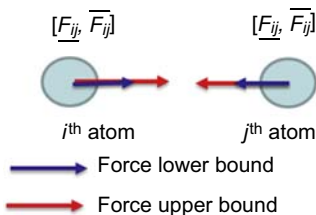


Figure 7.18 Newton's third law in generalized interval form.

force and interval position term, but not the kinetic term. Still, the epistemic uncertainty is too large to declare a meaningful approach for the UQ problem. In fact, the pressure UQ problem with constraint on the temperature uncertainty in this case study is a special case of another more general problem, which is a UQ problem with *uncertainty constraint* on related quantities.

The R-MD schemes with the midpoint–radius representation are limited in terms of capability. Specifically, these schemes only capture the uncertainty “at a snapshot” in the time dimension and cannot propagate them with respect to time. In contrast, the R-MD schemes with the lower–upper bound representation can quantify and efficiently propagate the uncertainty along time. In particular, the interval statistical ensemble scheme generalizes the classical MD simulation by first representing all the quantities under the interval representation, and second, propagating them efficiently, as in the traditional MD simulation.

Among the four different computational schemes, the total uncertainty scheme with classical intervals produces the most conservative yet overestimated results, as expected. The total uncertainty scheme with generalized intervals is less conservative and follows more closely with the interval statistical ensemble and other results. The α parameter was set to 0.001 through trials and errors. Reducing this α parameters will also reduce the width of the interval stress. It has also been observed that the uncertainty does not always grow larger during simulation. For the mechanical property prediction, the interval strain–stress curve becomes narrower toward the yield point. In the interval statistical ensemble scheme, the stress uncertainty, however, heavily fluctuates after the yield point. In our opinion, this behavior truly reflects the simulation uncertainty because in the interval statistical ensemble the system dynamics is preserved from the beginning to the end of the simulation. Therefore, the interval statistical ensemble is recommended for the propagating schemes. Regarding the completeness and soundness of the interval statistical ensemble, the interval stress is fairly sound, based on the fact that its estimated range provides at least 50% of the true solution set (Fig. 7.15(a)). Yet, it is not complete and only covers around 50% of the true solutions on average (Fig. 7.15(b)). For nonpropagating schemes, the total uncertainty scheme with classical intervals is recommended, because it demonstrates the worst-case scenario. However, right after the yield point deformation process, it represents almost 60% of the solution set (Fig. 7.15(a)). If one is concerned with the behavior of the stress right after the peak, then the total uncertainty scheme is

suggested. The completeness of the total uncertainty scheme with classical intervals is the highest and uniformly has the value of one, implying that it always covers more than all possibilities.

In general, an accurate estimation of the lower and upper bounds of the potential parameters depends on the first-principles models or experimental data that are used to calibrate them. However, since both computational and experimental data involve uncertainty, overestimation or underestimation is a common problem in UQ. An overestimation or underestimation of the parameters will lead to an overestimation or underestimation in the quantities of interests, respectively. Consider the true uncertain parameter range X , and the overestimated parameter range X^* , where $X \subseteq X^*$. If $f(\cdot)$ represents an MD simulation prediction of the quantities of interest, it is straightforward to verify that $f(X) \subseteq f(X^*)$. It is also true that if $X^* \subseteq X$ in underestimation, then $f(X^*) \subseteq f(X)$.

Note that the R-MD framework is to model a set of imprecise trajectories in the phase space simultaneously in an interval form. At each time step, the imprecise locations and velocities of all atoms are updated based on the ones at the previous time step. The interval-valued atomic positions correspond to the snapshots at one time step. Uncertainty is propagated along time, and the intervals can become wider. The R-MD framework thus is a generalization of classical MD simulation, where a collection of classical trajectories are tracked in the high-dimensional phase space. When the worst-case classical interval scheme is applied, the completeness of uncertainty estimation is ensured. That is, all possible trajectories from uncertain inputs are captured. When the trajectories are sensitively dependent on the interatomic potentials, the uncertainty level is high and the interval range can be wide. When large intervals of atomic positions are involved, uncertainty can propagate quickly along time and the estimated interval bounds for locations at one time step can be as large as the complete simulation cell or domain. If considered cumulatively for all time steps, every atom could visit the whole simulation domain with sufficient simulation time, should the statistical ensemble be ergodic, i.e., every point in phase space is visited given a sufficiently long time. The desired completeness leads to overestimation. Such overestimation problems are common in interval approaches. In order to provide different options, other schemes are also developed to effectively manage the global uncertainty.

Model calibration to find the optimal parameter values of interatomic potentials is an important component in MD simulations. Efficient optimization procedures are needed to search the optimum. Usually surrogate models are needed in optimization because there are no closed-form functions of physical properties. Surrogate-based optimization methods under uncertainty (e.g., Refs. [56,57]) are needed. Such frameworks help determine the best parameters within certain ranges. Interval representation of the surrogate models could be an interesting extension of the current work. It is also noted that interval-based optimization algorithms [58,59] are also available to solve global optimization problems.

Most of the existing UQ studies for MD applications in literature are probabilistic approaches, including Bayesian and frequentist statistics. On one hand, examples of Bayesian approaches, which assign a priori probability and use Bayes' rule to update

as more data are available, include Sethna et al. [12,60], Angelikopoulos et al. [16,61]. On the other hand, the statistical approaches, including polynomial chaos expansion and stochastic collocation, are more widely used based on the Smolyak algorithm [62], which has been applied in MD simulations [17,20]. Different from the above statistical approaches, the interval-based approach extends a real number to an interval to capture the variation ranges due to uncertainty. The interval approach is complementary with other statistical approaches, in the sense that the extension of the probabilistic methods with interval representation is possible with the differentiation of different sources of uncertainty.

One of the most challenging issues in using interval approaches for UQ is the overestimation, which can be partly mitigated by using generalized intervals instead of the classical intervals. However, the issue is not completely resolved. Further extensions are needed and remain as an open question for future research.

7.6 Conclusions

The major source of uncertainty in MD simulation is the imprecision associated with the interatomic potential function. Other approximations and numerical treatments during simulation also introduce additional errors in predictions. Quantifying the input uncertainty and providing error bounds associated with the predicted physical properties are important to maintain the reliability of MD simulation. In this chapter, a novel R-MD framework that quantifies the input uncertainty and performs sensitivity analysis on-the-fly is introduced. The intrusive approach based on generalized interval significantly improves the efficiency of UQ, compared to nonintrusive approaches. This requires the introduction of interval interatomic potential functions. The uncertainty in tabulated EAM potential is captured by analytical forms of error generating functions, whereas interval Lennard-Jones potential is a simple interval extension of the original one.

Four different computational schemes for R-MD simulation have been implemented. The total uncertainty and the lower–upper bound schemes are nonpropagating, whereas the midpoint–radius and the interval statistical ensemble are propagating schemes. For the nonpropagating schemes, at every time step, the uncertainty of the simulated system is estimated, but not carried forward to the next time step. That is, the uncertainty of the output due to the uncertainty of the interatomic potentials is computed at every time step in the nonpropagating schemes. For propagating schemes, the uncertainty of the simulated system is quantified and propagated toward the end of the simulation. The midpoint–radius scheme and total uncertainty scheme utilizes the midpoint–radius representation of intervals, whereas the lower–upper bound scheme and the interval statistical ensemble scheme use the lower–upper bounds to represent intervals. In the nonpropagating schemes, such as lower–upper bounds and total uncertainty schemes, the oscillations of uncertainty are expected. At different time steps in these nonpropagating schemes, the uncertainty of the system is quantified by the interval force, which originally comes from the interatomic potentials

uncertainty. Because the uncertainty does not propagate from the previous time step to the current time step, it fluctuates more heavily compared to that of propagating schemes.

Based on the experimental study, the interval statistical ensemble is recommended for investigating the uncertainty, because it preserves the simulation dynamics to the most extent. If the worst-case scenario is needed, the total uncertainty scheme with classical intervals is recommended. Even though the estimated ranges are overly pessimistic, this scheme can provide the most conservative and reliable estimation. However, the choice of the parameter α itself most requires a sensitivity study such that the overestimation can be controlled to a tolerable level.

The advantage of R-MD is that UQ is accomplished based on only one run of MD simulation. Although the estimated intervals associated with the output quantities do not have the same information or interpretation of confidence intervals in the statistical sense, they provide a quick revelation of how much the output quantities vary as a result of the imprecise interatomic potentials. Such quick evaluation of robustness is important in the materials design and decision-making process, where computational efficiency has a profound impact.

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Sensitivity analysis in kinetic Monte Carlo simulation based on random set sampling

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8.1 Introduction

Kinetic Monte Carlo (KMC) [1,2] is a discrete-event simulation mechanism where a system evolves according to events instead of continuous time. The system is described by a multidimensional state variable or state vector. The change of system states is triggered by a discrete sequence of events. At the atomistic scale, atoms' displacement, diffusion, and bond forming or breaking are examples of events of interest. Correspondingly, the positions of all atoms or the composition of all species form the state variable as an “image” of the system. During the simulation, an event of interest is randomly selected from a set of possible ones listed in a so-called event catalog. The state variable is then updated according to the event. Furthermore, the clock of the system, which keeps track of the physical time, advances based on another random sampling procedure. Therefore, for each iteration of KMC simulation, two random samples are taken. The first random sample is taken to select which event to occur next, whereas the second random sample is to advance the clock. Once the event catalog is updated according to the latest value of state variable, i.e., new possible events are inserted or impossible events are removed at the current state, the system proceeds to the next iteration of simulation.

Note that a different type of Monte Carlo (MC) simulation, which is often referred to as Potts model or Ising model, is different from the above KMC and not considered in this chapter. In the Ising model, a system-level energy as a function of state variable needs to be defined. The simulation process is done through the random sampling of state variable values so that the system energy is minimized. Thus, the Ising model captures only state transitions without modeling the physical time of a system.

In KMC, each event is associated with a kinetic rate constant. The major assumptions of the mathematical model in KMC include (1) the interoccurrence or interarrival time of each type of events is exponentially distributed with its respective kinetic rate and (2) the events are also independent with each other. These assumptions simplify the KMC stochastic simulation algorithm during the sampling process. During the simulation, two random numbers are generated for each iteration. The first random number for event selection, indicating the index of the event to be selected among all possible ones, is sampled according to a uniform distribution based on the kinetic rates. That is, the probability that one event is selected is the ratio of its corresponding

kinetic rate to the sum of all rates for all possible events. Mathematically, among M independent and exponentially distributed random variables T_i 's ($i = 1, \dots, M$) where $T_i \sim \text{Exponential}(a_i)$, the probability that a particular variable T_j is the minimum among all T_i 's can be analytically obtained as the ratio of kinetic rates. That is, it can be easily

verified that $P(T_j = \min\{T_1, \dots, T_M\}) = a_j / \sum_{i=1}^M a_i$. Therefore, the interarrival time

of a particular event is the minimum among several independent events follows a uniform distribution. The second random number for clock advancement, indicating how much time elapses between the current event and next event, is sampled according to an exponential distribution. The parameter or rate of the exponential distribution is the sum of all kinetic rates for all events. It can be easily proved that the minimum value among the above n independent and exponentially distributed random variables T_i 's is a random variable and follows an exponential distribution,

as $\min\{T_1, \dots, T_M\} \sim \text{Exponential}\left(\sum_{i=1}^M a_i\right)$. The earliest time that any event occurs,

among several independent and exponentially distributed interarrival times, also follows an exponential distribution with the sum of all rates as the parameter. As a result of the mathematical simplicity, KMC sampling algorithms elegantly take advantage of the major assumptions of independent exponential distributions associated with events, and thus ensure the computational efficiency.

The assumptions of independent exponential distributions however inevitably introduce model-form and parameter uncertainty in KMC simulations, where model-form uncertainty is associated with the type of probability distributions and parameter uncertainty is related to the parameters of distributions. First, the major underlying property for exponential distributions is the so-called memoryless property. In real physical systems, memory effect or temporal correlation exists in many materials. Time effects associated with aging and energy dissipation cannot be ignored if more accurate models are needed. Second, the independence assumption between events is fairly strong. Spatial correlation in materials such as crowding effect of reactions and coordinated diffusion for long ranges has been observed. Dependency between events is the reality. Third, the kinetic rates associated with events in KMC are typically assumed to be constant. The rates can dynamically change and are dependent on external loads of mechanical force, temperature, reactant density, etc. The simplification of constant rates causes inaccuracy. Fourth, more importantly, there is a lack of perfect knowledge about events. Our knowledge about the event catalog is mostly incomplete. It is likely that there are undiscovered transition or reaction paths corresponding to new events, which are not included in a KMC model. The knowledge about kinetic rates can also be incomplete. Typically these rates are calibrated empirically from experiments or from first-principles calculation. Errors associated with the rate calculation can be propagated during KMC simulation.

MC sampling itself is the most straightforward way to quantify uncertainty. However, the sampling does not capture epistemic uncertainty associated with probability distributions, i.e., the model-form and parameter uncertainty in simulations associated with the type of statistical distributions and their parameters, respectively. Instead, MC

sampling only models aleatory uncertainty, which is due to random variation and perturbation. Various approaches have been developed to incorporate epistemic uncertainty associated with the statistical sampling, such as the Bayesian method [3–5], bootstrap [6,7], and second-order MC [8,9]. Particularly, second-order MC simulation is a general approach and can be applied to assess the parameter uncertainty effect of KMC. It includes a double-loop sampling procedure, where the outer loop samples the input parameter values based on some distributions, and the sampled parameter values are applied to the regular KMC sampling as the inner loop. However, those approaches only quantify the confounded effect of both aleatory and epistemic uncertainty components. The robustness of KMC simulation predictions can be better assessed if the two components can be differentiated.

The effect of input parameter uncertainty associated with incomplete knowledge of event catalog and imprecise kinetic rates can be assessed with sensitivity analysis. With different settings of events and rates for different simulation runs, some predicted quantities of interest can be compared. If some events or rates cause the most significant difference in simulation results, they are regarded as the most sensitive input parameters. In addition to second-order MC, traditional one-factor-at-a-time local sensitivity analysis [10] can be applied here. For each simulation run, one input parameter is changed and others remain the same. Then the simulation results are compared. For instance, kinetic rates are the input parameters of KMC. To assess the sensitivity of the output prediction with respect to a kinetic rate, a different value from the original or nominal one can be applied for a separate KMC simulation run, while other rates remain the original. One-factor-at-a-time local sensitivity analysis however does not reveal the interaction between different input parameters. Alternatively, design of experiments with factorial experiments can be applied for local sensitivity analysis, where interaction between factors can be discovered with analysis of variance. As a further generalization, based on second-order MC simulation, global sensitivity analysis [11] can be applied to study how uncertainty in the output of a KMC model is attributed to different portions of uncertainty associated with model inputs.

In the above local or global sensitivity analysis, multiple runs of simulation are needed to assess the effect of parameter uncertainty. If the simulation is computationally expensive, sensitivity analysis can become a major burden for simulation practitioner. In addition, it is difficult to assess model-form uncertainty due to the assumptions of independent exponential distributions based on traditional sensitivity analysis of event catalogs, because the assumptions form the foundation of KMC sampling. To improve the efficiency of sensitivity analysis for KMC simulation, in this chapter, a new reliable kinetic Monte Carlo (R-KMC) scheme is described, where sensitivity can be assessed within the same run of KMC simulation on-the-fly. The mathematical foundation of the R-KMC simulation is random set sampling. Instead of sampling based on random numbers as in traditional MC sampling, a set of random numbers is sampled simultaneously to model the uncertainty associated with events and rates as the input of KMC. The random set sampling is based on imprecise probability distributions, in contrast to random number sampling based on traditional probability distributions. Based on the random set sampling, a new multievent selection

algorithm is developed, which allows for multiple events being fired so that the uncertainty about which event occurs is incorporated in the simulations. As a result, the clock advancement is also imprecise. The slowest and fastest time is modeled as an interval range, which is kept as the interval time in the system clock. The uncertainty associated with event selection and clock advancement is inherently recorded in the R-KMC model. Interval-valued propensities and probabilities are used as a result of imprecise transition rates. The interval width captures the epistemic portion of uncertainty. Not only the parameter uncertainty associated with the event catalog but also the model-form uncertainty associated with the exponential distribution assumption is also captured by the random set sampling scheme. The lower and upper bounds of the interval probability used in sampling follow two different exponential distributions. All probability distributions, which are not necessarily exponential, are enclosed by the exponential bounds and are considered during the simulation. In addition, a new sampling scheme is further developed to remove the independence assumption, where events in the event catalog can be correlated. This enables us to assess the effect of model-form uncertainty caused by the independence assumption.

The distinct advantages of applying interval probability over traditional probability in KMC simulations are twofold. First, it significantly improves the computational efficiency for sensitivity analysis, in comparison with traditional second-order MC simulation or one-factor-at-a-time local sensitivity analysis. Second, interval probability captures the effects of model-form uncertainty associated with the assumptions of exponential distributions and independence between events.

In the remainder of this chapter, in [Section 8.2](#), the background of interval probability and random set sampling is provided. In [Section 8.3](#), the new R-KMC mechanism, including the multievent selection, interval clock advancement, and event correlation, is described. The underlying mathematical model of R-KMC is also described, which shows that R-KMC is a generalization of KMC. In [Section 8.4](#), three examples are analyzed to demonstrate R-KMC.

8.2 Interval probability and random set sampling

Random set sampling is an efficient approach to predict the separate effects of epistemic and aleatory uncertainty. It is closely related to the concept of interval probability, where a lower bound and an upper bound are used to enclose a set of probability distributions. That is, when the probability measure associated with an event is not precisely known, it can be specified as an interval value $\mathbf{p} = [\underline{p}, \bar{p}]$. The width of the interval probability $[\underline{p}, \bar{p}]$ captures the epistemic uncertainty component. When $\underline{p} = \bar{p}$, the degenerated zero-width interval probability becomes a traditional one, without epistemic uncertainty. Therefore, interval probability can be regarded as a generalization of probability.

Different forms of interval probability have been proposed in the past five decades by researchers in applied mathematics, statistics, and engineering communities. These

different mathematical formalisms and theories are equivalent or similar by nature. The most well-known one is the Dempster–Shafer theory [12,13], where evidence is associated with a power set of discrete random events and quantified with basic probability assignments. The lower and upper bounds of probability are calculated from the basic probability assignments. The theory of coherent lower previsions [14] models uncertainties with the lower and upper previsions following the notations of de Finetti’s subjective probability theory. Probability box (p-box) [15] describes the interval probability $\mathbf{F} = [\underline{F}, \overline{F}]$ in terms of the lower and upper cumulative distribution functions (c.d.f.’s) directly where the nondecreasing functions enclose a set of all possible c.d.f.’s. F-probability [16] represents an interval probability as a set of classical probabilities that maintain the Kolmogorov properties. Generalized interval probability [17] incorporates generalized or directed intervals as probability bounds such that the probabilistic reasoning can be simplified. The interval probability is illustrated by the p-box in Fig. 8.2, where the lower and upper bounds of c.d.fs encapsulate a set of possible probabilities. In general, the lower and upper probabilities $\mathbf{p} = [\underline{p}, \overline{p}]$ themselves belong to the category of so-called nonadditive capacities instead of traditional Kolmogorov probability. Another well-known example of nonadditive capacities is the cumulative prospect theory [18].

Here the Dempster–Shafer theory is first used to introduce interval probability. In classical probability theory, the probabilistic measure is precisely assigned to each of the events in the event space. For instance, if the event space is $\Omega = \{A, B, C\}$, the probability assignments will be $P(A)$, $P(B)$, and $P(C)$, subject to constraint $P(A) + P(B) + P(C) = 1$. In the Dempster–Shafer theory, incertitude and indeterminacy are allowed. Therefore, probabilistic measures are assigned to the power set of events, $2^\Omega = \{\emptyset, \{A\}, \{B\}, \{C\}, \{A, B\}, \{A, C\}, \{B, C\}, \{A, B, C\}\}$. The assignments are called *basic probability assignments* (BPAs), as $m(\emptyset)$, $m(\{A\})$, ..., $m(\{A, B, C\})$, subject to $\sum_{x \in 2^\Omega} m(x) = 1$. That is, because of the imprecision of available information,

we are not required to assign probabilities to individual events precisely. Rather, probabilistic assignments are associated with a set of possible events. The above set of discrete events can also be extended to a set of continuous values as intervals. As a result, the probability that a particular event occurs becomes imprecise and can be enclosed by a lower bound and an upper bound. From the BPAs, the lower and upper probability bounds can be calculated. The lower limit of probability, also known as *belief*, is calculated as $\underline{P}(y) = \sum_{x \subseteq y} m(x)$. The upper limit of probability, also known

as *plausibility*, is calculated as $\overline{P}(y) = \sum_{x \cap y \neq \emptyset} m(x)$.

As an illustration, the calculation of interval probabilities from BPAs of discrete random sets is done as follows. Suppose that the BPAs are $m(\emptyset) = 0.1$, $m(\{A\}) = 0.1$, $m(\{B\}) = 0.1$, $m(\{C\}) = 0$, $m(\{A, B\}) = 0.2$, $m(\{A, C\}) = 0.2$, $m(\{B, C\}) = 0.3$, and $m(\{A, B, C\}) = 0$. The lower probabilities are $\underline{P}(A) = m(\emptyset) + m(\{A\}) = 0.2$, $\underline{P}(B) = m(\emptyset) + m(\{B\}) = 0.2$, and $\underline{P}(C) = m(\emptyset) +$

$m(\{C\}) = 0.1$. The upper probabilities are $\bar{P}(A) = m(\{A\}) + m(\{A, B\}) + m(\{A, C\}) + m(\{A, B, C\}) = 0.5$, $\bar{P}(B) = m(\{B\}) + m(\{A, B\}) + m(\{B, C\}) + m(\{A, B, C\}) = 0.6$, and $\bar{P}(C) = m(\{C\}) + m(\{A, C\}) + m(\{B, C\}) + m(\{A, B, C\}) = 0.5$.

The second example to illustrate the interval probability is using BPAs of continuous intervals. Suppose that BPAs are $m(0 \leq x < 1) = 1/6$, $m(0 \leq x < 2) = 1/6$, $m(1 \leq x < 3) = 1/3$, $m(2 \leq x < 4) = 1/6$, and $m(2 \leq x < 5) = 1/6$. The lower limit of c.d.f. is constructed as $\underline{P}(0 \leq x < 1) = m(0 \leq x < 1) = 1/6$, $\underline{P}(0 \leq x < 2) = m(0 \leq x < 1) + m(0 \leq x < 2) = 1/3$, $\underline{P}(0 \leq x < 3) = m(0 \leq x < 1) + m(0 \leq x < 2) + m(1 \leq x < 3) = 2/3$, $\underline{P}(0 \leq x < 4) = m(0 \leq x < 1) + m(0 \leq x < 2) + m(1 \leq x < 3) + m(2 \leq x < 4) = 5/6$, and $\underline{P}(0 \leq x < 5) = m(0 \leq x < 1) + m(0 \leq x < 2) + m(1 \leq x < 3) + m(2 \leq x < 4) + m(2 \leq x < 5) = 1$. The upper limit of c.d.f. is constructed as $\bar{P}(0 \leq x < 1) = m(0 \leq x < 1) + m(0 \leq x < 2) = 1/3$, $\bar{P}(0 \leq x < 2) = m(0 \leq x < 1) + m(0 \leq x < 2) + m(1 \leq x < 3) = 2/3$, and $\bar{P}(0 \leq x < 3) = \bar{P}(0 \leq x < 4) = \bar{P}(0 \leq x < 5) = m(0 \leq x < 1) + m(0 \leq x < 2) + m(1 \leq x < 3) + m(2 \leq x < 4) + m(2 \leq x < 5) = 1$. The resulting interval c.d.f. is shown in Fig. 8.1, where each of the BPAs can be regarded as a rectangle with the length as the value range of x and the height of BPA value.

The Dempster–Shafer theory helps establish the relationship between interval probabilities and random sets. In other words, random set and interval probability are just two views of the same system. Random set is from the perspective of events in the sampling space, whereas interval probability is from the perspective of probabilistic measure. Imprecision can be modeled as the lower and upper bounds of probability density functions or the bounds of c.d.f.’s as p-boxes. In simulation and sampling, p-box is more convenient because of the inverse transform method. The inverse transform method is a generic approach to generate a random variate when its c.d.f. is known. If the c.d.f. of random variable X is $F(x)$, a sample of X can be generated by first sampling a random number u uniformly between 0 and 1, then calculating $X = F^{-1}(u)$ based on the inverse function of c.d.f.

Among different forms of interval probability, generalized interval probability is based on generalized interval [19,20] in order to improve the algebraic property

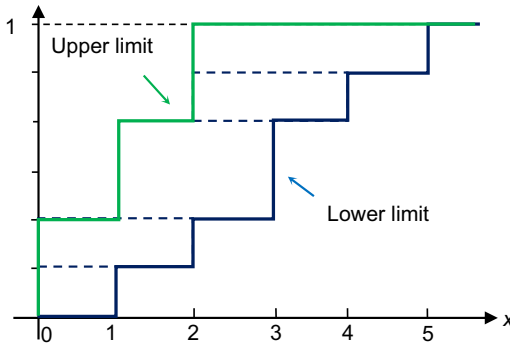


Figure 8.1 An example of interval c.d.f. from BPAs of continuous interval values.

and simplify the interval calculus. Different from classical interval, generalized interval allows the lower limit to be greater than the upper limit. A generalized interval $\mathbf{x} = [\underline{x}, \bar{x}]$ with *lower limit* $\underline{x}$ and *upper limit* $\bar{x}$ is called *proper* if $\underline{x} \leq \bar{x}$, and called *improper* if $\underline{x} \geq \bar{x}$. Kaucher interval arithmetic is defined to calculate generalized intervals. For instance, addition and subtraction of two intervals $[\underline{x}, \bar{x}]$ and $[\underline{y}, \bar{y}]$ are defined as $[\underline{x}, \bar{x}] + [\underline{y}, \bar{y}] = [\underline{x} + \underline{y}, \bar{x} + \bar{y}]$ and $[\underline{x}, \bar{x}] - [\underline{y}, \bar{y}] = [\underline{x} - \bar{y}, \bar{x} - \underline{y}]$, respectively. The width of interval $\mathbf{x} = [\underline{x}, \bar{x}]$ is defined as $\text{width} = |\bar{x} - \underline{x}|$. Particularly, the relationship between proper and improper intervals is established by a *dual* operator, defined as $\text{dual}([\underline{x}, \bar{x}]) = [\bar{x}, \underline{x}]$, which switches the lower and upper limits. We still call $\min(\underline{x}, \bar{x})$ the *lower bound* of the generalized interval, and $\max(\underline{x}, \bar{x})$ the *upper bound*.

The assignment of lower and upper probabilities is not arbitrary and is subject to several consistency constraints. For instance, there is an *avoid sure-loss* constraint, which states that for all possible events in the event space, the sum of all lower bounds of the probabilities should be less than one, and the sum of all upper bounds of the probabilities should be greater than one. In addition, the *coherence between previsions* requires that the sum of the upper probability bound associated with any one of the events and the lower probability bounds associated with all other events in the event space should be less than one. Another important constraint specifically for generalized interval probability is the *logic coherence constraint*, which states that the sum of all lower limits (not lower bounds) for all events is one, and the sum of all upper limits for all events is one. That is, $\sum_{j=1}^M \underline{p}_j = 1$ and $\sum_{j=1}^M \bar{p}_j = 1$ if there are a total of M possible events. It implies that there should be at least one proper probability interval and an improper one for all events in the event space.

Because the lower and upper bounds of c.d.f.'s are used to characterize the epistemic uncertainty, the knowledge about the event corresponding to a probability becomes imprecise. A random set [21,22] thus is associated with a probability measure, and inversely a measure similar to the basic probability assignment in the Dempster–Shafer theory is assigned to a set of events. The study of random set can be traced back to 1940s [23]. If sampling is conducted with the inverse transform method based on the interval c.d.f. in Fig. 8.2, random intervals will be generated. That is, after a random number u generated from a uniform distribution between 0 and 1, u is applied as the input of the inverse lower and upper c.d.f.'s and the random interval $[x_L, x_U]$ can be generated. For discrete cases, the sampling process will generate discrete random sets.

Random set sampling has been applied in stochastic simulations. Batarseh and Wang [24,25] developed an interval-based discrete-event simulation method and applied it to the M/M/1 queuing system. Interval-valued arrival and service times are generated from interval exponential distributions, where a generic parameterization procedure and a robustness measure were also developed. The random interval-based simulation was demonstrated in semiconductor material handling systems

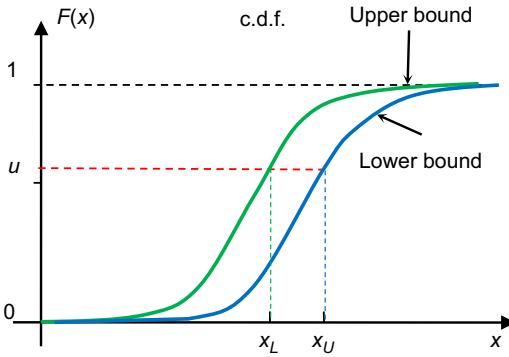


Figure 8.2 Random set sampling based on p-box.

[26]. Batarseh and Dashi [27] further extended it to stochastic Lancaster modeling. Zhang et al. [28,29] sampled interval-valued cross-section areas in structures according to probability box and applied it with interval finite-element analysis to evaluate structural reliability. Galdino [30] developed interval-based random set sampling for discrete-time Markov chains where state transitions are simulated with imprecise probabilities, and further extended to stochastic Petri net simulation [31]. Similarly, M/M/1 queuing systems under input uncertainty can be simulated with Markov chains under imprecise probabilities [32]. Recently, random set sampling was applied in simulating kinetic events of chemical reactions based on probability boxes, as a generalization of the classical KMC stochastic simulation algorithm [33].

8.3 Random set sampling in KMC

Without loss of generality, suppose that a system can be described by an n -dimensional state variable $x(t) = (x_1(t), \dots, x_n(t))$ as a function of time t . The state variable can be the amount of all n species in chemical reactions. It can also be the degrees of freedom or coordinates associated with the locations of all atoms, or the atom types for all n lattice sites in a crystal structure. State transitions can be modeled with a state change vector $\Delta(t) = (\Delta_1(t), \dots, \Delta_n(t))$ such that $x(t + \delta t) = x(t) + \Delta(t)$. For instance, in a simple water electrolysis system with reactions: $2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$, the state variable is formed by the amount of H_2O , H_2 , and O_2 as $(x_{\text{H}_2\text{O}}, x_{\text{H}_2}, x_{\text{O}_2})$. The state change vector for a forward reaction event is $(-2, 2, 1)$, whereas the vector for a reverse reaction is $(2, -2, -1)$. For simplification, the state change vector is assumed to be time independent. For a simple two-dimensional lattice structure with 16 sites, an example value of the state variable is

$$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 2 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

where “1” denotes a Type 1 atom, “2” denotes a Type 2 atom, and “0” denotes a vacancy. Some examples of state change vectors for diffusion events are

$$\begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & +1 & \cdot & \cdot \\ \cdot & -1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}, \begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & +2 & \cdot & \cdot \\ \cdot & \cdot & -2 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \text{ and } \begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & +1 & \cdot \\ \cdot & \cdot & -1 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

In a stochastic system, the value of the system state variable at a particular time is uncertainty and needs to be quantified by the probability, denoted by $P(x)$. The evolution of a stochastic system can be generally modeled by the Chapman–Kolmogorov equation [34,35], where the probability of state variable $P(x)$ evolves. When the epistemic uncertainty associated with the simulation model is incorporated, the probability of state variable is imprecise and becomes $\mathbf{P}(x) = [\underline{P}(x), \overline{P}(x)]$. Notice that the bold font denotes interval-valued functions. It has been shown that the generalized interval probability can be easily incorporated in the Chapman–Kolmogorov equation such that the kinetics of the system evolution can be concisely modeled by the interval-valued master equation [33]

$$\frac{d\mathbf{P}(x(t))}{dt} = \sum_{j=1}^M \mathbf{W}_j(x - \Delta_j) \mathbf{P}(x - \Delta_j) - \text{dual} \sum_{j=1}^M \mathbf{W}_j(x) \mathbf{P}(x) \quad (8.1)$$

as a special case of the generalized Chapman–Kolmogorov equation, where a total of M possible transitions can occur in the system, $\mathbf{W}_j(x)$ is the interval-valued transition probability associated with the j th transition or event ($j = 1, \dots, M$) when the system state is x , a state change vector Δ_j is associated with event j , and operator *dual* switches the lower and upper limits of an interval so that the group property of the generalized interval is maintained [17].

8.3.1 Event selection

The master equation in Eq. (8.1) is an equivalent view of KMC simulation under imprecise transition rates. When the transition rates a_i ’s are precisely known in classical KMC, the probability of the j th transition or event is $W_j = a_j / \sum_{i=1}^M a_i$. When

epistemic uncertainty is associated with transition rate $\mathbf{a}_j = [\underline{a}_j, \bar{a}_j]$, the interval-valued transition probability becomes $\mathbf{W}_j = [\underline{a}_j, \bar{a}_j]/a_0$ where a_0 is calculated as follows:

- (1) Sort all rates $[\underline{a}_1, \bar{a}_1], \dots, [\underline{a}_M, \bar{a}_M]$ based on their interval widths in an ascending order to $[\underline{a}^{(1)}, \bar{a}^{(1)}], \dots, [\underline{a}^{(M)}, \bar{a}^{(M)}]$ such that $[\underline{a}^{(1)}, \bar{a}^{(1)}]$ has the smallest interval, width while $[\underline{a}^{(M)}, \bar{a}^{(M)}]$ has the largest width. That is, $|\bar{a}^{(1)} - \underline{a}^{(1)}| \leq \dots \leq |\bar{a}^{(M)} - \underline{a}^{(M)}|$.
- (2) Calculate $a_0 = \max \left\{ \left(\underline{a}^{(1)} + \bar{a}^{(2)} + \underline{a}^{(3)} + \dots \right), \left(\bar{a}^{(1)} + \underline{a}^{(2)} + \bar{a}^{(3)} + \dots \right) \right\}$. That is, two sums of lower and upper limits of sorted rates in an alternating pattern are calculated. The total rate a_0 is the larger one among the two sums. Here, the summation of intervals $\mathbf{a}^{(j)}$'s with the alternating style is called the *-sum, denoted as $\sum_{1 \leq j \leq M}^* \mathbf{a}^{(j)}$.

This event sorting process is illustrated with the example in Fig. 8.3. The event catalog includes four possible events A, B, C, and D, which are associated with interval rates $[2, 4]$, $[3, 5]$, $[2, 3]$, and $[1, 4]$ respectively. First, the events are sorted based on the widths of the interval rates, as C, A, B, D. Then, the *-summations are performed to construct the imprecise empirical c.d.f., which are $[2, 3]$, $[2, 3] + [4, 2] = [6, 5]$, $[2, 3] + [4, 2] + [3, 5] = [9, 10]$, $[2, 3] + [4, 2] + [3, 5] + [4, 1] = [13, 11]$. As a result, $a_0 = 13$. The empirical c.d.f. is constructed as $\Pr(\{C\}) = [2, 3]/13$, $\Pr(\{C, A\}) = [6, 5]/13$, $\Pr(\{C, A, B\}) = [9, 10]/13$, $\Pr(\{C, A, B, D\}) = [13, 11]/13$. A null event is introduced with the rate $[0, 2]$. The null event does not change the system state. Its only purpose is to make the event space complete so that the interval probability converges to one, as $\Pr(\{C, A, B, D, N\}) = [13, 13]/13 = 1$.

The event selection in R-KMC is based on the following multievent algorithm.

Step 1. Construct the event list from the events with interval-valued rates. Sort the events based on the widths of the intervals in an ascending order.

Step 2. Calculate the *-sum of the sorted interval rates and a_0 .

Step 3. Construct the imprecise empirical c.d.f., which consists of two c.d.fs as lower and upper bounds.

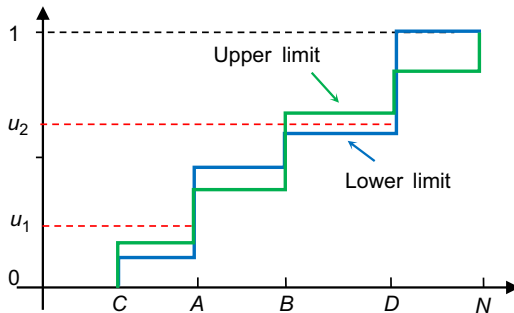


Figure 8.3 An example of imprecise c.d.f. constructed based on “*-sum” of sorted intervals.

Step 4. Generate a random number u and search the index of the event based on the inverse transform method. One or two events may be selected, depending on the value of u as well as the lower and upper c.d.f.'s.

As illustrated in the example in Fig. 8.3, the constructed lower and upper c.d.f.s show the zig-zag pattern. During the event selection process, if random number u_1 is generated, event A will be selected corresponding to the inverse transform method. If random number u_2 is generated, events B and D will be selected simultaneously.

The above event sorting and *-sum procedures are to ensure that the probability of a particular event being selected follows the interval rates. That is, $P(\text{event } j \text{ is elected}) = [a_j/a_0, \bar{a}_j/a_0]$. Mathematically it can be verified that for two proper intervals x and y with $widx \leq widy$, $dualx + y$ is not improper and $wid(dualx + y) \leq widy$. Therefore, the *-sum of the sorted interval rates always leads to the alternating pattern between the lower and upper limits of c.d.f. in Fig. 8.3. Since the probability that an event is randomly selected is proportional to the rate ratio as $[a_j/a_0, \bar{a}_j/a_0]$, the alternating pattern that guarantees the ratio is accurately implemented in sampling.

8.3.2 Clock advancement

In the classical KMC clock advancement scheme, the simulation clock is advanced by the earliest time approach. For each iteration, the clock advances with the earliest possible time among the random variants as the interarrival time between consecutive events, where the random variants are independently and exponentially distributed, as $T_i \sim \text{Expontial}(a_i)$ for $i = 1, \dots, M$. Because $P(T_i \leq \tau) = 1 - \exp(-a_i\tau)$ for $i = 1, \dots, M$, $P(\min(T_1, \dots, T_M) \leq \tau) = 1 - P(\min(T_1, \dots, T_M) > \tau) = 1 - \exp\left(-\left(\sum_{i=1}^M a_i\right)\tau\right)$. That is, the earliest possible time $\min(T_1, \dots, T_M)$ follows an

exponential distribution with rate $\sum_{i=1}^M a_i$. The random variant for clock advancement

is sampled as $-\ln\rho / \left(\sum_{i=1}^M a_i\right)$ with the inverse transform method, where ρ is a random number sampled uniformly between 0 and 1.

In R-KMC, the assumptions of precisely known kinetic rates and independence between events are relaxed. The uncertainty of kinetic rates affects not only event selection but also clock advancement. Two different cases are considered. For the first case, when multiple events are selected as a result of imprecise rates, the clock can be advanced with the assumption that the events are independent. For the second case, when the events are correlated, the clock advancement is not based on the assumption of independent exponential distributions.

8.3.2.1 When events are independent

In the multievent algorithm, multiple events can be chosen and fired for each iteration. How much time is needed for these random events to occur varies and includes both components of epistemic and aleatory uncertainty. To estimate the epistemic uncertainty component, the worst and best scenarios need to be given.

The least time for a set of events to fire is when all of them occur at the same time. Given the assumption of independence between events and the event selection scheme with one or two events fired at a time, the lower bound of the time increment is

$$T_L = -\ln \rho / \left(\sum_{i=1}^M \bar{a}_i \right) \quad (8.2)$$

The longest possible time for a set of events to fire is when the events occur consecutively one by one. Suppose that the respective rates of the firing sequence of n out of N events from a random set are $[\underline{a}^{(1)}, \bar{a}^{(1)}], \dots, [\underline{a}^{(n)}, \bar{a}^{(n)}]$. In the worst-case scenario, the total elapsed time for the sequence of n events is $T^{(n)} = X^{(1)} + X^{(2)} + \dots + X^{(n)}$, where the interarrival times $X^{(1)}, X^{(2)}, \dots, X^{(n)}$ are exponentially distributed with the respective rates of $\underline{\alpha}_0, \underline{\alpha}_1, \dots, \underline{\alpha}_{n-1}$ where

$$\left\{ \begin{array}{l} \underline{\alpha}_0 = \sum_{i=1}^N \underline{a}_i \\ \underline{\alpha}_1 = \sum_{i=1}^N \underline{a}_i - \underline{a}^{(1)} \\ \vdots \\ \underline{\alpha}_{n-1} = \sum_{i=1}^N \underline{a}_i - \sum_{j=1}^{n-1} \underline{a}^{(j)} \end{array} \right. \quad (8.3)$$

The rates are changing because after each event is fired, the earliest time for any of the left events to occur depends on the number of the rest events. The c.d.f. of $T^{(n)}$ is

$$P(T^{(n)} \leq \tau) = 1 - \sum_{j=0}^{n-1} A_j \exp(-\underline{\alpha}_j \tau) \quad (8.4)$$

where $A_j = \prod_{i=0, i \neq j}^{n-1} [\underline{\alpha}_i / (\underline{\alpha}_i - \underline{\alpha}_j)]$. Instead of sampling based on Eq. (8.4), it is easier to sample each of $X^{(j)}$'s as exponential distributions and the sum of the samples will be a sample of $T^{(n)}$. Therefore, the upper bound of time increment is

$$T_U = -\ln \rho / \left(\sum_{j=0}^{n-1} \alpha_j \right) \quad (8.5)$$

where ρ is the same random number as in Eq. (8.2) and α_j 's are defined as in Eq. (8.3).

The clock advancement is to update the current system time $[t_L, t_U]$ to $[t_L + T_L, t_U + T_U]$ by adding the interval time increment $[T_L, T_U]$. The interval time in the simulation clock provides the estimate of the best- and worst-case time so that the speed of the system state change can be tracked. The slowest and fastest times for a system to reach a particular state provides the same information of the possible states when the clock reaches a particular stage.

8.3.2.2 When events are correlated

When the events are correlated, either positively or negatively, the correlation effect needs to be considered in the clock advancement. The traditional sampling method based on the minimum of multiple independent random variables is not valid any more. The new sampling scheme proposed here is based on the copula. A copula is a functional mapping from marginal probability distributions to joint probability distributions, which is a useful analysis tool for random variables that are correlated. That is, the copula of random variables $(X_1, \dots, X_n)$, denoted by C , is defined in such a way that $F(X_1, \dots, X_n) = C(F_1(X_1), \dots, F_n(X_n))$, where F is the joint c.d.f. and F_i 's are the marginal c.d.f.'s of individual random variables.

Instead of directly using copulas, which usually have complex forms, here we perform sampling based on the lower and upper bounds of copulas. The Fréchet–Hoeffding theorem states that any copula $C(\cdot)$ is bounded by a lower bound and an upper bound. The lower bound $C_L(\cdot)$ is

$$\begin{aligned} C(F_1(X_1), \dots, F_n(X_n)) &\geq C_L(F_1(X_1), \dots, F_n(X_n)) \\ &= \max \left\{ 1 - \sum_{i=1}^n (1 - F_i(X_i)), 0 \right\} \end{aligned} \quad (8.6)$$

and the upper bound $C_U(\cdot)$ is

$$C(F_1(X_1), \dots, F_n(X_n)) \leq C_U(F_1(X_1), \dots, F_n(X_n)) = \min\{F_1(X_1), \dots, F_n(X_n)\} \quad (8.7)$$

For the correlated n events, where the interarrival time follows an interval exponential distribution with rate $[\underline{a}_i, \bar{a}_i]$, the copula lower bound is

$$\begin{aligned}
C_L(\cdot) &= \max \left\{ 1 - \sum_{i=1}^n \exp(-[\underline{a}_i, \bar{a}_i]\tau), 0 \right\} = \max \left\{ 1 - \sum_{i=1}^n \exp(-\underline{a}_i\tau), 0 \right\} \\
&\geq \max \{ 1 - n \exp(-\min(\underline{a}_1, \dots, \underline{a}_n)\tau), 0 \}
\end{aligned} \tag{8.8}$$

Similarly, the copula upper bound is

$$\begin{aligned}
C_U(\cdot) &= \min \{ 1 - \exp(-[\underline{a}_1, \bar{a}_1]\tau), \dots, 1 - \exp(-[\underline{a}_n, \bar{a}_n]\tau) \} \\
&\leq 1 - \exp(-\min(\underline{a}_1, \dots, \underline{a}_n)\tau)
\end{aligned} \tag{8.9}$$

Notice that the case of C_U corresponds to the comonotonicity with perfect positive dependence between those n events.

The clock advancement for M events, n out of which are correlated, is thus based on

$$\begin{aligned}
P(\min(T_1, \dots, T_M) \leq \tau) &= 1 - (1 - [C_L, C_U]) \exp \left(- \left(\sum_{j=n+1}^M [\underline{a}_j, \bar{a}_j] \right) \tau \right) \\
&= \left[1 - n \exp \left(- \left(\min(\underline{a}_1, \dots, \underline{a}_n) + \sum_{j=n+1}^M \underline{a}_j \right) \tau \right), 1 \right. \\
&\quad \left. - \exp \left(- \left(\min(\underline{a}_1, \dots, \underline{a}_n) + \sum_{j=n+1}^M \bar{a}_j \right) \tau \right) \right].
\end{aligned}$$

The sampling procedure is to apply the inverse functions of the lower and upper copula bounds to obtain

$$T_L = -\ln \rho / \left(\min(\underline{a}_1, \dots, \underline{a}_n) + \sum_{j=n+1}^M \bar{a}_j \right) \tag{8.10}$$

and

$$T_U = -\ln \rho / \left(n \min(\underline{a}_1, \dots, \underline{a}_n) + \sum_{j=n+1}^M \underline{a}_j \right) \tag{8.11}$$

8.3.3 R-KMC sampling algorithm

The pseudocode of the R-KMC sampling algorithm is listed in [Table 8.1](#). In each iteration, the *-sums are updated first. Then a random number is generated, and the corresponding random set of events is selected based on the lower and upper c.d.fs. The selected set of events are fired, and the lower and upper time increments are generated to update the system clock. The lower and upper bounds of time

Table 8.1 The pseudocode of R-KMC sampling algorithm for each iteration.

```

INPUT: The list of propensity_interval
OUTPUT: The list of events to fire and the interval-valued clock increment
Sort propensity_interval in the ascending order based on the widths of intervals;
// calculate the *sum of interval propensities to build the cumulative distributive function
sum_interval[1]=propensity_interval[1];
FOR i=2: numEvents
    sum_interval[i]=dual(sum_interval[i-1])+propensity_interval[i];
END
sum_interval[numEvents+1]=dual(sum_interval[numEvents])+propensityOfNullEvent;
// sampling a random set of events
Generate a random number u ~ Uniform(0,1);
Fraction=u×sum_interval[numEvents+1]
FOR i=1:numEvents
    Find the smallest i as index_L such that Fraction≤sum_interval[index_L].UBound;
END
FOR i=numEvents: 1
    Find the largest i as index_U such that Fraction≥sum_interval[index_U-1].LBound;
END
Calculate the lower bound of time increment T_L;
Calculate the upper bound of time increment T_U;

RETURN the event set corresponding to propensity_interval[index_L:index_U] and time increment
[T_L, T_U]

```

increment for clock advancement can be estimated based on the different cases in Section 8.3.2. The R-KMC mechanism is implemented in C++ and integrated with SPPARKS [36], which is an open-source KMC toolbox developed at the Sandia National Laboratories. In the input script for R-KMC, events are defined. All events are specified with the lower and upper rates instead of precise values. The correlated events are also specified in the input script. The implementation of R-KMC is available as an open-source tool [37].

In the R-KMC sampling, the probability density function of interarrival time between the *j*th events at the current state *x* is

$$f_j(x, t) = \mathbf{W}_j(x) a_0(x) \exp(-a_0(x)t) = \mathbf{a}_j(x) \exp(-a_0(x)t) \quad (8.12)$$

where $\mathbf{W}_j(x) = \mathbf{a}_j(x)/a_0(x)$ is the interval-valued transition probability in the interval master equation Eq. (8.1). The probabilities converge to the ones in the traditional KMC sampling algorithm when the widths of the interval propensities $\mathbf{a}_j$'s reduce to zeros, as the epistemic uncertainty vanishes.

The R-KMC simulation can be regarded as a generalized Poisson process where the state variable is updated as

$$X(t) = x_0 + \sum_{i=1}^M P_i \left(\int_0^t \mathbf{a}_i(x(\tau)) d\tau \right) \Delta_i \quad (8.13)$$

where $P_i \left(\int_0^t \mathbf{a}_i(x(\tau)) d\tau \right)$ is a generalized Poisson or counting process to fire a random number of events i 's, $\int_0^t \mathbf{a}_i(x(\tau)) d\tau$ is the mean firing rate between time 0 and time t , x_0 is the initial state vector at time 0, Δ_i is the state change vector associated with event i , and $X(t)$ is the state vector as a random interval. The expectation of the state vector is

$$\mathcal{E}[X(t)] = \left[x_0 + \sum_{i=1}^M \Delta_i \int_0^t \underline{a}_i(\tau) d\tau, x_0 + \sum_{i=1}^M \Delta_i \int_0^t \bar{a}_i(\tau) d\tau \right] \quad (8.14)$$

In Ref. [33], it has been shown that R-KMC with interval rates is a generalization of KMC. When the epistemic uncertainty vanishes and the interval rates become real values as $\underline{a}_i = \bar{a}_i$, it is seen that the expected state variable values in R-KMC as shown in Eq. (8.14) are the same as the ones in KMC, and R-KMC converges to traditional KMC. It has also been shown that the interval master equation, as the equivalent probabilistic description of R-KMC simulation, also converges to the classical chemical master equation when interval-valued rates degenerate to real-valued rates. The chemical master equation captures the state evolution in jump processes by probability distributions, which equivalently models the dynamics of KMC simulation in a continuous form.

R-KMC provides an on-the-fly sensitivity analysis approach to assess the robustness of simulation prediction under input uncertainty, without relying on traditional second-order MC simulation for sensitivity assessment. The developed multievent selection and clock advancement algorithms convert imprecise propensities to the imprecise time of reaching a particular state. Therefore, the robustness of R-KMC prediction can be quantified as the *probability of time enclosure*

$$P(\underline{G}(x) \leq G(x) \leq \bar{G}(x)) \quad (8.15)$$

for a particular state x , where random variables $\underline{G}(x)$, $G(x)$, and $\bar{G}(x)$ are the first-passage times that x is reached for the lower-bound, real-valued, and upper-bound scenarios, respectively. All of the three first-passage time variables follow the Erlang distribution with c.d.f.'s as

$$P(G(\cdot) \leq t) = 1 - \sum_{k=0}^{n-1} e^{-a_0 t} (a_0 t)^k / k! \quad (8.16)$$

where n is the number of events to occur by time t .

8.4 Demonstration

Three examples are analyzed to demonstrate R-KMC in this section, including an *Escherichia coli* reaction network, ethanol decomposition on Cu, and a microbial fuel cell (MFC) model.

8.4.1 *Escherichia coli* reaction network

The classical model of the *E. coli* reaction network [38] is shown in Fig. 8.4, where the arrows indicate the reactant–product relationships and the associated real-valued kinetic rate constants are also shown. In R-KMC, the interval rates are used. Different interval ranges are tested in this example to demonstrate the effects of interval rates and random set sampling. Within each iteration, a random set of reaction events are selected according to Section 8.3.1. The interval time advancement is sampled based on the clock advancement described in Section 8.3.2.

In this example, the interval rate constants are generated by varying the original nominal values with $\pm 1\%$, $\pm 10\%$, and $\pm 20\%$. For instance, the rates of the reaction $PLacRNAP \rightarrow TrLacZ1$ at the right-bottom corner of Fig. 8.4 become $[0.99, 1.01]$, $[0.9, 1.1]$, and $[0.8, 1.2]$, respectively, for the three scenarios. At $t = 0$, the initial counts

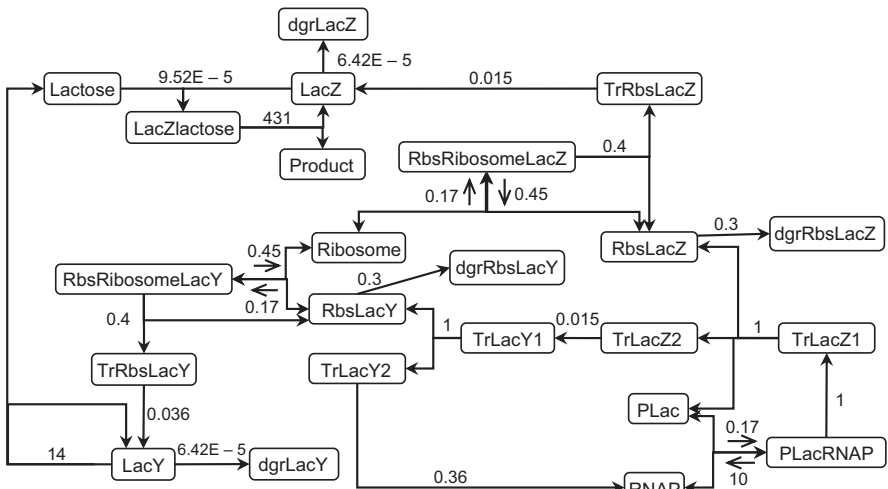


Figure 8.4 The reaction channels of LacZ and LacY proteins in *E. coli* [38].

of species are 1 for PLac, 35 for RNAP, and 350 for Ribosome. All others are zeros. The predicted amounts of *product* and *Ribosome* species are shown in Fig. 8.5, where the predictions along time from the original KMC and R-KMC are plotted. The curves with box markers are the upper bounds, whereas the ones with triangle markers are the lower bounds. The dot lines, solid lines, and long dash dot lines correspond to the interval rates of $\pm 1\%$, $\pm 10\%$, and $\pm 20\%$, respectively. To consider the effect of aleatory uncertainty during sampling, all simulations are run 10 times and the averages are plotted. Here the independence cases are considered and compared with the real-valued one. It is seen that the R-KMC provides the lower and upper bounds of predictions simultaneously. The interval bounds mostly enclose the KMC real-valued predictions when events are assumed to be independent, especially for the wider intervals. Notice that the real-valued, lower bound, and upper bound predictions are all random trajectories in nature as a result of the separate stochastic processes. The interval enclosure thus is not deterministic. For the narrow interval rate with $\pm 1\%$ deviation, the probability of enclosure is low. As the interval rates get wider, the probability of enclosure becomes higher.

The correlation case is also simulated and compared with the independence case, as shown in Fig. 8.6, where the results from the correlation case are plotted with dot lines. Here only the case of minimal correlation is considered, where only the two events selected in the multievent selection algorithm for one step are correlated, and the rest of events are still assumed to be independent. The sampling in the correlated case is based on the copula formulation in Section 8.3.2.2. The lower and upper bounds of predictions for species *product*, *Ribosome*, *Lactose*, and *TrLacZ2* are shown for the minimal correlation and independence cases. The interval rates of $\pm 10\%$ are used. It is seen that when events are correlated, traditional KMC simulation based on the independence assumption is likely to result in biases in predictions. That is, the KMC predictions tend to either under- or overestimate the amounts of species at a given time. The results from R-KMC simulations with interval rates and the independence assumption are also biased. The bias can be easily seen when the amount of species increases or decreases monotonically. When the amount fluctuates along time, such as *TrLacZ2* in Fig. 8.6(d), the bias is not obvious. R-KMC results do not bound real-valued KMC predictions either.

8.4.2 Methanol decomposition on Cu

The second example is the reaction network of methanol decomposition on Cu surface. The purpose is to further study the effect of correlation between events. Cu-based catalysts have attracted attention for methanol decomposition and synthesis as a possible source of energy for the hydrogen economy. Mei et al. [39] searched saddle points on the potential energy surface calculated from first-principles density functional theory and identified the reaction channels and reaction rates of methanol decomposition on Cu(110), which are shown in Fig. 8.7. A total of 26 reactions, with corresponding kinetic rate constants denoted by r_i 's, are identified. The differences between rates are significant. The largest one is $r_{15} = 6.9 \times 10^{11}$, whereas the smallest one is $r_{20} = 2.4 \times 10^{-11}$.

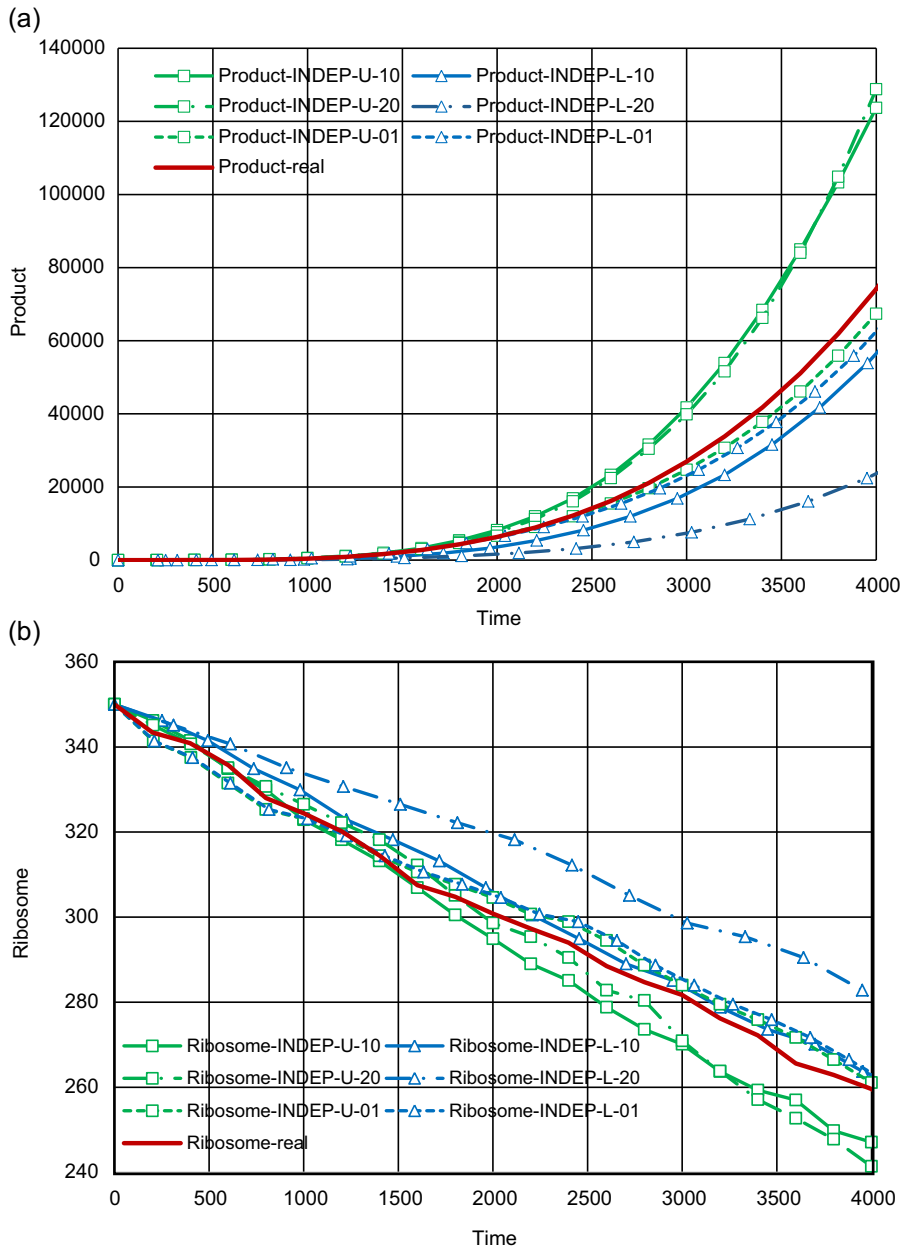


Figure 8.5 Prediction comparisons between the KMC and R-KMC simulations of the *Escherichia coli* reaction network, with interval reaction rates of $\pm 1\%$, $\pm 10\%$, and $\pm 20\%$ corresponding to “01,” “10,” and “20” in the legend, respectively, with the assumption of independence between events. (a) Product; (b) Ribosome.

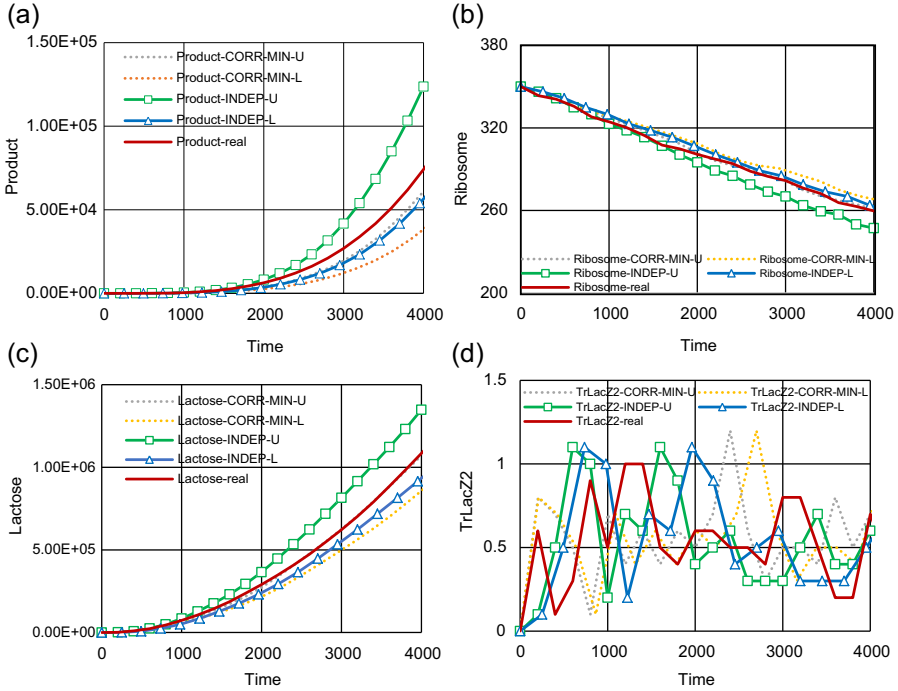


Figure 8.6 Prediction comparisons between the KMC and R-KMC simulations of the *Escherichia coli* reaction network, where the cases of independence and the minimal correlation are shown. “CORR-MIN” in the legend corresponds to the minimal correlation, “INDEP” corresponds to the independence case, and “real” refers to the traditional KMC simulation prediction. All interval reaction rates are $\pm 10\%$. (a) Product; (b) Ribosome; (c) Lactose; (d) TrLacZ2.

The discrepancy between the classical KMC simulation under the independence assumption and the R-KMC simulation with event correlation is revealed. Again, the R-KMC sampling with event correlation is based on the formulation in [Section 8.3.2.2](#). The interval time advancement is based on [Eqs. \(8.10\) and \(8.11\)](#). Several scenarios of correlation are compared. The first one is the minimal correlation, where only two events that are simultaneously selected at one step are correlated. The second scenario is when some of the major decomposition events are correlated, including events with rates r_1 , r_3 , r_5 , and r_7 . The third scenario is that the events with the 10 largest rates are correlated, including r_2 , r_4 , r_6 , r_{10} , r_{12} , r_{15} , r_{18} , r_{19} , r_{21} , and r_{26} . The amounts of four species, CH_3OH , CH_3O , H , and CH_3OH , are shown in [Fig. 8.8](#). The amounts of other species are zeros during simulation. It is seen that the difference between the results of independence and correlation cases becomes more apparent as the extent of correlation increases. The evolution of systems with highly correlated events could be slower than what KMC predicts. Therefore, the error of prediction from KMC could be high when the independence assumption is not valid.

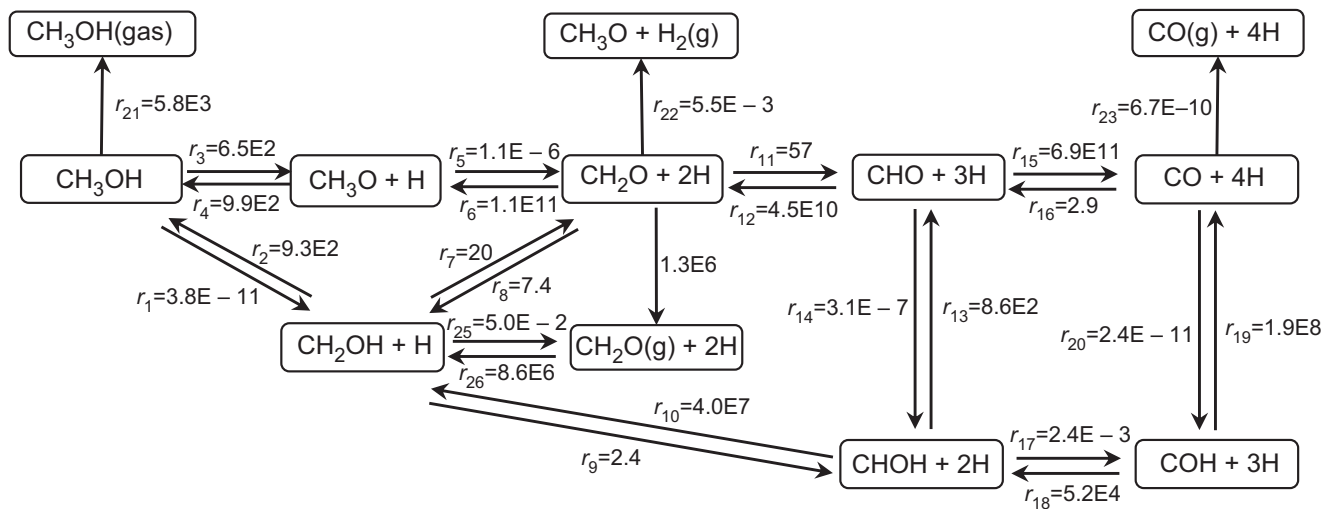


Figure 8.7 The reaction channels of methanol decomposition on Cu(110) [39].

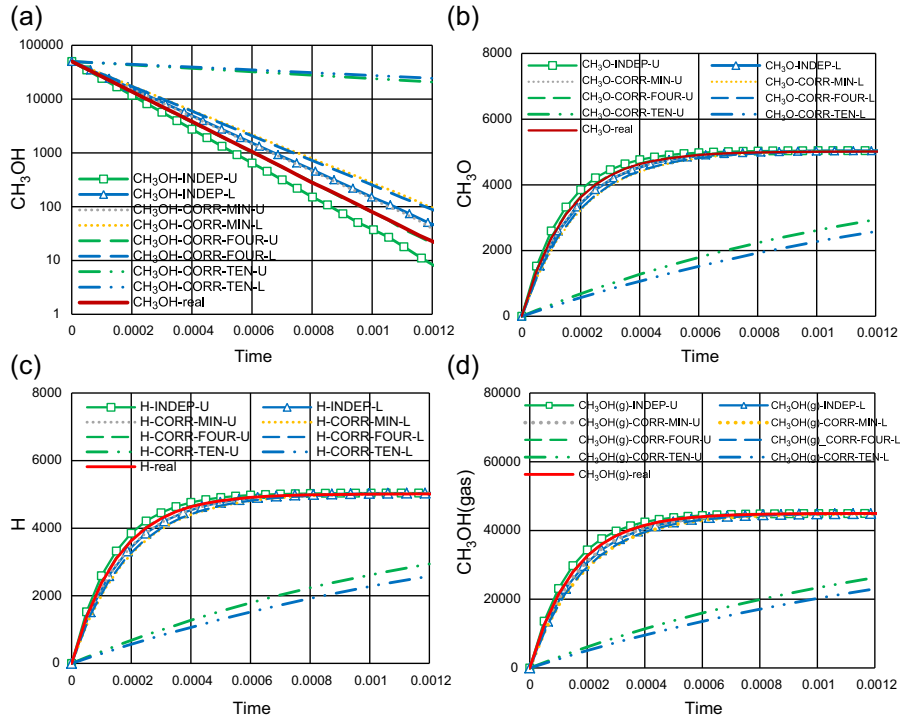


Figure 8.8 The R-KMC simulations of methanol decomposition on Cu(110) with three different scenarios of correlation and the independence case, where “CORR-MIN” in the legend corresponds to the minimal correlation, “CORR-FOUR” to the correlation between four major decomposition events, “CORR-TEN” to the correlation between the 10 largest kinetic rate constants, “INDEP” to the independence case, and “real” to the traditional KMC simulation prediction. All interval rates are $\pm 10\%$. (a) CH_3OH (y-axis is in the $\log_{10}$ scale); (b) CH_3O ; (c) H ; (d) $\text{CH}_3\text{OH}(\text{gas})$.

8.4.3 Microbial fuel cell

The MFC [40] converts the chemical energy contained in organic matter to electricity with the assistance of bacteria, where organic wastes and renewable biomass are used as the energy source. An MFC includes two chambers, an anaerobic anode chamber and an aerobic cathode chamber, which are separated by a proton exchange membrane. Here, a simplified model of MFC reaction networks [41,42] is used to demonstrate R-KMC. The events and rate constants are listed in Table 8.2. There are nine reactions (R1-R9) occurring in the anode chamber, whereas four reactions (R10-R13) are in the cathode chamber. Four example outputs, including the amounts of water, proton at anode side, proton at cathode side, and the power generated, are shown in Fig. 8.9. Six cases are compared, including the traditional KMC predictions, R-KMC

Table 8.2 The reactions of a two-chamber microbial fuel cell used in the R-KMC model.

Number of sites involved	Reaction/transition event	Rate constant
R1: water dissociation	$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$	10^{-1}
R2: carbonic acid dissociation	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$	10^1
R3: acetic acid dissociation	$\text{AcH} \rightarrow \text{Ac}^- + \text{H}^+$	10^1
R4: reduced thionine first dissociation	$\text{MH}_3^+ \rightarrow \text{MH}_2 + \text{H}^+$	10^1
R5: reduced thionine second dissociation	$\text{MH}_4^{2+} \rightarrow \text{MH}_3^+ + \text{H}^+$	10^1
R6: acetate with oxidized mediator	$\text{Ac}^- + \text{MH}^+ + \text{NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{X}_{\text{Ac}} + \text{MH}_3^+ + \text{HCO}_3^- + \text{H}^+$	10^1
R7: oxidation double protonated mediator	$\text{MH}_4^{2+} \rightarrow \text{MH}^+ + 3\text{H}^+ + 2\text{e}^-$	10^1
R8: oxidation single protonated mediator	$\text{MH}_3^+ \rightarrow \text{MH}^+ + 2\text{H}^+ + 2\text{e}^-$	10^1
R9: oxidation neutral mediator	$\text{MH}_2 \rightarrow \text{MH}^+ + \text{H}^+ + 2\text{e}^-$	10^1
R10: proton diffusion through PEM	$\text{H}^+ \rightarrow \text{H}_-^+$	10^{-2}
R11: electron transport from anode to cathode	$\text{e}^- \rightarrow \text{e}_-^-$ (+power)	10^{-2}
R12: reduction of oxygen with current generated	$2\text{H}_-^+ + 1/2\text{O}_{2-} + 2\text{e}_-^- \rightarrow \text{H}_2\text{O}_-$	10^5
R13: reduction of oxygen with current generated	$\text{O}_{2-} + 4\text{e}_-^- + 2\text{H}_2\text{O}_- \rightarrow 4\text{OH}_-^-$	10^3

predictions with interval rates, and the independence assumption, with interval rates and the correlation among the nine reactions at anode side, with interval rates and the correlation among the four reactions at the cathode side, with real-valued rates and correlation at anode side, and with real-valued rates and correlation at cathode side. Strong correlation may exist because of the common environment at the respective anode and cathode chambers. The results show that R-KMC predictions with independence assumption can provide the ranges that enclose the real-valued KMC predictions. There are significant discrepancies between independence cases and correlation cases. Even with the same real-valued rates, simulations with the independence assumption and with the consideration of correlations may give very different predictions. In this example, the independence assumption can introduce large biases if events at the anode side are strongly correlated.

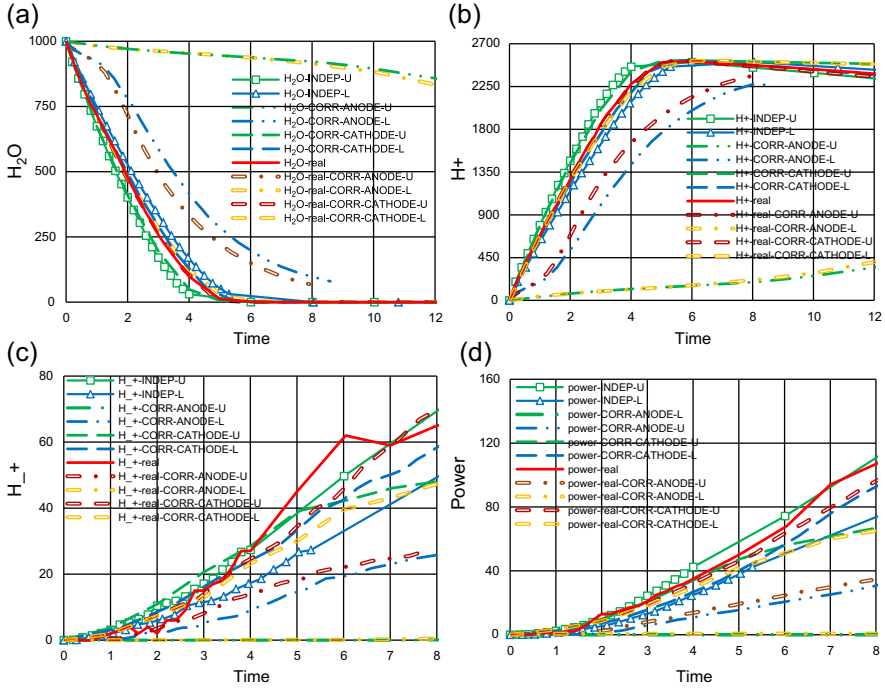


Figure 8.9 Comparisons of the numbers of species over time in the MFC reaction network between the traditional KMC and R-KMC simulations, where the interval reaction rates are $\pm 10\%$. “CORR-ANODE” in the legend corresponds to the cases of correlation at anode side, “CORR-CATHODE” to the correlation between events at cathode side, “INDEP” to the independence case with interval rates, “real” to the traditional KMC, and “real-CORR” to the correlation cases when rates are real values. (a) Water (H_2O); (b) proton (H^+) at anode side; (c) proton (H^+) at cathode side; (d) power generated.

8.5 Summary

In this chapter, we introduce an R-KMC mechanism which can assess the effects of parameter and model-form uncertainty in KMC simulation. The sensitivity analysis is conducted on the fly without relying on traditional second-order MC simulation. The mathematical foundation of R-KMC is random set sampling, where a discrete set of events is sampled in each iteration of simulation. Random set sampling is equivalent to interval probability. The lower and upper bounds of probabilities capture the epistemic uncertainty or imprecision associated with probability distributions, whereas probability distributions themselves represent aleatory uncertainty of MC simulations.

The new R-KMC mechanism simulates systems where multiple possible states can be reached at one step according to a multievent algorithm. Equivalently, the first passage time for a system reaching a particular state is imprecise. The simulation clock thus is kept as an interval which indicates the fastest and slowest pace to reach a state.

It has been demonstrated that the R-KMC sampling converges to traditional KMC sampling when the rates become precisely known as real values. Therefore, random set sampling is a generalization of random number sampling, and R-KMC can be regarded as a generalization of KMC.

Traditional KMC relies on the assumption that events are independent from each other. This assumption was made to simplify the sampling procedure. However, it could lead to major prediction errors. In this work, correlation between events is introduced in the R-KMC simulation. It is seen that the independence assumption results in biased prediction in KMC when events are highly correlated. This on-the-fly sensitivity analysis for correlation quantifies the effect of model-form uncertainty from the independence assumption.

The R-KMC mechanism has been implemented for the chemical reaction simulation. The simulation of other processes such as diffusion will be similar. Events of diffusion are associated with interval rates. The multievent selection algorithm is applied similarly to select events to fire. The interval clock advancement for the scenarios of independence and correlation will also be the same. Similarly, the shortest and longest first-passage time will be sampled and recorded during simulation. Future work will include such implementation for diffusion process simulation. The key element of the proposed R-KMC mechanism is the interval clock advancement. Thus the mechanism is not applicable for Potts or Ising models, where the physical time of system evolution is not simulated. For Ising models, model-form and parameter uncertainty is mainly from the definitions of energy or Hamiltonian functions. Therefore, MC simulations based on such models will be formulated according to the uncertainty associated with Hamiltonian functions. Future work will also include the development of Ising models under uncertainty. The basic principle will be similar to the one in R-KMC, where epistemic and aleatory uncertainty components are differentiated.

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Quantifying the effects of noise on early states of spinodal decomposition: Cahn–Hilliard–Cook equation and energy-based metrics

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9.1 Introduction

While the necessity of random fluctuations in nature is rarely contested, the subsequent inclusion of these processes into classical deterministic models is often neglected. The argument for this has been to omit unnecessary complexity that adds little benefit. However, in some cases the influence of random inhomogeneities cannot be ignored, as certain phenomena may be unobservable in the absence of random processes. Examples include the classic “*escape from a metastable*” state in chemical kinetics and numerous scenarios in the study of phase transitions and critical phenomena [1–4]. We are specifically interested in the Cahn–Hilliard equations that describe a wide variety of phase-separating behavior. Fluctuations (compositional and thermal) are known to play an essential role in precipitating phase separation. The primary ingredient for spinodal decomposition to occur (once inside the spinodal region) is a symmetry-breaking composition fluctuation of sufficient magnitude. Cook [5] asserted that the solely deterministic Cahn–Hilliard model [6,7] may be inadequate at early stages, due to observed discrepancies with experiments. As a result, and in analogy to Brownian motion, Cook proposed a revised formulation with an added stochastic noise term to account for fluctuations, i.e., the Cahn–Hilliard–Cook (CHC) equation (cf. Eq. (9.6) below) [5].

Among the earliest numerical studies of domain coarsening events in spinodal decomposition were performed by Rogers and Elder [8], and Puri and Oono [9], for a conserved order parameter (“Model B” [10]). The authors observed consistent growth in the characteristic length scale ($R(t) \sim t^{1/3}$), confirming the Lifshitz–Slyozov (LS) growth law [8]. They further asserted that noise facilitates faster domain growth in the early and intermediate stages, but had little effect on the late-stage coarsening events.

Since fluctuations are primarily felt at the interface, the authors noted that the interfacial width plays an important role throughout the early and intermediate scales. However, as Glotzer points out, once the characteristic domain size becomes the dominant length scale, perturbations become insignificant to the underlying growth mechanisms [11]. Hence, fluctuations have been consistently reported to have little influence on scaling functions or growth laws [12,13], *which primarily focus on late-stage behavior*. Elder et al. studied the effects of initial (*prequench*) and persistent noise (*postquench*) and found that under weak (or no) continuous noise, the initial condition plays a crucial role in the early time development process [14]. Given a sufficient magnitude, this initial perturbation is enough to initiate phase separation. Based on this assessment, and in light of computational limitations, many authors have chosen to neglect the “Cook” noise term altogether. It has become common practice to simulate these perturbations by including random fluctuations into the initial grid field [11–13,15,16].¹

Alternatively, the above observation makes no mention of boundary conditions or other competing forces. In experiments, a thin film is likely to be asymmetrically quenched due to contact with an interface (e.g., substrate or air). The close proximity to a surface is likely to impose various symmetry-breaking interactions in the form of surface energies, roughness, and temperature gradients [18]. Shortly after the works by Elder et al. [14], several papers exploring the surface interaction on a thin film began to emerge—with and without the presence of noise. Among the first to study this topic is attributed to Ball and Essery [18], which applied temperature gradients at the boundaries in a finite difference scheme to study the effects of quenching from one edge. This led to observable oscillations in the volume fraction emanating from the surface (i.e., surface enrichment layers). Shortly thereafter, Marko [19] conducted a more detailed study (in two and three dimensions) of surface-induced phase separation for varying levels of noise. In that work, a damping effect in the amplitude and depth of penetration in the surface oscillations were reported—indicating a competition between noise and surface energy. This phenomenon was also observed by Glotzer et al. [11] while studying phase separation in the presence of immobile filler particles. In this work, damped composition waves were observed to propagate outward from the particle, in which weaker noise allowed for deeper propagation than that of stronger noise [20]. However, power law scaling, $R(t) \sim t^{1/3}$, was still observed in the presence of noise and surface energy [21]. Hence, while the specific nature of the morphology maintains clear dependencies on the Cook noise term, growth laws remain insensitive, regardless of competing energy sources. Therefore, for studies primarily focused on late-stage scaling properties, fluctuations are often neglected, unless the nature of the study requires so. In addition, the topic of random number generation is often viewed as a major bottleneck [11,16].

In more recent years, there has been a renewed interest in studying the effects of noise on spinodal decomposition. In part, this growth in interest is due to exceedingly more accessible and powerful computational resources and visualization techniques.

¹ Some have included noise at evenly spaced intervals throughout the length of the simulation as well, though this is not as common [17].

This allows investigators to approach the full CHC model from a variety of new perspectives. For instance, Puri et al. [22] used the CHC extension to investigate the effect of heating–cooling cycles in attempts to control structure formation in phase-separating systems [23]. The group also investigated the effect of an initial concentration gradient on presence of surface forces and thermal noise in a thin film. It was found that in some cases the noise broke up the initial concentration gradient and a final equilibrium was reached regardless of initial conditions [24]. Keyes et al. [25] studied several numerical algorithms and methods for solving the CHC equation for large datasets [25]. Hawick studied higher dimensional visualization techniques as well as critical aspects of numerical implementation [26]. In addition to these numerical works, there remains a relatively deep collection of mathematical literature, as the CHC equation provides a model equation for studying existence and solvability associated with the stochastic term. For more information, we refer the interested reader to Refs. [27–30] (and references therein).²

In light of the interest in control of phase-separating systems, we are primarily interested in the *short-term* dynamics of spinodal decomposition. This relatively short regime encompasses the most rapid of changes throughout the morphology evolution (see Fig. 9.1). Here, an influential perturbation may lead to a larger spectrum of solutions and potentially new venues for morphology control. While there exists a rich history of work in the field as a whole, comprehensive numerical studies in this regime remain few, leaving several questions unexplored. Among these include the proper treatment and efficient implementation of the noise term as these are critical to the accurate development of extended models and subsequent morphology tailoring.

Our contributions in this chapter include the following:

1. Massively parallel finite element framework with scalability on the order of 100,000 CPUs,
2. Higher-order backwards difference time scheme and efficient methods for noise implementation,
3. Comprehensive study of the effects of noise via parametric analysis using macroscale energy-based descriptors of morphology, and
4. Identifiable statistical features and behavior in morphology evolution as a function of noise.

This work is organized as follows. In Sections 9.2 and 9.3, we briefly introduce the CHC model and discuss the development of an efficient and scalable finite element formulation. Time discretization and related concerns are addressed therein. Section 9.4 discusses several existing techniques for morphology characterization. In particular, we discuss the formulation and significance of energy-based metrics for characterization. Section 9.5 discusses the numerical aspects of the above-discussed formulation. Specifically, we focus on space–time discretization and noise generation on parallel computing architectures. We also present a brief scalability analysis for the present formulation. Finally, we show the effect of noise on several microstructural features in Section 9.6.

² Beyond *binary* phase separation, ternary and higher-order systems may require noise at differing points throughout the simulation. Depending on the relative component volume fractions (conserved or non-conserved) and resulting domain sizes, noise may maintain critical influence throughout the evolution and lead to widely different structures [31–33].

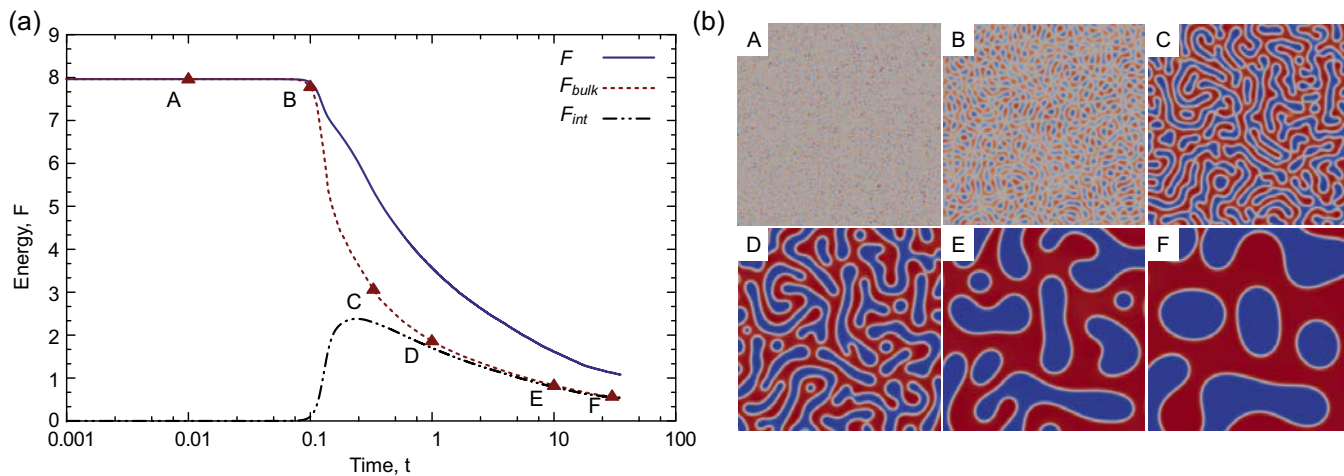


Figure 9.1 A representative morphology evolution depicting rapid phase separation followed by gradual coarsening: (a) Time evolution profiles for the *Total*, *Bulk*, and *Interfacial* free energy components (Eqs. 9.4 and 9.5); (b) Two-dimensional renderings (*top-down*), sampled at several points of interest (from initial distribution (A), through the initiation of phase separation (B), and progression of phase separation (C, D, E), followed by coarsening (F)) throughout the evolution.

9.2 Cahn–Hilliard–Cook model

The CHC model for an immiscible binary blend describes the spatial and temporal dependence of the order parameter (volume fraction) $\phi(\mathbf{x}, t)$ through the mass flux $\mathbf{J}(\mathbf{x}, t)$, as described by the continuity equation:

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{x}, t) + \xi(\mathbf{x}, t) = 0. \quad (9.1)$$

This mass flux is related to the chemical potential, μ , by

$$\mathbf{J}(\mathbf{x}, t) = M \nabla \mu, \quad (9.2)$$

where M denotes the species mobility. We rewrite Eq. (9.1) and subsume the noise term into the flux expression. This enables a simple numerical treatment of noise satisfying constraints arising from the fluctuation–dissipation theorem. The effective mass flux then becomes

$$\mathbf{J}(\mathbf{x}, t) = M \nabla \mu + \mathbf{j}_T(\mathbf{x}, t), \quad (9.3)$$

where the noise term, $\xi(\mathbf{x}, t)$, is related to the noise-induced mass flux, $\mathbf{j}_T(\mathbf{x}, t)$, as $\xi(\mathbf{x}, t) = \nabla \cdot \mathbf{j}_T(\mathbf{x}, t)$. Here, the chemical potential, μ , quantifies free energy changes with respect to volume fraction. The mobility M measures the system's response to chemical potential fluctuations and is generally defined as $M = D\phi(1 - \phi)/k_bT$, in which D is the material diffusivity. For simplicity, however, it is common to remove the order parameter dependence and assume M to be constant.³ For a *binary* system, in a domain $\Omega \in \mathbb{R}^d$, for $d = 2$ or 3 , in which the order parameter is conserved (i.e., $\phi_1 + \phi_2 = 1$), the total system energy may be written as follows:

$$\mathcal{F}[\phi(\mathbf{x})] = \int_{\Omega} \left[f(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] d\Omega. \quad (9.4)$$

This construction consists of two additive components, a *homogenous* free energy and an *interfacial* contribution. The homogeneous free energy of mixing, $f(\phi)$, depends solely on local volume fractions, whereas the remaining interfacial component depends on the composition gradient scaled by an interfacial coefficient, ε^2 .

In this chapter, we assume the free energy of mixing is of the following polynomial form:

$$f(\phi) \simeq \frac{1}{4} \cdot \phi^2 (1 - \phi)^2. \quad (9.5)$$

³ We note that for many physical systems, this may be an inadequate assumption. The species mobility is known to be highly phase dependent—often maximized near interfacial regions and zero elsewhere.

When substituted into Eq. (9.4), we have the widely used Ginzburg–Landau free energy functional. Combining the above equations, we arrive at the CHC equation:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left[M \nabla \left(\frac{\partial f}{\partial \phi} - \epsilon^2 \nabla^2 \phi \right) \right] + \xi(\mathbf{x}, t), \quad (9.6)$$

where $\xi(\mathbf{x}, t) = \nabla \cdot \mathbf{j}_T$. Strictly speaking, this is a fourth-order, nonlinear partial differential equation, in which the final term on the RHS is often referred to as the “Cook” noise term, subject to the following *Fluctuation Dissipation* (FDT) constraints [2,11]:

$$\langle j_T(\mathbf{x}, t)_m \rangle = 0, \quad (9.7)$$

$$\langle j_T(\mathbf{x}, t)_m, j_T(\mathbf{x}', t')_n \rangle = \sigma \cdot \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \delta_{mn}. \quad (9.8)$$

where $\sigma > 0$ characterizes the intensity of the fluctuations, and the subscripts denote the m -th and n -th component of the vector.

The CHC formulation effectively describes how the total energy in Eq. (9.4) dissipates throughout a conserved system. From a physics perspective, the solution space simultaneously captures a rapid phase separation, resulting in the creation of numerous thin boundaries (or interfaces), followed by a very slow coarsening stage in which phase-separated domains gradually evolve toward a steady-state solution. Characteristic solutions are provided in Fig. 9.1(b). Here, figures (A)–(F) provide representative snapshots throughout the morphology evolution—each corresponding to a significant point along the bulk energy profile shown in Fig. 9.1(a). More specifically, points (A) and (B) represent a disordered phase prior to bulk segregation. The short moments thereafter are characterized by significant bulk energy dissipation as component-rich domains rapidly begin to emerge, triggering the creation of boundaries and maximizing the interfacial energy. Then, as the system continues to evolve toward an equilibrium, interfaces slowly diminish and component-rich domains coarsen—resulting in further energy dissipation, now at a much slower rate. This *coarsening* phase is reflected in points (D), (E), and (F) of Fig. 9.1.

Although originally proposed for binary alloys, the Cahn–Hilliard [6,7] and CHC [5] equations have applications in topics ranging from image processing [34], planetary formation [35], and polymer blends [36]. Fig. 9.1 shows representative solutions and energy profiles for a typical evolution.

9.3 Methodology

In previous works, we have primarily focused on the deterministic phase field model and have presented scalable and efficient methodologies for its solution [37]. These efforts have been expanded to include evaporation-induced and substrate-induced phase separation for ternary systems, in which the inclusion of the noise term is essential for phase separation to occur [32]. However, this stochastic addition poses several numerical challenges that will be addressed in the following sections.

9.3.1 Formulation

We consider the split form of the CHC equation, as discussed in Refs. [37,38]. Consider an open domain $\Omega \subset \mathbb{R}^d$ ($n \leq 3$), with a sufficiently smooth boundary $\Gamma = \partial\Omega$. We seek to find $\{\phi, \mu\} : \Omega \times [0, T] \rightarrow \mathbb{R}$, such that

$$\frac{\partial \phi}{\partial t} = \nabla \cdot [M \nabla \mu] + \xi \quad \in \Omega \times [0, T], \quad (9.9)$$

$$\mu = \frac{\partial f}{\partial \phi} - \varepsilon^2 \nabla^2 \phi \quad \in \Omega \times [0, T]. \quad (9.10)$$

Here, the order parameter, ϕ , is the primary quantity of interest and μ is introduced as an auxiliary variable describing the chemical potential. Boundary conditions are represented in Eq. (9.11), which constitute general Neumann boundary conditions (BC_N , assumed to be homogeneous, i.e., $h_\mu = h_\phi = 0$). While this will be a topic of discussion at a later point, we will also consider the use of periodic boundaries (BC_P).

$$(BC_N) \equiv \begin{cases} M \nabla \mu \cdot \mathbf{n} = h_\mu & \text{on } \Gamma_q \times [0, T], \\ M \nabla \phi \cdot \mathbf{n} = h_\phi & \text{on } \Gamma_q \times [0, T], \end{cases} \quad (9.11)$$

$$(BC_P) \equiv \begin{cases} \phi(0) = \phi(L) & \text{on } \Gamma_p \times [0, T], \\ \mu(0) = \mu(L) & \text{on } \Gamma_p \times [0, T]. \end{cases} \quad (9.12)$$

9.3.2 Weak formulation

Next, we introduce the test functions $w \in \mathcal{V} \subset \mathcal{H}^1(\Omega)$ and integrate by parts to derive a weak form of the split CHC equation. Find $\{\phi, \mu\} \in \mathcal{V}(\Omega)$, such that for all $w \in \mathcal{V}(\Omega)$:

$$(w, \phi_t) + (\nabla w, M \nabla \mu) + (\nabla w, \mathbf{j}_T) = (w, h_\mu)_\Gamma, \quad (9.13)$$

$$- (w, \mu) + (w, f'(\phi)) + (\nabla w, \varepsilon^2 \nabla \phi) = (w, h_\phi)_\Gamma. \quad (9.14)$$

Here, $(\cdot, \cdot)$ denotes the L_2 inner product on Ω , h_μ , and h_ϕ define natural boundary conditions. The conserved noise term is now represented by $\mathbf{j}_T$, which is an n -dimensional vector ($n = 2$ or 3) of stochastic flux components representing a Gaussian space–time white noise subject to the above FDT constraints.

9.3.3 Galerkin approximation

To discretize this system with a continuous Galerkin finite element approximation, we let $\mathcal{V}^h \subset \mathcal{V}$, be a finite dimensional subspace spanned by $w^h \in \mathcal{V}^h$. Here we choose

$w^h \in P^1(\Omega_e)$ to be a set of linear basis functions on element Ω_e . We now find $\phi^h, \mu^h \in \mathcal{V}^h \times [0, T]$, such that $\forall w^h \in \mathcal{V}^h$:

$$(w^h, \phi^h_t) + (\nabla w^h, M \nabla \mu^h) + (\nabla w^h, \mathbf{j}_T) = 0, \quad (9.15)$$

$$-(w^h, \mu^h) + (w^h, f'(\phi)) + (\nabla w^h, \varepsilon^2 \nabla \phi^h) = 0. \quad (9.16)$$

Here, the Cook noise term is discretized by generating Gaussian-distributed random numbers for each component of $\mathbf{j}_T$. To ensure these components satisfy FDT constraints and are uncorrelated in time and space, we discretize Eqs. (9.7) and (9.8) in similar fashion to that described by Karma and Rappel [2]:

$$\langle \mathbf{j}_T(\mathbf{x}, t)_m, \mathbf{j}_T(\mathbf{x}', t')_n \rangle = 2Mk_B T \delta_{mn} \frac{\delta(\mathbf{x} - \mathbf{x}')}{W^d} \frac{\delta(t - t')}{\Delta t}. \quad (9.17)$$

In which T is the temperature, M is the mobility, k_B is the Boltzmann constant, δ is the Kronecker delta, and W^d is a spatial scaling parameter described by Karma and Rappel [2]. Here, treating the Cook noise as a numerical flux enables clean integration into established Galerkin formulations and ensures rigorous thermodynamic consistency. In this work, all constant terms in Eq. (9.9) will be described by a single quantity, σ . A detailed investigation of the FDT is provided in Section 9.6.4.

9.3.4 Time scheme

Due to the stiff, nonlinear nature of the CHC equation, explicit time schemes are often difficult to implement with efficiency. Depending on the specific formulation (particularly the free energy selection), such methods may impose severe time step restrictions to maintain numerical stability. For this reason, our previous works have studied several implicit schemes coupled with a nonlinear solver [37]. This approach guarantees stability and grants more flexibility when considering system configurations.⁴ Ideally, we would select a set of implicit schemes that allow for adaptive time strategies—as this is the most desirable way to address the multiscale nature of the CHC equation. However, this remains a relatively unexplored territory for both the CH and CHC equations. Furthermore, the added noise term has time discretization dependencies, as seen in Eq. (9.17), which further complicates most adaptive strategies.

Under these constraints, we formulate an implicit strategy that is conducive for future adaptive measures. Here we have chosen a higher-order, backwards differentiation formulation (BDF). In particular, we employ a third-order scheme, of the form:

⁴ For the CH and CHC equations, commonly used implicit time schemes are that of the Euler Backward (EB) or Crank–Nicholson (CN), coupled with a Newton–Raphson nonlinear solver, see Ref. [37] for more details.

$$u_{n+3} - \frac{18}{11}u_{n+2} + \frac{9}{11}u_{n+1} - \frac{2}{11}u_n = \frac{6}{11}\Delta t F(t_{n+3}, u_{n+3}). \quad (9.18)$$

Selection of this method was based upon an exploration of various time discretization schemes, in which results were consistent across all BDF- n , $n \leq 4$, methods. In addition, this approach offers flexibility for future adaptive schemes, with and without a uniform Δt over the BDF- n range.

9.4 Morphology characterization

Next, we briefly outline our approach toward morphology quantification. In many studies involving spinodal decomposition, a primary focus has generally been placed on the growth kinetics by tracking the structure factor, $S(\mathbf{k}, t)$, throughout the evolution (see Refs. [14,39] for a complete description).

$$S(\mathbf{k}, t) = \left\langle \frac{1}{L^d} \sum_x \sum_{x'} e^{i\mathbf{k} \cdot \mathbf{x}} \left[\phi(\mathbf{x} + \mathbf{x}', t) \phi(\mathbf{x}', t) - \langle \phi \rangle^2 \right] \right\rangle. \quad (9.19)$$

A particularly appealing quality of the structure factor is the fact that it may be obtained numerically and experimentally (via various scattering techniques), which provides a convenient bridge for direct comparison. Hence, in much of the literature, a strong effort has been made to assess the behavior of the structure factor. In both CH and CHC simulations, a *growth law* of $R(t) \sim t^{1/3}$ has been observed, exhibiting a LS trend [14,40]. This observation is often used as justification for neglecting noise in simulations, as the long-term growth behaviors generally remain unchanged. However, as is clear from Figs. 9.1 and 9.2, the CHC model exhibits highly complex spatio-temporal pattern formations throughout the morphology evolution. While the growth laws may be insensitive to noise, the specific nature of these morphologies is directly dependent on the Cook noise term—particularly throughout the early stages. Hence, in order to effectively assess the impact of the noise term (or other forces) and identify distinctive features, other characterization strategies must be considered.

Popular alternative strategies include statistical moments [41], energy-based metrics, homological descriptors (such as the Euler characteristic and Betti number) [39,42], as well as graph-based approaches [43]. In this work, we seek the use of a physically meaningful, macroscale descriptor to assess the kinetics of phase separation in the presence of a stochastic noise term. We therefore perform a thorough *energy-driven* analysis, focusing primarily on changes in the bulk energy (see Fig. 9.1), as this directly correlates to microstructural changes.⁵ Drawing from Eq. (9.4) above,

⁵ The microstructure evolution can be uniquely mapped to the (bulk) energy as pure domains have substantially lower energy than mixed domains. Hence, the effect of noise to create domains of different sizes and purity will be reflected in the evolution of the system energy.

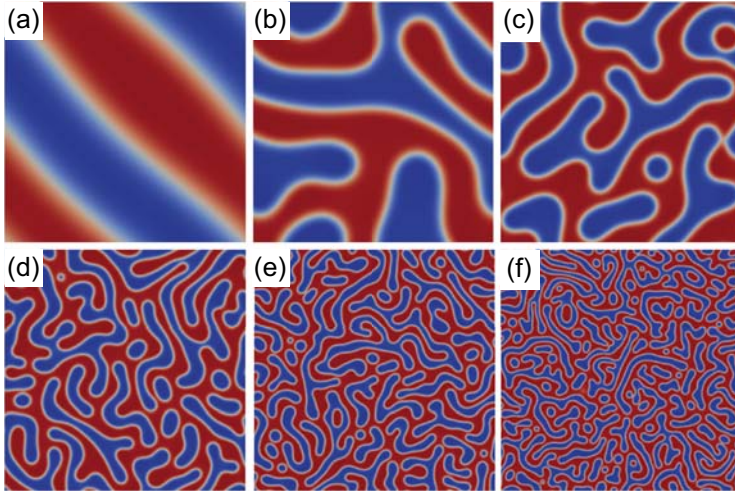


Figure 9.2 Typical CHC solutions showing increasing complexity as computational domain size, L_n , grows. The figures correspond to $n = 1, 3, 5, 10, 20, 30$, respectively, where $L_n = n.L$ (as described in 9.5.1).

we calculate the total system energy as a summation of *homogeneous* and *interfacial* energies, $E_T(t) = E_H(t) + E_I(t)$. In which E_H and E_I are calculated as follows:

$$E_H(t) = \int_{\Omega} f(\phi) d\Omega, \quad (9.20)$$

$$E_I(t) = \int_{\Omega} \frac{\varepsilon^2}{2} |\nabla \phi|^2 d\Omega.$$

9.5 Numerical implementation

Next, we discuss the most critical aspects of numerical implementation, including discretization, computational domain size, parallel noise generation, and scalability.

9.5.1 Spatial discretization

The multiscale nature of our application requires relatively fine resolution throughout the early stages to effectively capture the intricate details of rapid interface creation and subsequent phase separation. For this work, we consider a two-dimensional problem on the unit square: $L = [0, 1] \times [0, 1]$, which is uniformly discretized by approximately $N = \left(1/\sqrt{\varepsilon^2}\right)^2 \approx 30 \times 30$ elements. This selection adheres to the simple *4-elements-per-interface* criteria derived in Ref. [37], which has been shown to be

an efficient discretization to adequately capture both phase separation and coarsening processes. We then explore incremental expansions of this unit domain: $n \cdot L = L_n$ with discretization: $n \cdot N = N_n = \left(n / \sqrt{\varepsilon^2}\right)^2$, for $n = \{1, 3, 5, \dots, 30\}$. However, as observed in Fig. 9.2, as the domain expands, more interesting and complex phenomena are allowed to enter the scope. This has clear implications for our morphology descriptors as well as computational efficiency.

9.5.2 Time discretization

As discussed in Section 9.3.4, we have implemented a third-order BDF scheme with a constant time step. In our application, the selection of this time step is primarily governed by rapid changes throughout the early stages of the evolution—as this is when most of the system energy is dissipated (see Fig. 9.1). Since this regime is also our primary interest, we choose a conservative time step of $\Delta t = 1\text{E}-3$ to ensure all aspects are captured.

9.5.3 Parallel space—time noise generation

To generate the Gaussian-distributed random numbers, as required by Eq. (9.17), we seek a pseudo-random number generation (PRNG) scheme that meets the following requirements:

- Long period with no discernible structure or correlation (*Crush* resistant⁶),
- Low computational overhead (memory and CPU cycles),
- Consistent with domain decomposition scheme, and
- Reproducible results across computing platforms.

Many open-source and proprietary software packages exist that generally meet these requirements. In this work, we have opted to implement the *Sitmo* “C Parallel Random Number Engine” [45]. Designed for very broad usage, this is a multithreaded uniform PRNG based on the *Three-fish cryptographic cipher*. It provides a large periodicity of up to 2^{256} parallel random streams of length 2^{256} each and passes the *BigCrush* test battery. Further, the C++ implementation is fully contained in one header file and seamlessly integrates into our existing framework. Noise generation and conversion to a Gaussian sequence is done with little overhead using the Ratio of Uniforms approach [46].

Proper implementation of this package requires some attention to detail, as we must take a few measures to ensure that our noise generation scheme is physically meaningful and meets the above requirements. Of particular concern is obtaining consistency across decomposed domain boundaries. As part of our parallelization strategy, we partition our mesh into subdomains through the use of parMETIS [47], in conjunction with PETSc [48]. As with many parallel function evaluations, this decomposition

⁶ The “BigCrush” test, or more generally “TestU01,” is an extensive statistical battery for uniform RNGs that was designed to assess quality, period length, and structure of random bit sequences [44].

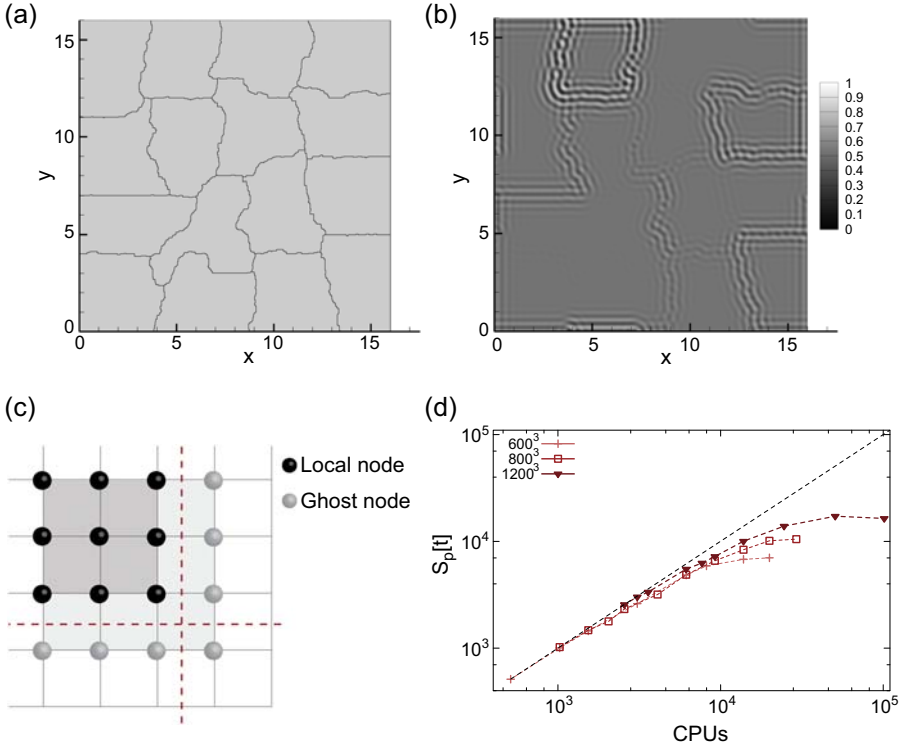


Figure 9.3 (a) Partitioned mesh with 16 subdomains; (b) unphysical results generated by inconsistencies in the overlapping region between decomposed domains (low noise $\sigma = 1\text{E} - 9$); (c) *ghost* nodes description; and (d) relative speed up for large-scale simulations on the Blue Waters supercomputer.

spawns the creation of *ghost* nodes in order to satisfy unknowns that lie on CPU domain boundaries, as seen in Fig. 9.3(b). When solving for system unknowns, these *ghost* values generally converge on the same solution. However, when considering node-based random number generation, these ghost nodes provoke an additional call to the PRNG. To maintain consistency, these boundary values must be synchronized. Conflicting ghost values can cause difficulties for the solver or simply generate nonphysical results, as shown in Fig. 9.3(c). This is particularly true for low levels of noise. To circumvent this issue, we take advantage of the multithreading capabilities of the *Sitmo* PRNG and assign a unique *stream* for each nodal value, with the initial seed directly dependent on the global node ID, $N_{id}^{g\ell}$. Then, for each time step, a random number is pulled from each of these unique streams. Hence, for any given point in time and space, the unique seed may be described as follows:

$$\mathcal{S}_0(\mathbf{x}, t) = f_s \left(f_0, N_{id}^{g\ell} + \varrho_0^d \right) + n_{ts}. \quad (9.21)$$

Here, $f_s : \mathbb{Z} \rightarrow \mathbb{Z}$ is a seeding function that takes an initial value f_0 , and the global node ID, $N_{id}^{s\ell}$, shifted by a factor ϱ_0^d , which depends on the spatial dimension, d . The initial value, f_0 , may be used to produce a nonreproducible stream (e.g., by time of day or process ID) and n_{ts} is the time step number. Since this PRNG has a very large period, this seeding scheme may be generalized to produce several independent, yet reproducible, streams simply by shifting the seeding function:

$$\mathcal{S}_n(\mathbf{x}, t) = f_s\left(f_0, N_{id}^{s\ell} + \varrho_n^d(n_{ts}^{\max})\right) + n_{ts}. \quad (9.22)$$

Now, n is the independent seed number, and ϱ_n^d is the shift that now must take into account $n_{ts}^{\max}$, the maximum number of time steps to ensure no overlap. This approach ensures that ghost values are synchronized without having to communicate any information beyond initialization across processors. This is particularly important for large simulations requiring thousands of processors, as communication can become a major bottleneck. In addition, this approach also provides a complete “noise record” which is critical for any future time strategies.

9.5.4 Scalability analysis

Finally, we briefly detail the numerical implementation and performance. The discretized set of equations described by Eq. (9.13) are solved using an in-house, C++ , finite element library in conjunction with PETSc, a suite of scalable linear algebra routines supported by Argonne National Laboratory [48]. Results are obtained using the generalized minimal residual method with an additive Schwarz preconditioner. This solves the linearized system via Newton’s method, coupled with an iterative Krylov-subspace minimal residual solver.

To gauge the efficiency of this framework, we choose a large three-dimensional problem and perform a scalability analysis, as seen in Fig. 9.3(d). Here, we solved the CHC equation for 10 time steps, using the same PRNG seed. The reference configuration for this study consists of 600^3 elements, or $\sim 432\text{M}$ degrees of freedom (DOF). We also considered configurations of 800^3 and 1200^3 elements, with 1024M and 3456M DOF, respectively. The significance of studying problems of this size is twofold: (a) this shows that our PRNG period is large enough to accommodate nearly $\sim 3.5\text{B}$ DOF and (b) problems of this size require 64-bit integers to handle more than 2^{31} unknowns. These are two primary numerical challenges associated with scaling up simulations to study more realistic systems.

For these tests, T_p denotes the averaged runtime for a single time step on p -processors. The speed up S_p is defined as $S_p = (T_{p_{\min}}/T_p)$, where $p_{\min}$ is the minimum number of processors required to solve the problem. The results in Fig. 9.3(d) indicate that our framework scales sufficiently up to 25k processors, with the ability to scale up to 100k processors before communication becomes a limiting factor.

9.6 Results

Next, we quantify and interpret the effect of thermal noise on the evolving morphology. Choosing a representative system of $\phi_0 = 1 : 1.1$, $\varepsilon^2 = 0.001$, and a noise range of $1\text{E} - 13 \leq \sigma \leq 1\text{E} - 4$, we perform a comprehensive parametric analysis to investigate the influence of the noise term on the CHC solution space. More specifically, through the lens of energy-based descriptors, several critical aspects of proper model development are explored, including domain size and discretization, boundary conditions, and noise implementation. To ensure statistical significance, the results in the following sections were obtained by running over 6400 two-dimensional simulations using five unique PRNG seeds.

9.6.1 Energy-driven analysis and noise effects

Simulations of spinodal decomposition typically focus on three distinct time regimes [11,14]: (I) the *early* stage immediately following a quench, in which composition fluctuations grow exponentially with time; (II) the intermediate or *scaling* regime, in which the average domain size becomes significantly larger than the interfacial width; and (III) the very late stage in which coarsening substantially slows and effectively ceases. Distinctions between these stages are often driven by apparent changes in the aforementioned structure factor (Eq. 9.19). However, in the following sections, we forgo the structure-based analysis in favor of a more simplistic energy-driven approach, which primarily focuses on the transition between stages I and II—an era of critical interest for accurate model development. By simply placing markers at key points along the bulk energy profile and observing how these markers change under varying levels of noise, we have a quantifiable metric that accurately assesses the early-stage kinetics.

Fig. 9.4(a) provides an illustrative example. Here, several energy profiles are provided for varying levels of noise, with markers highlighting specified levels of bulk (or *homogeneous*) energy dissipation ($E_H^{97.5\%}$ refers to a 97.5% decrease in bulk energy, $E_H^{80\%}$ refers to an 80% decrease, etc.). Fig. 9.4(a) also provides a clear depiction of the influence that the thermal noise has on the evolution—particularly throughout the early stages. Markers $E_H^{97.5\%}$, $E_H^{80\%}$, and $E_H^{50\%}$ observe a general shift toward earlier timeframes as the thermal noise increases. Hence, the kinetics of phase separation is accelerated under increasing levels of noise. However, as the bulk system energy dissipates, the noise becomes less influential, as observed by the $E_H^{20\%}$ marker, which sees a convergence of all noise magnitudes. Thus, late-stage coarsening events are indifferent to the noise amplitude—an observation that is consistent with structure factor analysis performed in other studies [14].

To further illustrate the phase separation kinetics in the presence of thermal noise, Fig. 9.4(b) compares the *time* to reach each marker with the imposed noise amplitude. For each incremental increase in noise amplitude, the required time to reach a given marker begins to linearly decrease with a log-linear slope of $\approx 10^{-1.40}$. Here we observe a direct correlation between noise and the phase separation kinetics.

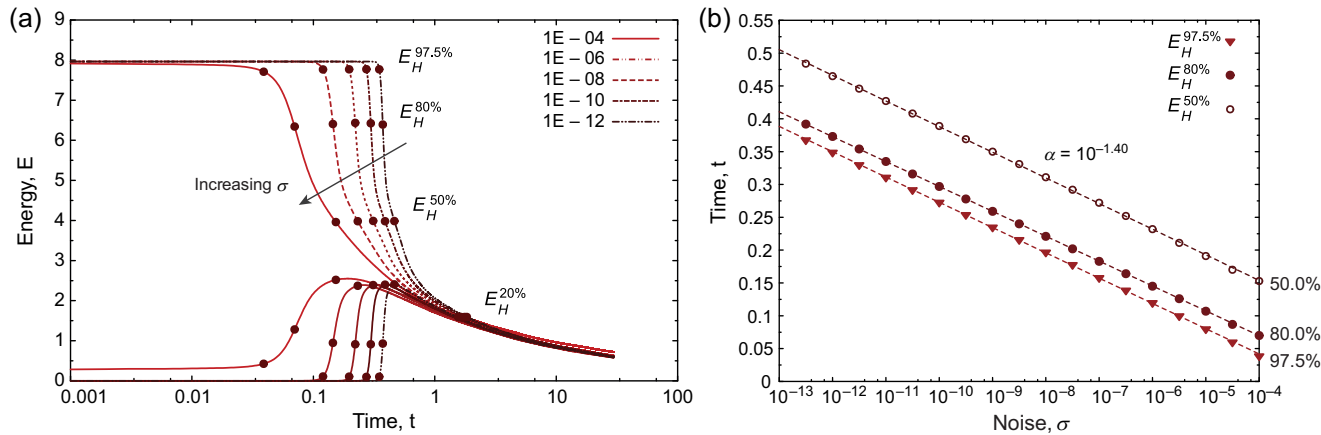


Figure 9.4 (a) Energy profiles for increasing levels of thermal noise: $1E-12 \leq \sigma \leq 1E-4$. (b) Time required to reach 97.5%, 80%, 50% of bulk energy for varying degrees of noise magnitude, σ .

9.6.1.1 Effect of initial noise

Next, we take a brief look at the initial conditions. In the previous case, we applied a uniform initial field of $\phi_0 = 1 : 1.1$. However, in deterministic phase field simulations, it is common to add a small perturbation about the mean value to initiate phase separation: $\phi_0 = 1 : 1.1 \pm \delta \cdot \sigma_0$, where $\delta \in \mathcal{N}(0, 1)$. For this analysis, we introduce a new quantity, τ_x , which represents the *time* to reach the respective level of bulk energy dissipation (τ_{ps} refers to the time to reach phase separation, or $E_H^{97.5\%}$; $\tau_{80\%}$ refers to the time required to reach $E_H^{80\%}$, or 80% bulk energy dissipation, etc.).

Including such perturbations into our analysis and plotting the time to reach each marker, we observe similar scaling behavior, see (Fig. 9.5). Here, we notice a consistent shift between steady initial noise levels, σ_0 , as well as a critical point in which the required time begins to linearly decrease with a similar log—linear slope observed Fig. 9.4(b). This inflection point describes the level of noise required to overcome the effects of the initial perturbation with high consistency. However, as observed in Fig. 9.4(b), this trend begins to deteriorate at later stages, with an increasingly high variability, as observed in Fig. 9.5(d).

9.6.2 Domain size analysis

Next we investigate the significance of increasing the computational domain size, as it relates to varying levels of thermal noise. From Fig. 9.2, it is clear that larger computational domain sizes lead to more intricate and complex microstructures—although this comes with steep costs, requiring considerably more computational resources. Hence, there is often a trade-off. More importantly, however, the effect of the stochastic noise term should be examined at lower resolutions to rule out any finite size effects.

As discussed in Section 9.5, this work explores incremental expansions of the unit square, $L = [0, 1] \times [0, 1]$, which is uniformly discretized, adhering to the 4-elements-per-interface criteria outlined above. Thus, domain size and resolution increase proportionally. For this analysis, we assume periodic boundary conditions (PBCs) and track the time of phase separation, τ_{ps} , to study the effects of varying noise levels ($\sigma = \{1\text{E} - 05, 1\text{E} - 08, 1\text{E} - 11\}$), with increasing grid size. For simplicity, $\mathcal{E}_x$, depicts the number of elements in the x -direction only.

The results from this analysis are shown in Fig. 9.6. Here we observe large inconsistencies for low grid resolutions ($\mathcal{E}_x < \sim 100$), which is followed by a rapid convergence onto a consistent profile thereafter. Moreover, this high initial variability appears to have some noise magnitude dependence, although this trend quickly diminishes for larger grid sizes, as shown in Fig. 9.6(c) which depicts the average spread of the data for various noise magnitudes. Since the quantity of interest here is temporal in nature (time to reach phase separation, τ_{ps}), the driving force behind the kinetics is a chance perturbation(s) that will trigger phase separation. The probability of breaching this “energetic” threshold is potentially higher for larger noise magnitudes at low grid resolutions. For higher grid resolutions, however, the moment when this chance perturbation occurs becomes more predictable.

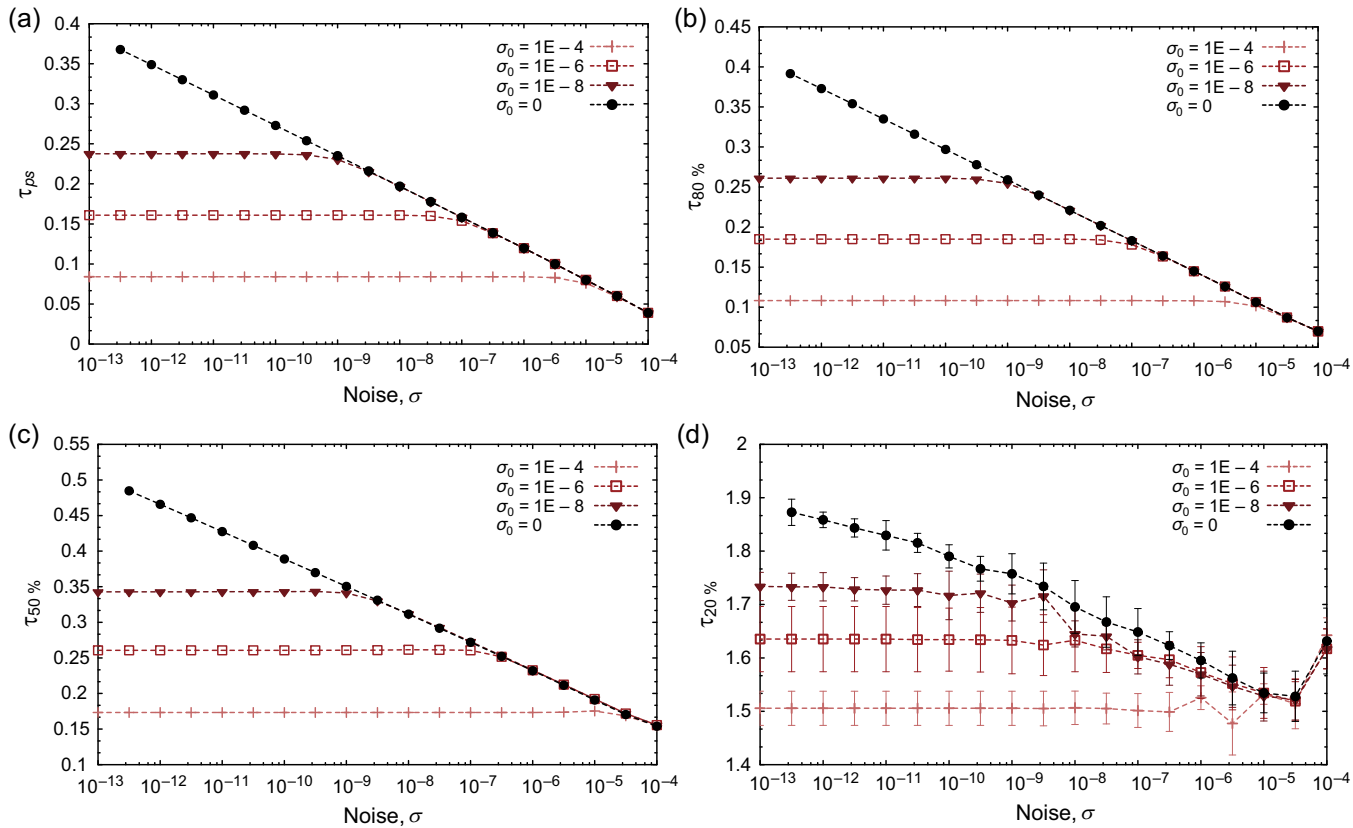


Figure 9.5 Time required to reach respective energy levels, with an initial perturbation applied: (a) 97.5%: time of phase separation (τ_{ps}); (b) 80.0% bulk energy dissipation; (c) 50.0%; and (d) 20.0%. Each figure depicts consistent scaling behavior throughout phase separation, which breaks down during coarsening events.

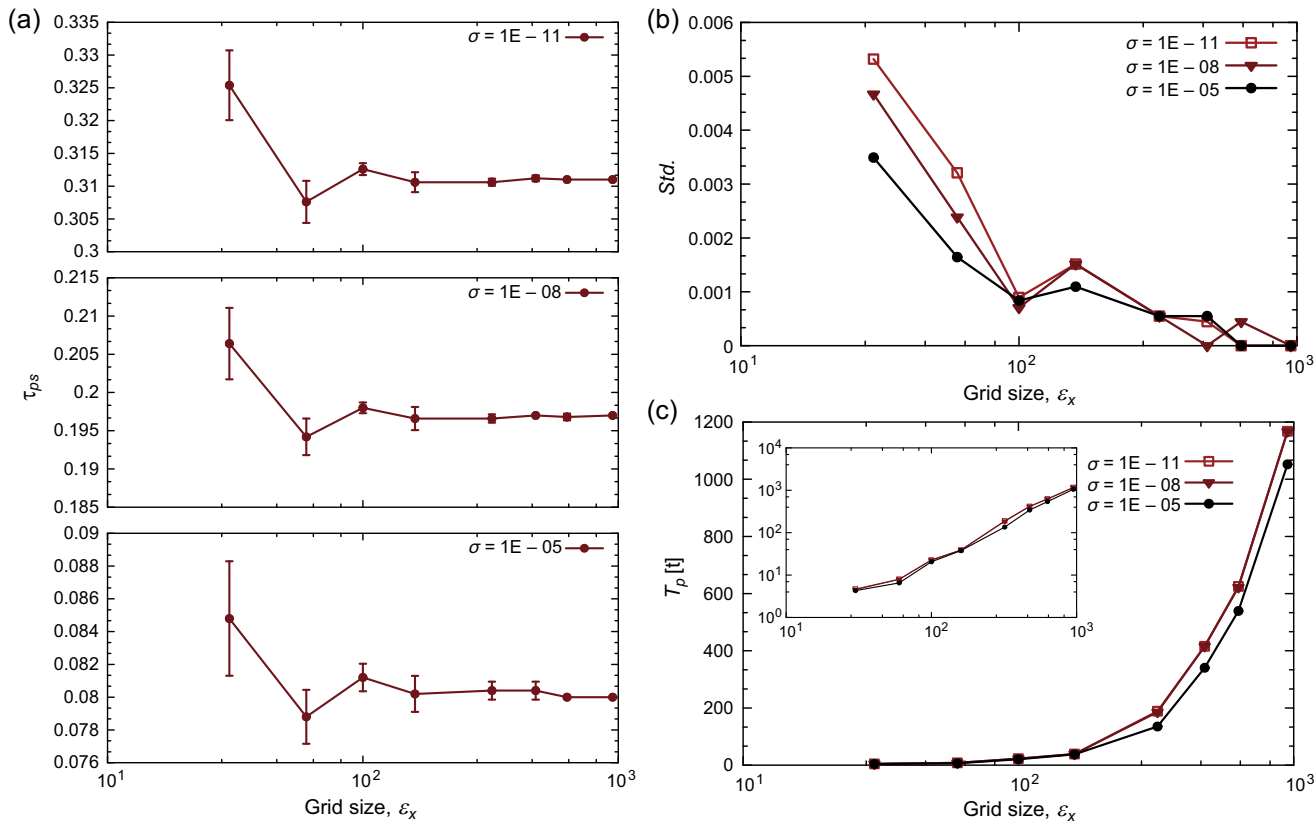


Figure 9.6 Domain size analysis: (a) time of phase separation, τ_{ps} , for high ($\sigma = 1e-05$), medium ($\sigma = 1E-08$), and low ($\sigma = 1E-11$) noise levels; (b) standard deviation with varying noise levels; and (c) total job completion time for increasing problem size (eight processors on a local desktop machine).

From these observations, it is clear that for simulations involving the stochastic noise term a baseline domain size analysis should be performed to avoid finite size effects and make efficient use of computational resources. In Fig. 9.6(d), we plot the total completion time for several noise levels and grid sizes. This provides a quick measure for the computational effort required to solve a typical problem.

9.6.3 Nonperiodic domains

For many intriguing problems, PBCs are not necessarily practical. Many interesting phenomena are often introduced through the boundaries as a source term or simply as a hard surface (e.g., substrate or wall). Therefore, we next consider nonperiodic boundary conditions (nPBCs)—specifically focusing on the Neumann (zero-flux) conditions described by Eq. (9.11).

In previous cases, boundary values were synchronized with corresponding “partners” across computational domain boundaries; this ensures complete continuity (in the noise as well as the order parameter) and effectively extends the computational domain to a semiinfinite medium, ensuring periodicity in all directions. However, with nonperiodic, zero-flux boundaries, no such synchronization takes place and a current-restricting barrier is now introduced at the edge nodes. Due to this lack of continuity at the perimeter, any perturbation propagating through the domain will eventually be obstructed by a zero-flux “barrier.” This disruption can be sufficient to initiate phase separation—although not necessarily at the locations along the perimeter. Furthermore, as the ratio of surface area to volume increases, the boundary elements gain influence over the morphology evolution. Depending on the chosen nature of the boundary, this may significantly affect the solution.

Building on the domain size analysis above, we now examine the time of phase separation, τ_{ps} , and grid resolution, $\mathcal{E}_x$, for nonperiodic boundaries. The results from this analysis are shown in Fig. 9.7. Here we again observe large inconsistencies for low grid resolutions, with large discrepancies between boundary conditions for the time of phase separation, as well as for $\tau_{50\%}$, as shown in Fig. 9.7(a,b). It should be noted, however, that this discrepancy is not unexpected. The higher surface area to volume ratio for smaller domains gives the boundary conditions greater influence, which dissipates accordingly. This discrepancy, however, is only mildly dependent on noise magnitude, as shown in Fig. 9.7(c), in which high and low noise magnitudes are compared (for simplicity, the results have been normalized by the largest grid resolution). Finally, the data variance is compared in Fig. 9.7(d), in which the nonperiodic boundary conditions provide slightly more consistency in the time of phase separation.

9.6.4 Enforcing fluctuation–dissipation

Finally, we investigate the validity of the FDT relation, described by Eqs. (9.7) and (9.8). Not adhering to these requirements may result in a nonphysical residual “drift” in the system. In particular $\langle \xi(\bar{r}, t) \rangle = 0$ may need to be enforced, as described by Hawick [49]. The authors suggest that this FDT requirement may not be inherently satisfied and that the overall mean value may need to be removed to ensure that no unintended

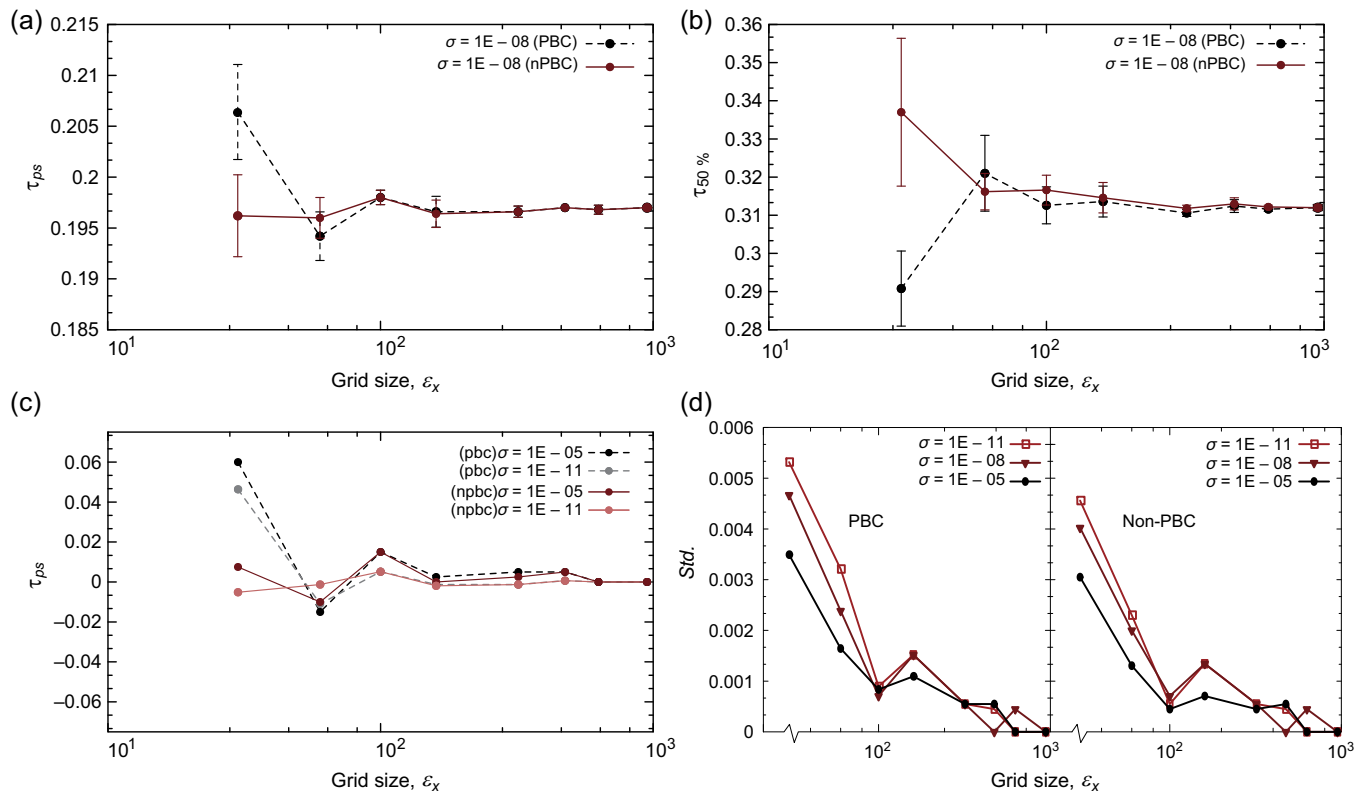


Figure 9.7 Domain size analysis for nonperiodic boundary conditions: (a): Time of phase separation for $\sigma = 1E-08$; (b) Time to reach 50% bulk energy dissipation; (c) Normalized time of phase separation for high and low noise levels; and (d) Standard deviation with varying noise levels.

drift is applied [49]. Clearly, given a sufficiently large grid resolution, a normal distribution with a mean value of zero should be expected in the noise field. However, as discussed in the previous sections, finite geometries are of particular concern and a “sufficiently large” number of points may not be computationally realistic. Therefore, we investigate and gauge when it is appropriate to enforce this relation.

For this analysis, we again examine the time of phase separation, τ_{ps} , and grid resolution, $\mathcal{E}_x$, for both PBC and nPBC conditions. However, for this section, we artificially enforce the above FDT relation, by removing any excess noise. The FDT requirements are enforced as follows:

$$\tilde{\xi}_{i,j} = \xi_{i,j} - \langle \bar{\xi}(\Omega) \rangle, \quad (9.23)$$

where $\langle \bar{\xi}(\Omega) \rangle = 1/n_{\mathcal{E}} \int_{\Omega} \xi \, d\Omega$ is an integrated average over the entire domain. Here, the new noise term, $\tilde{\xi}_{i,j}$, is a random field shifted by the overall residual.

To gauge the effect of this mass current, Fig. 9.8(a) shows the time of phase separation for periodic (PBC) and nonperiodic (nPBC) boundaries for cases in which the average noise has been removed (NR) and has not been removed (nNR).

At this early stage, there is no apparent difference in the energy-based metrics for PBCs, but a slight deviation is observable for nonperiodic boundaries. This minor variation then propagates through to later stages, as observed in Fig. 9.8(b). This trend is relatively consistent for all noise levels (not shown here), but lower magnitudes appear to be more susceptible, as shown in Fig. 9.8(c). While no significant discrepancy between NR and nNR datasets is apparent—particularly at higher grid resolutions—the fact that these values are not *exactly* the same is concerning. Furthermore, Fig. 9.8(d) shows the global average of the noise; and while the values sufficiently converge to zero at high grid resolutions, it is clear that a persistent residual mass current will exist in the system for practical systems.

To visualize this discrepancy, we directly subtract nNR and NR datasets for the order parameter, ϕ , shown in Fig. 9.9(a,b). In the nPBC case, there exists large areas of contrast in close proximity to the boundaries that do not exist in the PBC case. These discrepancies originate at the boundaries and propagate inward until a point of sufficient interface creation. At that moment, the discrepancies mirror the characteristic domain interfaces. This effect is consistent for increasing domain sizes; however, the impact on the energy profile is suppressed due to the increase in volume.

As briefly mentioned in the previous section, the zero-flux “barrier” creates a discontinuity for system perturbations. However, since we are directly subtracting nNR and NR datasets, this effect will not be apparent. In this observation the boundary conditions create an added constraint for the solver on an elemental basis. In conjunction with the random noise, this produces a residual flux in order to meet these constraints. Hence, to properly implement these boundary conditions, an additional term must be added to Eq. (9.7) to counter the created residual flux. While the overall effect of this phenomena is not well recognized by the energy-based metrics, other morphology characterization techniques, such as the Betti number or many graph-based approaches, will be much more sensitive. This has implications for confined geometries and other boundary-based phenomena in the presence of a white noise.

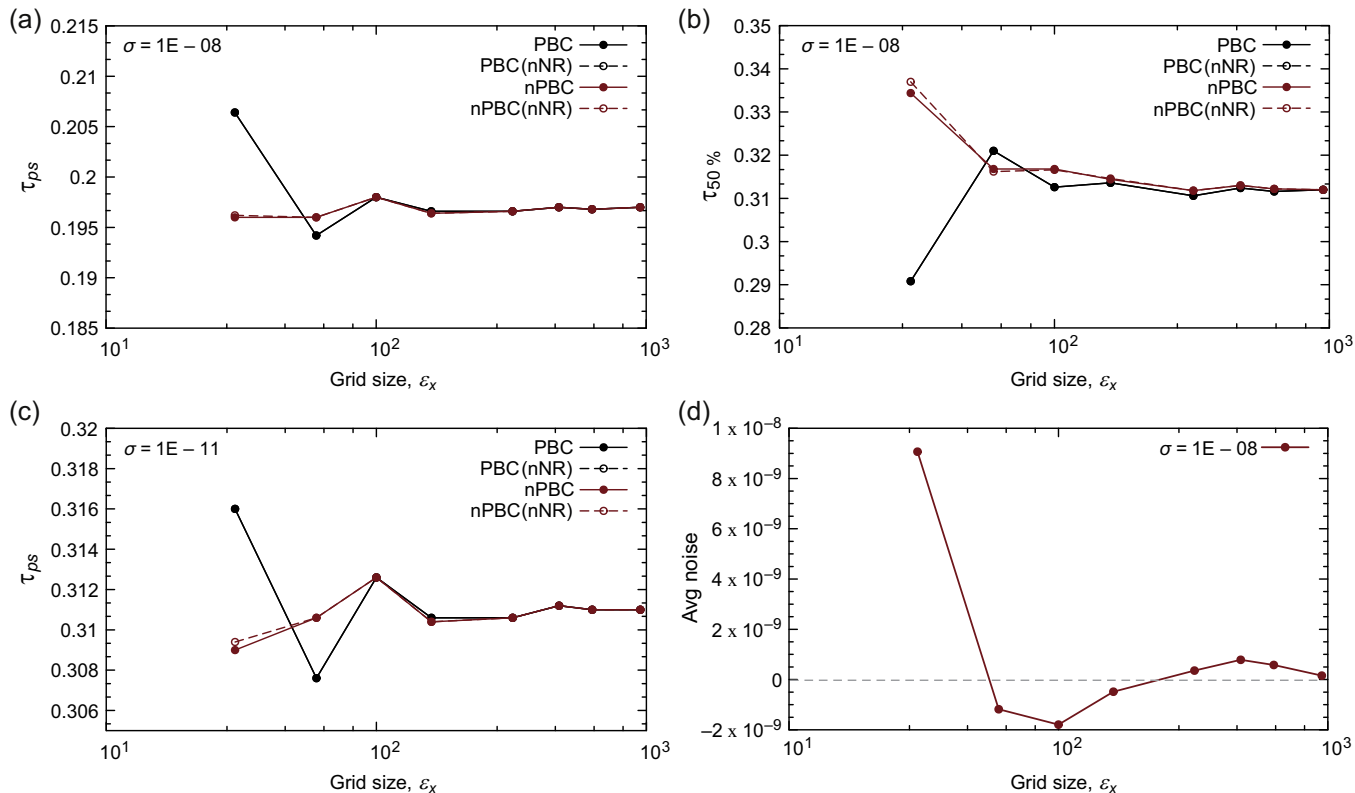


Figure 9.8 Effect of noise removal for periodic (PBC) and nonperiodic (nPBC) boundary conditions; dotted lines indicate no noise removal (nNR) applied: (a) Time of phase separation for $\sigma = 1E-08$; (b) Time to reach 50% bulk energy dissipation, $\tau_{50\%}$, for nNR and NR datasets; (c) Time to reach phase separation for low noise levels, $\sigma = 1e-11$; and (d) Average noise across entire grid field.

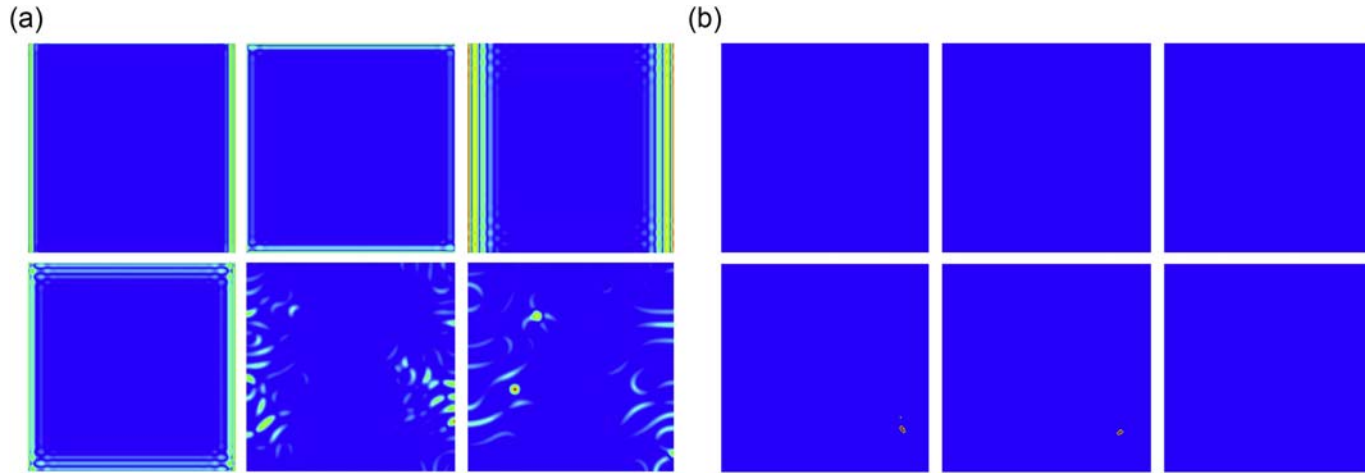


Figure 9.9 Relative difference between NR and nNR morphologies: (a) for nonperiodic boundary conditions and (b) periodic boundary conditions.

9.7 Conclusions

In this work, we analyze the stochastic Cahn–Hilliard system describing phase-separating behavior in material systems. Although noise and fluctuations are necessary for initiating phase separation, traditional treatments often neglected fluctuations due to the ensuing computational simplicity. Neglecting stochastic fluctuations is usually reasonable if one is interested in the late-stage behavior of the system. This is however not a reasonable assumption when one is interested in early-stage behavior. Specifically, in the context of process control to achieve tailored morphologies, it has been shown that early-stage control of morphologies may be important [50,51]. It thus becomes important to characterize the effect of noise on the dynamics of phase separation. In this work, we propose energy-based metrics that help in quantifying the effect of noise on initiation and propagation of phase separation. We show that this metric works particularly well for characterizing early-stage behavior, especially since standard metrics like structure factor are known to be insensitive to noise. We also address several numerical issues that arise with a massively parallel implementations of the CHC model. Often, such implementations of stochastic PDEs suffer from scalability and inconsistent (nonoverlapping) treatment of the noise term across processors. To this end, we show scalability of this implementation on the NCSA Blue Waters supercomputer up to $\sim 10,000$ CPUs. We additionally suggest a simple approach to visualize if the noise implementation is consistent across processor boundaries. Finally, we discuss enforcing the fluctuation–dissipation theorem during numerical discretization of the noise. Using this fast, scalable framework, we performed an exhaustive parametric analysis of the effect of various levels of initial noise, space–time noise, spatial discretization, and the effect of boundary conditions (periodic vs. Neumann) on the evolution pathway. The effect of these phenomena was characterized in the early stage of phase separation using energy-based metrics.

Implications, limitations, and future work: This study provides insights into the effect of noise on early-stage control of morphology evolution. This is especially promising for soft materials [50,52–54], where multistage processing [50,51,55] can be used to effectively control the evolution pathway that the system takes. Additionally, this study provides one approach to investigate the sensitivity of the morphology pathway on space–time noise, thus establishing the relative utility of different processing avenues. Limitations of the current study include two simplifying assumptions that are made: (a) that the mobility is constant, instead of the more physically meaningful degenerate mobility [56] and (b) that the free energy takes a polynomial form, instead of the more physically representative Flory–Huggins form.

Future work could be along several avenues. One avenue is to extend the approach to account for correlated or pink noise. This is naturally possible to do via methods like the Karhunen–Loève expansion or its variants [57]. A second avenue is to leverage GPU-based parallelization to solve the CHC set of equations. GPU-based approaches are especially promising when used in conjunction with higher-order basis functions. In a third possible avenue, one could develop consistent numerical schemes to treat the noise term under spatial and temporal adaptivity. Adaptive discretization is a very

commonly used numerical technique to intelligently deploy computational resources. The presence of the noise term complicates such treatment of the CHC equation, especially when the space–time noise terms have to satisfy the fluctuation–dissipation theorem. This is a very promising area for additional research. Yet another avenue would be to utilize promising developments in generative models (variational encoders and adversarial networks) to reduce the computational effort needed to simulate these morphologies [58]. Such techniques are very promising due to their ability to account for noise as well as their computational speed (for inference after training).

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Uncertainty quantification of mesoscale models of porous uranium dioxide

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10.1 Introduction

Mesoscale modeling and simulation provides a powerful means of bridging from atomic scale simulations to the engineering scale. One example of such work is the development of advanced materials models for reactor fuel performance codes [1], in which the development of the necessary evolution models and structure property relationships is accelerated by using lower length-scale modeling and simulation. First-principles methods are used to determine single crystal and point defect properties [2–4]; molecular dynamics (MD) simulations are used to determine the properties of linear and planar defects, how properties change with temperature, and the properties governing behaviors that occur over time [5–7]; mesoscale simulations (modeling material behavior at length scales ranging from 100 nm to 100 microns) are used to investigate microstructure evolution and the impact of microstructure on various material properties [8–17]. The MARMOT tool has been developed for such mesoscale simulations [18], coupling the phase field method, used to predict evolution of the microstructure, with heat conduction and solid mechanics, to include the impact of stress and temperature and to determine effective thermal and mechanical properties. While the development of these new models is far from complete, preliminary results are promising [13].

The safety requirements for nuclear reactors are extremely high; therefore, it is very important to carefully validate reactor simulations and to understand the impact of uncertainty on their predictions. While uncertainty quantification (UQ) methods have been applied to tools to model the entire reactor for many years [19–22], they have only been applied to fuel performance codes more recently [23–25]. In the new microstructure-based approach to materials models for reactor fuel, UQ becomes even more important due to the use of lower length-scale simulations to assist in the development of the materials models [1], as these simulations also introduce uncertainty that must be quantified. This requires both UQ and rigorous validation against experimental data. Indeed, UQ has been called out as a major concern that must be addressed in all forms of multiscale modeling [26]. Many of the existing UQ methods have been developed for deterministic models that solve differential equations, which

are not directly applicable to first-principles methods or MD [27], but can be applied to many mesoscale approaches. While some such work has been carried out in the nuclear materials area [28], much more is needed.

In this chapter, we present three case studies of the application of UQ on three mesoscale modeling efforts that are being used to develop microstructure-based materials models for the macroscale fuel performance tool BISON [29]. Each is focused on a different behavior of porous UO_2 grain growth simulations to determine the evolution of the average grain size with time, mesoscale heat conduction simulations to determine the relationship between the thermal conductivity and the fuel microstructure, and fracture simulations to determine the relationship between the fracture stress and the fuel microstructure. We begin with a general introduction to standard UQ methods and demonstrate how they are applied to the mesoscale simulations and the mechanistic materials models. We then focus individually on the three simulation areas.

10.2 Applying UQ at the mesoscale

The purpose of UQ is to quantify the impact of uncertainty on the predictions of a simulation, including uncertainty in the values of input parameters, uncertainty in the form of the model, and numerical error. In essence, UQ considers the fact that, due to uncertainty, simulation predictions are not deterministic but rather are stochastic and can be characterized by a distribution rather than a single deterministic value. The goal of UQ is to accurately propagate uncertainty through the simulation and to quantify the distribution of the resultant prediction. Uncertainty can be broadly separated into two categories: aleatoric uncertainty, which results from inherent randomness and can be described by a probability distribution, and epistemic uncertainty, which results from incorrect or incomplete understanding of the system being modeled and cannot be described by a distribution [30]. Aleatoric uncertainty is easier to include in UQ methods, but both types of uncertainty can and should be considered. While UQ has been well developed and widely applied to some engineering fields, such as computational fluid dynamics, it has only rarely been applied to nuclear materials simulation [25,28].

In this work, we apply standard UQ methods to mesoscale MARMOT simulations of UO_2 behavior and to mechanistic microstructure evolution models that have been informed by the mesoscale simulations. Standard UQ methods can be readily applied to the mechanistic models, as they predict a single scalar value. However, applying UQ to the mesoscale simulations is more difficult because they spatially resolve the microstructure of the material, meaning that they predict variable fields that vary throughout the spatial domain. Quantifying the uncertainty of a variable field can be difficult, as is visualizing that uncertainty. While there are typically scalar values of interest that we extract from the spatial variable field, such as an average or homogenized value, for which we can quantify the uncertainty, there is not typically a unique relationship between the variable fields and the scalar value. Thus, UQ should be applied to the unique variable field whenever possible. However, for the case studies in this work, we will only characterize the uncertainty of scalar values of interest, and we will leave quantifying the uncertainty of the variable fields as future work.

UQ is carried out in this work using the open source Dakota toolkit [31]. There are various approaches for carrying out UQ on the predictions of existing codes. The approaches that are easiest to implement involve using an external code or toolbox that uses Monte Carlo (MC) methods and repeatedly runs the existing code using different input parameters. Specific parameter values that correctly represent the parameter's uncertainty are typically selected by the UQ tool and the various results are also collected and analyzed by the tool. Various tools exist for such use [32,33]. One widely used tool is Dakota, which is developed by Sandia National Laboratory. Dakota is a robust, useable software for optimization and UQ that enables design exploration, model calibration, risk analysis, and quantification of margins and uncertainty with existing codes. It also provides a flexible and extensible interface between existing codes and its iterative systems analysis methods. The user determines which methods from Dakota they will employ, defines a distribution for each input parameter, and creates a script that Dakota uses to run the code. Dakota then repeatedly runs the code and quantifies the final uncertainty. Various manuals and tutorials are available on the Dakota website: <https://dakota.sandia.gov/>.

Three separate analyses were carried out for each simulation or model: sensitivity estimation for each uncertain parameter, calculation of the mean and standard deviation using a linear approximation with the sensitivities, and a full MC UQ analysis.

Sensitivity analysis is the study of the relative impact of each parameter on a value of interest computed by a model or simulation [34]. There are various approaches available for sensitivity analysis, varying in computational expense, difficulty to implement, consideration of correlated inputs, and their handling of nonlinearity. In this work, we use the local sensitivity, which is the partial derivative of the value of interest (represented by the function f) with respect to one of the input parameters c_i ,

$$S_{c_i}^f = \frac{\partial f}{\partial c_i}. \quad (10.1)$$

The local sensitivity is a simple means of estimating the relative impact of a parameter at a single point, but does not consider correlated inputs or nonlinearity. The local sensitivity is typically calculated using the mean value of all the input parameters. The sensitivities can be calculated exactly for an analytical model by taking partial derivatives of the equations, but for a simulation the sensitivities must be estimated. There are various methods available for such estimation [35], but in this work we sample a single parameter from a normal distribution using Latin Hypercube sampling (LHS) [36] and then determine the sensitivity from the slope of a linear fit to the value of interest. It is often useful to compare sensitivities, to determine which parameters have the largest impact on a given result. Each sensitivity has different units and cannot be directly compared; however, they can be normalized for comparison. In this work, normalized sensitivities are calculated according to

$$\tilde{S}_{c_i}^f = \frac{\bar{c}_i}{f} \frac{\partial f}{\partial c_i}, \quad (10.2)$$

where $\bar{x}$ denotes the mean values of x .

The uncertainty in the calculated value f can be estimated using the mean $\bar{f}$ and the standard deviation σ_f . The mean is determined by evaluating the model or simulation using the mean value for all input parameter values. σ_f can be estimated using the sensitivity values according to

$$\sigma_f = \sqrt{\sum_i S_{c_i}^2 \sigma_{c_i}^2}. \quad (10.3)$$

However, this equation assumes that the model is a linear function of each input parameter and that there is no significant covariance between the various parameters. These assumptions are rarely correct, so this approach can be inaccurate.

A more accurate, but much more computationally expensive, approach to UQ is the MC approach. When using MC for UQ, the function is evaluated many times (can require tens to hundreds of thousands of evaluations for accurate distribution estimation [37]), with input parameter values sampled from their corresponding distribution. For large simulations, using a sufficient number evaluations is typically cost prohibitive. When a reduced number is used, the distribution will not be accurately determined and will typically underestimate the uncertainty. These costs can be reduced using approaches such as importance sampling [38], control variates [39], or multilevel MC [40]. It is also possible to construct surrogate models and conduct UQ on those [41], and Dakota has tools for creating such surrogates. The Dakota toolkit was used in this work to carry out the MC UQ analysis of the MARMOT simulations. The parameter sampling is done using LHS and we assume a normal distribution for all parameters.

10.3 Grain growth

10.3.1 Introduction

The average grain size of fresh fuel pellets is typically around 10 microns. However, during reactor operation, a large temperature gradient forms in the fuel pellets, with the temperature at the outer radius (where the radius is about 0.5 cm) being around 800K and the centerline temperature reaching as high as 1600–1800K. The high center temperatures are high enough to allow grain boundary (GB) migration to occur, resulting in grain growth. Thus, the average grain size increases with time in the hotter regions of the fuel. Many of the other behaviors in the fuel are directly impacted by the grain size, including fission gas release, fracture, and creep. Thus, the average grain size is an important microstructure variable in the microstructure-based materials models for fuel performance codes. Currently, only empirical models of the change of the average grain size are available for UO_2 [42]. Thus, a mechanistic model is needed; however, the model must also include the impact of porosity on the grain growth, as they will impede GB migration.

Before a mechanistic grain growth model could be developed, a better understanding was needed with regard to how GB migration is impacted by various conditions

within the fuel during reactor operation, including fission gas bubbles. Mesoscale simulations of grain growth in UO_2 were conducted using a quantitative phase field model [43] in MARMOT. The rate of grain growth is impacted by the GB mobility and the magnitude of all driving forces. The GB energy provides a driving force for grain growth that is always present. MARMOT grain growth simulations discovered that the temperature gradient found in LWR fuel pellets is not sufficient to provide an additional significant driving force for grain growth [9]. Fission gas bubbles and second-phase particles provide an additional force that resists the driving force, slowing grain growth. MARMOT simulations that coupled grain growth with bubble behavior were used to quantify this resistive force [17,44].

10.3.2 Model summaries

The phase field grain growth model implemented in MARMOT is taken from Moelans et al. [43]. An example 2D simulation domain is shown in Fig. 10.1.

This is a fully quantitative model that assumes isotropic GB properties, such that the only material properties needed in the model are the average GB mobility M_{GB} and the average GB energy γ_{GB} . The GB mobility is a function of temperature according to

$$M_{\text{GB}} = M_0 e^{\frac{-Q}{k_b T}}, \quad (10.4)$$

where M_0 is the mobility prefactor, Q is the activation energy, k_b is the Boltzmann constant, and T is the temperature. The model is solved using the finite element method with implicit time integration.

The mechanistic grain growth model that has been developed to predict the change in the average grain size of the fuel over time is based on theory that the velocity of a GB v_{GB} can be approximated as

$$v_{\text{GB}} = M_{\text{GB}}(P_d - P_r), \quad (10.5)$$

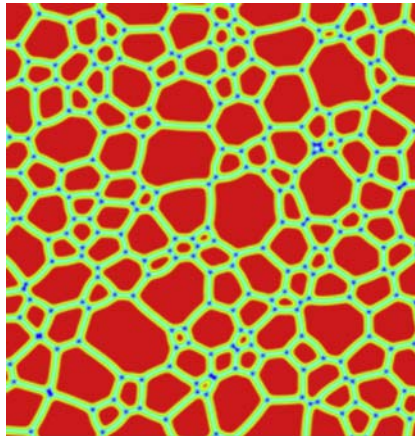


Figure 10.1 Mesoscale simulation of grain growth domain, where the red regions are the grains, the green are the GBs, and the blue are the triple junctions.

where M_{GB} is the GB mobility, P_d is the sum of all significant driving force, and P_r is the sum of all resistive pressures. Note that if $P_r > P_d$, the value of $(P_d - P_r)$ is set to zero. We assume, with some input from mesoscale simulations [9], that the only significant driving force is the GB energy, such that

$$P_d = \frac{\gamma_{GB}}{R}, \quad (10.6)$$

where γ_{GB} is the GB energy and R is the radius of curvature of the GB. The resistive pressure of second-phase particles can be defined using models adapted from Zener pinning theory [13]; however, such models are not appropriate for bubbles at elevated temperatures, as the GBs are never fully pinned and drag the bubbles along. When dealing with bubbles, an effective mobility M_{eff} can be used that includes the effects of the GB and bubble mobilities rather than a resistive pressure P_r . If we consider a polycrystal with an average grain size D , we can assume a linear relationship with the average GB curvature to obtain

$$\bar{D} = \sqrt{\alpha} \bar{R} \quad (10.7)$$

where α is a shape parameter that is assumed to be constant with time during normal grain growth. The change in the average grain size with time can be defined according to

$$\dot{\bar{D}} = \sqrt{\alpha} \dot{\bar{R}} \quad (10.8)$$

$$= \sqrt{\alpha} M_{eff} \frac{\gamma_{GB}}{\bar{R}} \quad (10.9)$$

$$= \alpha M_{eff} \frac{\gamma_{GB}}{\bar{D}}. \quad (10.10)$$

Thus, given the initial average grain size $\bar{D}_0$, the grain size can be predicted at a given time t by integrating Eq. (10.10). This integral must be done numerically, since the M_{eff} will be changing with time as the fission gas bubbles evolve. However, in this case study, we assume that there is no porosity, such that $M_{eff} = M_{GB}$. Thus, we can integrate Eq. (10.10) to obtain

$$\bar{D}^2 - \bar{D}_0^2 = 2\alpha M_{GB} \gamma_{GB} t, \quad (10.11)$$

where t is the time.

The range of the GB energy of UO_2 is 1.04–1.86 J/m² at room temperature according to MD calculations using the Basak potential [45]. However, the GB energy decreases rapidly with temperature. The GB energy at high temperature has been measured [46–48] between 1200 and 1800K. These data were fit with a linear relationship to give the equation

$$\gamma_{GB} = -0.000728T + 1.657 \quad (10.12)$$

where T is temperature. According to this expression at 1700K $\gamma_{GB} = 0.419$ J/m².

For our UQ analysis, we need to know the uncertainty of the GB energy in terms of each distribution due to various sources such as measurement error, variability between samples, and variability in experimental conditions. However, as is common in older data like these, none of this information is reported or available [46–48] and no newer data GB energy is available. Twelve experimental data points and four points from MD are available, each at different temperatures and slightly different stoichiometry. With this limited amount of data, only a rough approximation of the distribution is possible. Therefore, we assume a normal distribution. The standard deviation of the fit from Eq. (10.12) is assumed to be independent of temperature and is determined such that bounds of $\pm 3\sigma_{\gamma_{\text{GB}}}$ contain all but one of the data points. Using this approach, we obtained $\sigma_{\gamma_{\text{GB}}} = 0.088 \text{ J/m}^2$.

The average GB mobility is determined by measuring the average grain size over time; however, it cannot be measured directly. Rather, the data are used to determine the rate constant K using the empirical equation

$$\overline{D}^2 - \overline{D}_0^2 = 2Kt. \quad (10.13)$$

The relation between the GB mobility and rate constant is obtained by equating Eq. (10.11) and Eq. (10.13) to obtain

$$M_{\text{GB}} = \frac{K}{\alpha\gamma_{\text{GB}}}. \quad (10.14)$$

M and K share the same temperature dependence which leads to

$$K = K_0 e^{-\frac{Q}{k_b T}}. \quad (10.15)$$

Thus, the relation between the GB mobility prefactor and the rate constant prefactor is

$$M_0 = \frac{K_0}{\alpha\gamma_{\text{GB}}}. \quad (10.16)$$

The rate constant has been measured for fully dense UO_2 at temperatures ranging from 1273 to 2273K [42], but no uncertainty or error information was reported. Therefore, as with the GB energy, we assume a normal distribution. We calculate the mean value $\overline{K}_0 = 1.44 \times 10^{-8} \text{ m}^2/\text{s}$ and the standard deviation $\sigma_{K_0} = 3.06 \times 10^{-11} \text{ m}^2/\text{s}$ from the available data. The shape parameter was determined to be $\alpha = 0.55$ using MARMOT grain growth simulations. From these values, we determined the mean value of the mobility prefactor to be $\overline{M}_0 = 6.26 \times 10^{-8} \text{ m}^4/\text{Js}$ with standard deviation $\sigma_{M_0} = 1.76 \times 10^{-8} \text{ m}^4/\text{Js}$.

The mean and standard deviations of the model parameters used in our simulations are summarized in Table 10.1. The initial average grain size was $\overline{D}_0 = 1.327 \text{ }\mu\text{m}$, and the final average grain size was calculated after 1000 sat 1700K.

Table 10.1 Uncertainties of parameter in grain growth model.

Parameter	Mean	Standard deviation
γ_{GB} (J/m ²)	0.4194	0.088
M_0 (m ⁴ /Js)	6.2604×10^{-8}	1.7554×10^{-8}
Q (eV)	2.614	0.0831

10.3.3 Sensitivity analysis

We conducted a sensitivity analysis on both the mesoscale phase field grain growth model and the mechanistic model of the average grain size with time.

In the mechanistic model, the local sensitivities are obtained by taking partial derivatives of Eq. (10.11) to obtain

$$S_{\gamma_{GB}}^D = \frac{\partial D}{\partial \gamma_{GB}} \quad (10.17)$$

$$S_{M_0}^D = \frac{\partial D}{\partial M_0} \quad (10.18)$$

$$S_Q^D = \frac{\partial D}{\partial Q} \quad (10.19)$$

The mean parameter values shown in Table 10.1 are used in these expressions to determine the sensitivities. The normalized sensitivities (normalized according to Eq. 10.2) are shown in Table 10.2 and Fig. 10.2.

The local sensitivities of the average grain size predicted by the phase field grain growth model in MARMOT with respect to the model parameters were estimated in Dakota, and the normalized sensitivities from the mesoscale MARMOT model are also shown in Table 10.2 and Fig. 10.2. The values of the normalized sensitivities from the MARMOT grain growth model and the mechanistic average grain size model show good agreement, demonstrating that the two models represent the grain growth physics in a similar manner.

The sensitivities illustrate which parameters have the largest impact on the simulation results. In both the mesoscale simulations and the macroscale model, the GB activation energy Q was nearly 20 times more sensitive than the other two parameters. Thus, uncertainty in the values of Q will result in the most uncertainty in the average grain size.

Table 10.2 Normalized sensitivities of the grain growth models at 1700K.

Sensitivity	Macroscale model	Mesoscale simulation
$\tilde{S}_{\gamma_{GB}}^D$	0.11	0.15
$\tilde{S}_{M_0}^D$	0.11	0.14
$\tilde{S}_Q^D$	-2.01	-2.75

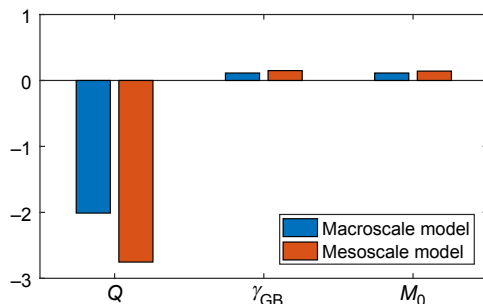


Figure 10.2 The normalized sensitivities of the macroscale model and the mesoscale simulations at 1700K.

10.3.4 Uncertainty quantification

In addition to the sensitivity analysis, we also conducted UQ on both the macroscale mechanistic model of the average grain size and the mesoscale grain growth model in MARMOT. The uncertainty was quantified using the linear approximation from Eq. (10.3) and it was estimated using the MC method with Dakota. The linear approximation determines the mean and the standard deviation of the average grain size, while the MC method provides an estimate of the full distribution. When applying the MC method to the MARMOT simulations, only 500 evaluations were carried out, where each parameter was sampled using the LHS method from a normal distribution. This small number was used to reduce the computational expense and is not sufficient to predict the final distribution with any accuracy. However, it does provide a means of comparing the results from the macroscale and mesoscale models and of estimating how well the linear approximation works for the grain growth models.

Fig. 10.3 shows the distribution of the average grain size of the macroscale model and the MARMOT simulations calculated using the MC method. The solid line shows the model prediction when using the mean of each parameter. The dashed lines show the mean value $\pm$ the standard deviation calculated using Eq. (10.3) with the parameter standard deviations from Table 10.1 and the sensitivity values from Table 10.2.

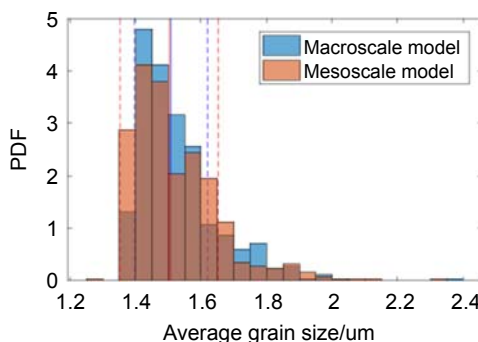


Figure 10.3 Uncertainty quantification comparison of the macroscale model and the mesoscale MARMOT simulations at 1700K. The *solid lines* are the mean value of the average grain size and the *dashed lines* are the mean $\pm$ standard deviation calculated from the linear approximation.

Table 10.3 Linear approximation and MC simulation of the mean and standard deviation of average grain size at 1700K.

	Standard deviation	Mean
Linear approximation		
Macroscale model	0.11 μm	1.51 μm
Mesoscale model	0.15 μm	1.50 μm
MC simulation		
Macroscale model	0.13 μm	1.53 μm
Mesoscale model	0.14 μm	1.52 μm

For both the macroscale model and the MARMOT simulations, the mean and standard deviation calculated using the linear approximation and the MC method are shown in Table 10.3. The mean values from both approaches are similar, as are the standard deviations (within the error resulting from our small number of MC evaluations). This indicates that for modeling isotropic grain growth, the simulation uncertainty may be estimated using the linear approximation. To estimate the relative impact of the three parameters on the uncertainty, we use the variance calculated using the linear approximation (see Fig. 10.4). In both the macroscale model and the mesoscale simulations, the activation energy was the largest contributor to the variance. Reducing the uncertainty in the value of Q would have the largest impact on reducing the uncertainty of the calculated average grain size.

With the MC method, the macroscale model and the mesoscale simulations both predicted a distribution of the average grain size that is skewed to the left, with a long tail to the right, though the distribution from the mesoscale simulations had a smaller tail. The macroscale model and the mesoscale simulations have similar mean value and standard deviation, along with the similarity of the sensitivities, indicating that the macroscale model is a good representation of the physical behavior represented in the mesoscale simulations. The uncertainty in the calculation is fairly large, with a standard deviation that is about 10% of the mean, primarily due to uncertainty in the activation energy. Thus, the accuracy of the model would be improved by additional grain growth data to reduce the uncertainty in the value for Q .

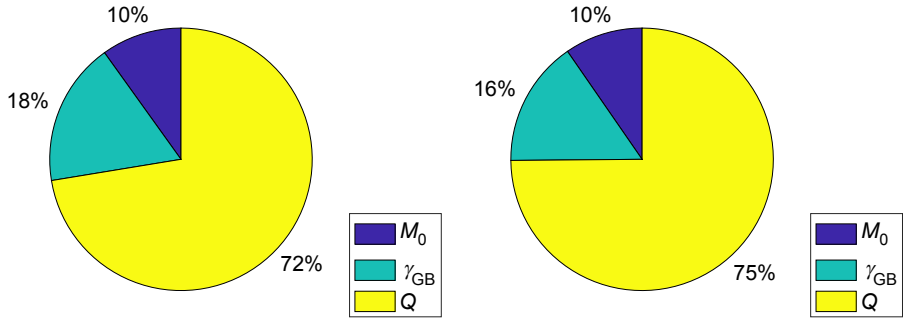


Figure 10.4 Pie chart of parameter uncertainty contributions of the macroscale model (left) and mesoscale model (right).

10.4 Thermal conductivity

10.4.1 Introduction

The most critical consideration with regard to both reactor efficiency and safety is how well the fuel can conduct the heat that is generated within it out to the cladding. Unfortunately, the thermal conductivity of UO_2 is very low and gets lower due to microstructure changes that occur during reactor operation. While there are various empirical thermal conductivity models that are functions of temperature and burnup, a new mechanistic model is needed that calculates the thermal conductivity as a function of temperature and the values of the microstructure variables. Various lower length-scale simulations are being used to accomplish this, including MD simulations to calculate the impact of small defects on the thermal conductivity and mesoscale heat conduction simulations to determine the impact of larger microstructure features, such as the grain size and fission gas bubbles.

The mesoscale simulations have primarily focused on determining how fission gas bubbles impact the thermal conductivity of the fuel. The fission gas is present in the fuel in three general forms [49]: individual atoms distributed in the UO_2 crystal lattice, intragranular bubbles that are typically small except at high burnup, and intergranular bubbles that can grow to much larger sizes. The intergranular bubbles grow and interconnect, and eventually provide pathways for the fission gas to escape the fuel pellets. These bubbles are filled with Xe, Kr, and other fission product gases that do not conduct heat efficiently. Thus, the fuel thermal conductivity goes down with time, but each form of fission gas impacts the thermal conductivity in a different way. Mesoscale simulations have focused on determining the impact of the intergranular gas bubbles on the thermal conductivity [50]. All of this information has been put together to create a mechanistic thermal conductivity model that accounts for the three forms of fission gas [13,14].

10.4.2 Model summaries

The effective thermal conductivity of a UO_2 microstructure is determined using a homogenization approach based on solutions of the steady-state heat conduction equation. In MARMOT, the effective thermal conductivity for a given microstructure is determined using asymptotic expansion homogenization [51]. The microstructure of the material is spatially represented in 2D or 3D, and different local thermal conductivities are assigned inside of each feature. The microstructure is randomly generated using a Voronoi tessellation for the grains with spherical bubbles randomly distributed along the GBs. The effective thermal conductivity depends on the values of the local conductivities, the fraction of the overall material taken up by each feature, and the configuration of the features within the material. An example simulation domain is shown in Fig. 10.5. These types of simulations can be carried out in 2D or 3D, where 3D simulations are not only more accurate but also much more computationally expensive. In this work, we carry out 2D simulations, and 3D simulations will be carried out in the future.

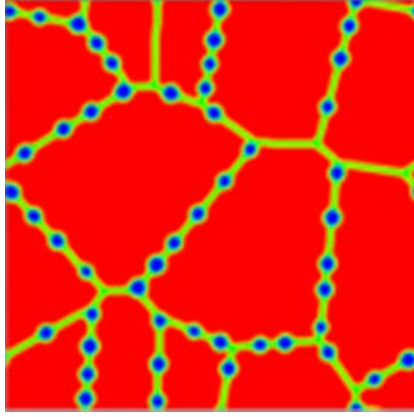


Figure 10.5 Example of mesoscale domain used to estimate the effective thermal conductivity, where the red regions are bulk UO_2 , the green regions are the GBs, and the blue regions are the bubbles.

The mesoscale simulation model describes three types of features: bulk UO_2 , GBs, and fission gas bubbles. The thermal conductivity of bulk UO_2 k_{UO_2} is determined from semiempirical functions of the temperature T and stoichiometry x [52]

$$K_{\text{bulk}} = \frac{1}{0.0257 + 3.336x + (2.206 - 6.85x)10^{-4}T + \frac{6400}{(T/1000)^{5/2}} \exp\left(\frac{-16350}{T}\right)}. \quad (10.20)$$

The thermal conductivity of the GB is a function of the thermal resistance of the GB R_{GB} (Kapitza resistance), the bulk UO_2 conductivity, and the width of the GB used in the mesoscale representation of the microstructure w_{GB} according to the expression [13]

$$k_{\text{GB}} = \frac{k_{\text{UO}_2} w_{\text{GB}}}{R_{\text{GB}} k_{\text{UO}_2} + w_{\text{GB}}}, \quad (10.21)$$

where values for the GB thermal resistance in UO_2 have been determined using MD simulations [14], shown in Table 10.5. The thermal conductivity within the bubbles k_{gas} is the thermal conductivity of Xe gas as a function of temperature [53],

$$K_{\text{gas}} = \sum_{i=0}^n a_i T^{i-1}, \quad (10.22)$$

where the values for the coefficients a_i are given in Ref. [53].

The mechanistic macroscale model presented by Tonks et al. [13] accounts for the dispersed gas atoms, intragranular bubbles, and intergranular bubbles. Each is included using a different portion of the model. The microstructure is defined in terms of the average grain size $\bar{D}$, the fractional coverage of the GBs by bubbles f_c , and the

average bubble radius r_b . Other parameters used in this macroscale model are k_{UO_2} , k_{gas} , x , R_{GB} , and the concentration of Xe gas atoms in the bulk c_{gas} .

In this work, results from the macroscale model were compared with those from the mesoscale simulation in both the sensitivity analysis and UQ. Therefore, the parameters must be consistent between the two for them to be comparable. Thus, the same values will be used for k_{UO_2} , k_{gas} , x , R_{GB} , and c_{gas} . The values used in the macroscale model for the variables defining the microstructure, $\bar{D}$, f_c , and r_b , were determined from the mesoscale microstructures to ensure a good comparison. The average grain size in the 2D microstructures was calculated according to

$$\bar{D} = 2\sqrt{\frac{A}{\alpha N}} \quad (10.23)$$

where A is the area of the simulation domain, N is the number of grains in the domain, and α is the shape parameter from Eq. (10.7). For the 2D domains used here, $\alpha = 0.6983$. The GB fractional coverage f_c is calculated using

$$f_c = \frac{N_B \pi r_B^2}{A_{\text{GB}}}, \quad (10.24)$$

where N_B is the number of bubbles in the mesoscale simulation, and A_{GB} is the GB area present in the simulation domain.

For all the simulations in this work, we neglect gas atoms within the UO_2 matrix, such that $c_{\text{gas}} = 0$. The impact of dispersed gas atoms will be investigated in future work.

10.4.3 Sensitivity analysis

Sensitivity analysis of the effective thermal conductivity k is conducted for both the macroscale model (referred to as “model”) and the mesoscale simulation (referred to as “simulation”). The local sensitivities of the model are represented by the partial derivative of the UO_2 effective thermal conductivity k with respect to each parameter as

$$S_{k_{\text{bulk}}}^k = \frac{\partial k}{\partial k_{\text{bulk}}} \quad (10.25)$$

$$S_{k_{\text{gas}}}^k = \frac{\partial k}{\partial k_{\text{gas}}} \quad (10.26)$$

$$S_{R_{\text{GB}}}^k = \frac{\partial k}{\partial R_{\text{GB}}} \quad (10.27)$$

$$S_{r_B}^k = \frac{\partial k}{\partial r_B}, \quad (10.28)$$

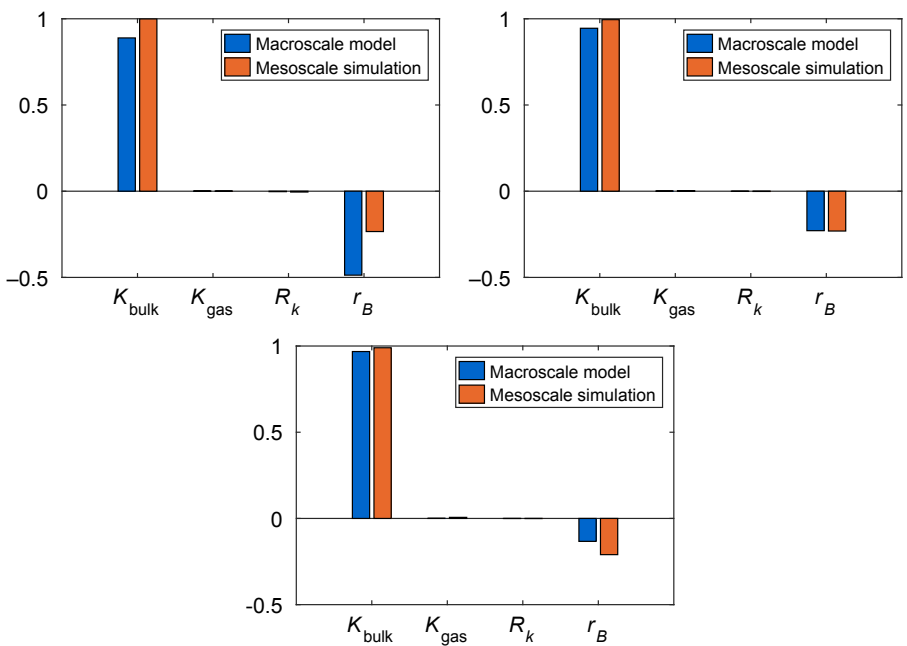


Figure 10.6 Normalized sensitivities of the effective thermal conductivity k with respect to the parameters from the model and simulation, where the values for 300K are shown on the top left, for 800K on the top right, and for 1200K on the bottom.

Table 10.4 Normalized sensitivities of the model and simulation at different temperatures.

	300K		800K		1500K	
	Model	Simulation	Model	Simulation	Model	Simulation
$\tilde{S}_{k_{\text{bulk}}}^k$	0.89	1.00	0.95	1.00	0.97	0.99
$\tilde{S}_{k_{\text{gas}}}^k (\times 10^{-3})$	0.79	0.65	0.82	2.54	0.76	6.25
$\tilde{S}_{R_{\text{GB}}}^k (\times 10^{-3})$	-2.66	-4.77	-0.83	-1.44	-0.33	-0.56
$\tilde{S}_{r_B}^k$	-0.49	-0.23	-0.23	-0.23	-0.13	-0.21

using Eq. (10.2) to normalize them. Dakota is used to determine the sensitivities, and normalized sensitivities of UO_2 at 300, 800, and 1500K are shown in Fig. 10.6 and also summarized in Table 10.4. k_{bulk} is the most sensitive and r_b roughly half as sensitive as k_{bulk} . The sensitivities of k_{gas} and R_{GB} are negligible compared with the other two. The sensitivities compare well between the model and simulation at high temperature, but vary significantly at 300K.

10.4.4 Uncertainty quantification

The uncertainty of the effective thermal conductivity k can be approximated using the linear approximation using Eq. (10.3) or using MC simulation. Here we carry out both approaches and compare the results.

For the linear approximation of the standard deviation of k , using Eq. (10.3), the values for the sensitivities are taken from Table 10.4. The standard deviation of the input parameters are the same for the model and simulation, with $\sigma_{k_{\text{bulk}}} = 0.06\bar{k}_{\text{bulk}}$, $\sigma_{k_{\text{gas}}} = 0.02\bar{k}_{\text{gas}}$, and $\sigma_{r_b} = 0.3\bar{r}_b$. The values for $\sigma_{k_{\text{bulk}}}$ and $\sigma_{k_{\text{gas}}}$ were determined directly from the experimental data [53,54] in a similar manner to that used in the previous section for the GB energy. Fig. 10.7 shows that assigning $\sigma_{k_{\text{bulk}}} = 0.06\bar{k}_{\text{bulk}}$ aligns well with the experimental data in the paper. σ_{r_b} was assumed to be one-third of the mean value. The value of $\sigma_{R_{\text{GB}}}$ changes with temperature, where the values are shown in Table 10.5 and were estimated from Ref. [14].

The mean value of the effective thermal conductivity is estimated by evaluating the value using the mean parameter values for the model and simulation. The mean and standard deviation obtained from the linear approximation for both the model and

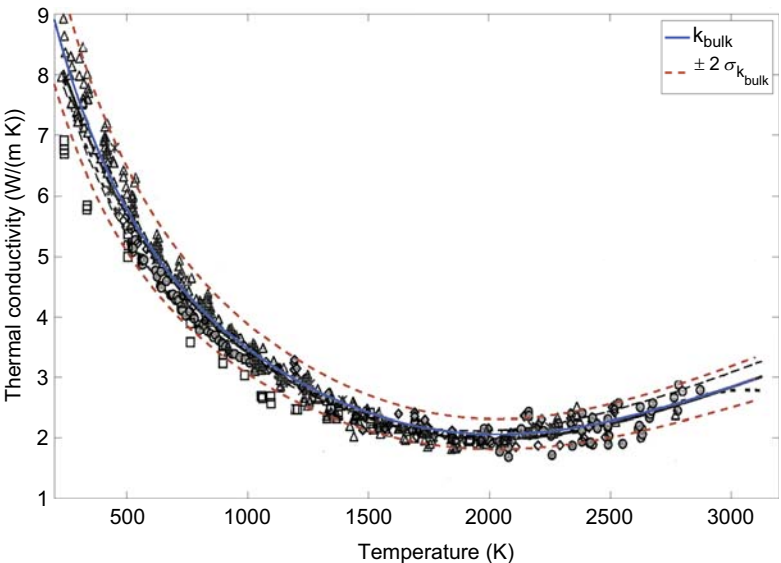


Figure 10.7 The standard deviation of the UO_2 thermal conductivity was determined from the scatter of the data from Ref. [54]. The dashed lines demonstrate the two standard deviation limits on the thermal conductivity fit.

Table 10.5 $\bar{R}_k$ and $\sigma_{R_{\text{GB}}}$ at different temperatures.

T (K)	300	800	1500
$\bar{R}_k$ ($\times 10^{-9}$) (W/mK)	1.48	0.97	0.66
$\sigma_{R_{\text{GB}}}$ ($\times 10^{-9}$) (W/mK)	0.13	0.057	0.087

Table 10.6 Linear approximation and MC simulation of the mean and uncertainty of thermal conductivity at different temperatures.

	300K		800K		1500K	
	Model	Simulation	Model	Simulation	Model	Simulation
Linear approximation						
$\bar{k}$ (W/mK)	9.16	8.99	4.44	4.11	2.62	2.36
σ_k (W/mK)	1.43	0.83	0.40	0.38	0.18	0.21
MC simulation						
$\bar{k}$ (W/mK)	9.15	8.89	4.43	4.07	2.62	2.35
σ_k (W/mK)	0.49	0.89	0.25	0.39	0.15	0.22

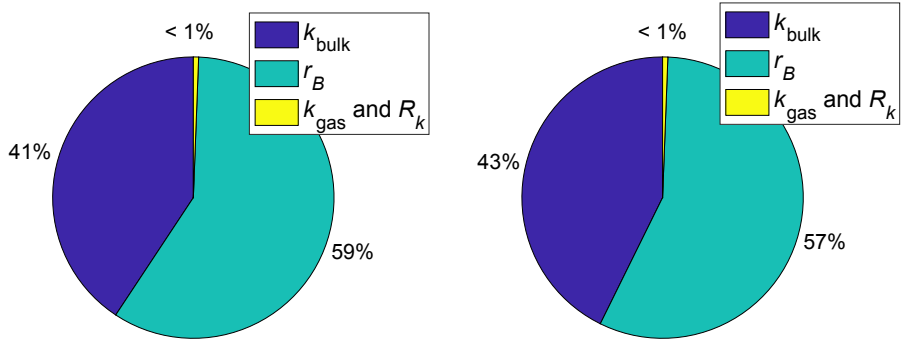


Figure 10.8 The relative contributions of each parameter to σ_k^2 for the model (left) and simulation (right). In the model, k_{bulk} makes up of 41% in the total uncertainty, and r_B is 59%. In the simulation, k_{bulk} is 43%, and r_B is around 57%. k_{gas} and R_k have very small contributions. The relative contributions do not vary significantly with temperature.

simulation at different temperatures are shown in Table 10.6. The relative contribution of each parameter to the overall variance σ_k^2 for the model and simulation are shown in Fig. 10.8.

Only 300 samples were used in the MC UQ analysis of the analytical model and the MARMOT simulations, which is much too small to accurately determine the distribution (as in the previous section). We use the MC UQ results to evaluate the effectiveness of the linear approximation and to compare the results from the macroscale model and the mesoscale simulations. The UQ comparison of the model and simulation at different temperatures are shown in Fig. 10.9. The mean and standard deviation values of the model are shown in Table 10.6.

Both the macroscale model and mesoscale simulation predict effective thermal conductivity distributions obtained by the MC analysis that are fairly symmetric and could be treated as normal. The $\bar{k}$ and σ_k values vary between the model and the simulation. The mean values vary by 3% at 300K, 9% at 800K, and 11% at 1500K; the standard

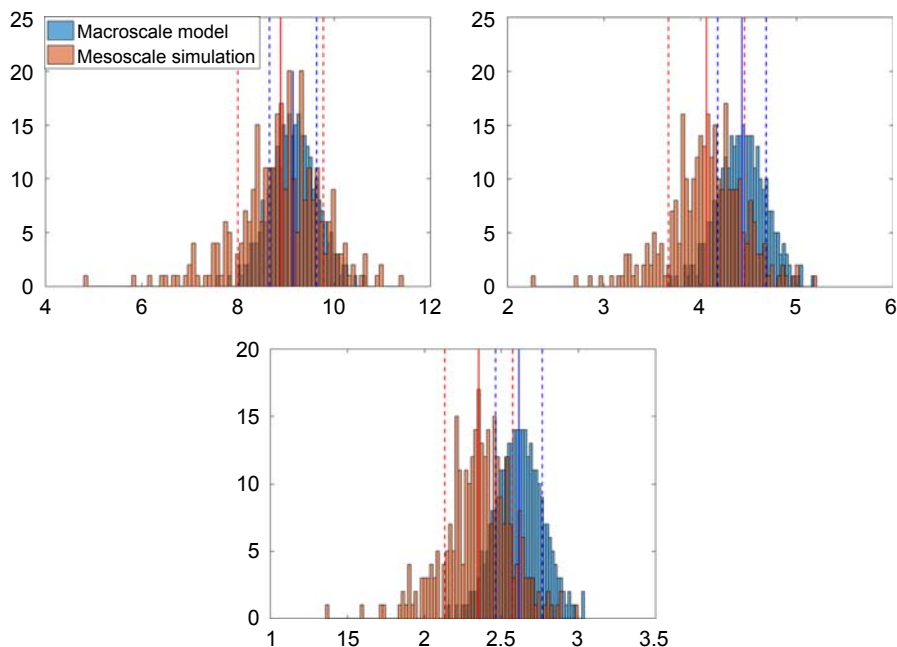


Figure 10.9 The distribution of the calculated effective thermal conductivity using the model and simulation at different temperatures, where 300K are shown on the top left, 800K on the top right, and 1500K on the bottom. The *solid lines* are the mean value of the effective thermal conductivity, and the *dashed lines* are the mean $\pm$ standard deviation.

deviation values vary by 45% at 300K, 36% at 800K, and 32% at 1500K, indicating that the straightforward mechanistic model captures the mean and the shape of the thermal conductivity distribution fairly accurately but that the standard deviation is predicted much less accurately. This may indicate that the approximations involved in the model may be an oversimplification of the actual material behavior.

In Table 10.6, it can be seen that the $\bar{k}$ and σ_k values from the linear approximation and MC simulation are very close for the mesoscale simulation, but not for macroscale model. Thus, in the future we can use the linear approximation to predict the uncertainty in predictions using the mesoscale simulations, but that MC analysis would be required for the macroscale model. This is acceptable, as the mesoscale simulations are much more computationally expensive.

As shown in Fig. 10.8, the linear approximation predicts that r_B has the largest impact on the variance of the thermal conductivity. This is different than what was shown by the sensitivity analysis (Fig. 10.6). This is because even though k_{bulk} has a higher sensitivity value than r_B , the standard deviation of r_B is 30% of the mean value, much higher than the standard deviation of k_{bulk} which is 6% of the mean value. The uncertainty in the predicted thermal conductivity depends on the sensitivities and the standard deviations of the parameters.

Since the simulation only has bubbles on the GB, future work needs to be done to add bubbles inside the grains in the MARMOT simulation and to include the

intragranular bubble effect multiplier in the model. To further compare the model and simulation with experiment, point defects need to be considered in the k_{bulk} equation.

10.5 Fracture

10.5.1 Introduction

UO₂ is a brittle ceramic. During reactor start-up, shut-down, and other transients, fuel pellets fracture primarily along GBs due to thermal stresses. Thus, as intergranular fission gas bubbles grow along the GBs, the fuel will crack at lower and lower stress. To accurately determine the fracture of irradiated fuel, it is necessary to include the impact of intergranular bubbles. Because fracture occurs due to intergranular fracture, grain size will also impact the fracture stress. Phase field fracture simulations using MARMOT have been used to quantify the impact of gas bubbles and grain size on the fracture stress of UO₂ [55]. The simulations so far have been in 2D, and the 2D results were used to fit a relationship between porosity and the fracture stress. However, 3D results will be needed to give a more accurate relationship between porosity and grain growth and the fracture stress. In addition, a mechanistic model is needed to predict the relationship rather than just empirical fits.

10.5.2 Model summaries

The phase field fracture model in MARMOT is summarized in the paper by Chakraborty et al. [55]. This is a fully quantitative model that assumes isotropic mechanical properties. The only material properties needed in the model are the elastic constants, E and ν , and the energy release rate, G_C . An example simulation domain is shown in Fig. 10.10. In this model, the damage region is described using the order parameter

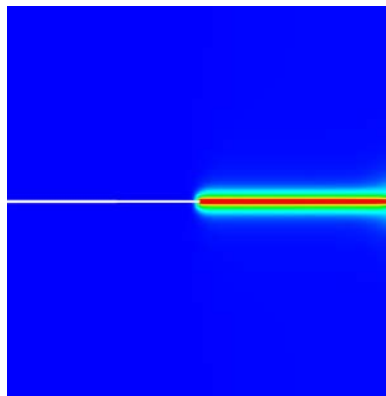


Figure 10.10 Example of mesoscale domain used to estimate the maximum stress before fracture on a SENT sample, and the color gradient from blue to red indicating the local value of damage variable c from 0 to 1, respectively.

c , where $c = 0$ in undamaged material and $c = 1$ within the crack. In the phase field method, the crack has a finite width l , which is a model parameter. As $l \rightarrow 0$, the accuracy increases but so does the computational cost, due to the small element size required to resolve the crack width. As the crack propagates, the value of c ahead of the crack evolves from 0 to 1, indicating that the crack has progressed. The model achieves rate independent behavior as the viscosity parameter $\eta \rightarrow 0$. Thus, in addition to the material properties, we also have to understand the fracture model's dependence on the model parameters l and η .

10.5.3 Sensitivity analysis

In this work, we conduct a sensitivity analysis on the phase field fracture model. A single edge notch tension system as described by Chakraborty et al. [55] was chosen as the test case. In this simulation, we assume the material to be isotropic, single crystal UO_2 . The elastic constant values were obtained from experimental data [56–59]. The G_C values were taken from a MD simulation paper by Zhang et al. [5].

The mean values for the model parameters η and l were chosen by decreasing their values in the MARMOT simulation until the output was relatively invariant with further decrease in the model parameter values. These values were found to be $\eta = 10^{-4}$ and $l = 9 \times 10^{-3} \mu\text{m}$. The model parameters were then sampled within $\pm 10\%$ of their mean values. The quantity of interest was chosen to be the maximum stress before fracture S_f , and the sensitivities were calculated using Dakota.

The linear sensitivity can be approximated as the slope of the output function with respect to an input parameter, using Eq. (10.1). Eq. (10.2) was used to normalize the sensitivities. The results of the sensitivity analysis are shown in Table 10.7 and Fig. 10.11. The most sensitive parameter was the energy release rate G_c , then Young's modulus E , and then Poisson's ration ν . The model parameters l and μ are the least sensitive, indicating that we were able to effectively select values that have little impact on the model predictions (a desirable behavior for model parameters).

Table 10.7 Normalized sensitivity of the fracture stress S_f with respect to the various model parameters.

Parameter	Sensitivity
$\tilde{S}_{G_c^{1/2}}^{S_f}$	1.00
$\tilde{S}_E^{S_f}$	0.51
$\tilde{S}_\nu^{S_f}$	0.30
$\tilde{S}_\eta^{S_f}$	-2.4×10^{-3}
$\tilde{S}_l^{S_f}$	-0.12

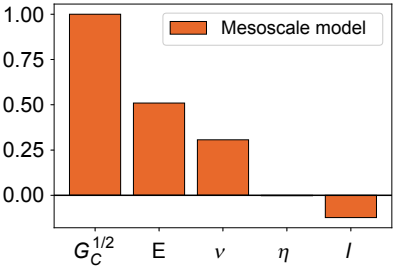


Figure 10.11 The normalized sensitivities of the fracture stress with respect to the various model parameters.

10.5.4 Uncertainty quantification

The uncertainty of the maximum stress before fracture S_f can be approximated using the linear approximation from Eq. (10.3). The sensitivity values are taken from Table 10.7. There are not sufficient data reported in the references to determine the standard deviations of the input parameters. Therefore, the standard deviations were estimated using the error bars shown in the source references [5,56–59]. In each case, the mean of the parameter was taken to be the average of the maximum and minimum reported values, while the standard deviation was taken to be one-sixth of the difference between the maximum and minimum values. The mean and standard deviation values for the input parameters are shown in Table 10.8.

The calculated mean and standard deviation of the fracture stress are shown in Table 10.9. The relative contribution of each parameter to the overall variance $\sigma_{S_f}^2$ is shown in Fig. 10.13.

MC UQ of the MARMOT simulation was performed using Dakota, where each parameter was assumed to follow a normal distribution. Only 500 samples were used to generate the S_f distribution shown in Fig. 10.12, which is not enough to accurately estimate the distribution of the computed fracture stress, but is sufficient for us to evaluate the effectiveness of the linear approximation method. The mean and uncertainty values of the MC UQ analysis are shown in Table 10.9.

In Table 10.9, it is seen that the results of the linear approximation of $\bar{S}_f$ and σ_{S_f} are very close to the MC values. Therefore, for future studies it may be enough to use the linear approximation method, and not necessary to do the full MC UQ analysis.

Table 10.8 Mean and uncertainty values of input parameters.

Parameter	Mean	Standard deviation
G_C (GPa $-\mu\text{m}$)	2.785×10^{-3}	3.1833×10^{-4}
E (GPa)	201.9344	15.2767
ν	0.32	0.01
η	1×10^{-4}	3.33×10^{-6}
l (μm)	9×10^{-3}	3×10^{-4}

Table 10.9 The mean and standard deviation of the fracture stress S_f predicted by the MARMOT fracture model. Results are provided from the linear approximation and the MC analysis.

Statistics	Linear approximation	MC UQ
$\bar{S}_f$ (GPa)	0.76	0.76
σ_{S_f} (GPa)	0.0529	0.053

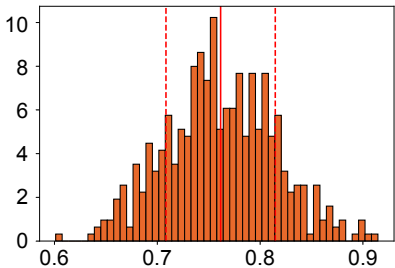


Figure 10.12 The distribution of S_f calculated using the MC method with the MARMOT simulation. The *solid red line* is the mean value, and the *dashed lines* are the mean $\pm$ standard deviation.

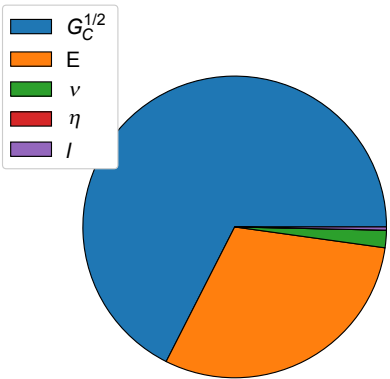


Figure 10.13 Relative contributions of each parameter to the variance of the fracture stress σ_f .

Fig. 10.13 shows that $G_C^{1/2}$ is the major contributor to $\sigma_{S_f}^2$, followed by E and then ν . These results are consistent with the sensitivity analysis results. The overall variation in the predicted fracture stress was rather high, with the standard deviation about 7% of the mean. To lower this variation, the uncertainty of the energy release rate needs to be reduced, using a combination of more MD simulations and experimental data. More data are also needed to reduce the uncertainty in Young’s modulus.

However, this simulation only looks at single grain fracture with no intergranular bubbles. Future work needs to be done to simulate a polycrystalline material using a 3D mesh to properly study the effect of porosity on fracture behavior. In addition, a mechanistic macroscale model needs to be developed, and its uncertainty investigated.

10.6 Conclusions

In this work, we have applied preliminary sensitivity analysis and UQ to three types of models of the behavior of porous UO_2 grain growth, the effective thermal conductivity, and fracture. In the areas of grain growth and the effective thermal conductivity, we employed both mesoscale simulations using the MARMOT tool and macroscale mechanistic models, while for fracture we only employed a mesoscale MARMOT model.

The sensitivity analysis identified the parameter that has the largest impact on the value of interest: the GB activation energy for grain growth, the bulk thermal conductivity of UO_2 for the effective thermal conductivity measurement, and the energy release rate for fracture. For the grain growth, both the mesoscale simulations and the macroscale model had similar parameter sensitivities, indicating that the macroscale model represents the physics in a similar way to the mesoscale models. For the thermal conductivity model, the sensitivities were only similar at high temperature.

UQ was carried out using both a linear approximation based on the sensitivities and using the MC method (though with a small number of MC evaluations). The standard deviation predicted by the linear approximation differed significantly from the MC calculated value for the macroscale thermal conductivity model, but for all other models the linear approximation provided a sufficiently accurate prediction of the uncertainty. The linear approximation was also used to estimate the relative impact of the various parameters on the final variance. The parameter that had the largest impact on the uncertainty also had the largest sensitivity for the grain growth and fracture models, but in the thermal conductivity model the average bubble radius had the largest impact rather than the bulk thermal conductivity.

The UQ analysis carried out in this work is an important step to understanding the uncertainty in the model predictions being used as part of the NEAMS-funded effort to improve our fuel performance codes. However, much work is still needed. In particular, the predicted model distributions need to be compared to experimental data to validate the models and provide a confidence level on their predictions.

Acknowledgments

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Multiscale simulation of fiber composites with spatially varying uncertainties

11

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11.1 Background and literature review

Uncertainty sources are generally categorized as aleatory and epistemic [1]. While the former uncertainty source is inherent to the system (and hence irreducible), the latter is generally due to lack of knowledge or data and may be reduced by conducting more simulations, experiments, or in-depth studies. In case of materials, both sources are present and may be introduced in the design and constituent selection stages, manufacturing processes, or operation. Such uncertainties manifest as, e.g., mechanical (e.g., Young's modulus, Poisson ratio, yield stress, damage evolution parameters, ...) or geometrical (e.g., reinforcement distribution, fiber misalignment in composites) variations. To elaborate more on materials uncertainty, we take woven fiber composites as an example. These materials have been increasingly used in aerospace, construction, and transportation industries because of their superior properties such as high strength-to-weight ratio, noncorrosive behavior [2], enhanced dimensional stability [3], and high impact resistance [4]. Woven fiber composites possess, as illustrated in Fig. 11.1, a hierarchical structure that spans multiple length scales. At the finest scale, nanoscale, the constituent properties and the interaction between them (e.g., the interphase) are modeled. The fibers (and their relative position within the yarns) and the matrix belong to the *microscale*. The individual yarns and their architecture (i.e., their dimension and relative spatial arrangement, see Fig. 11.2(a,b)) in the laminates are modeled in the *mesoscale*. The overall mechanical performance under some external loading conditions is evaluated at the *macroscale*. This is the highest (i.e., coarsest) length scale in this example where characteristics such as fiber and yarn (aka tow or bundle) volume fractions, effective properties, and part geometry are of interest.

* Equal contribution.

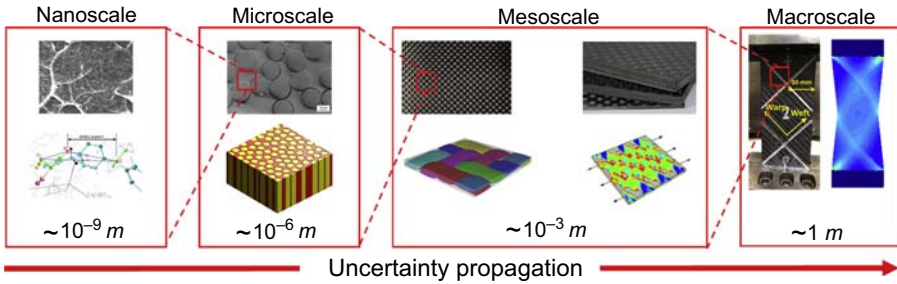


Figure 11.1 Multiscale structure. Schematic view of a four-scale woven fiber composite with polymer matrix. In computational modeling of this structure, each integration point (IP) at any scale is a realization of a structure at the next finer scale.

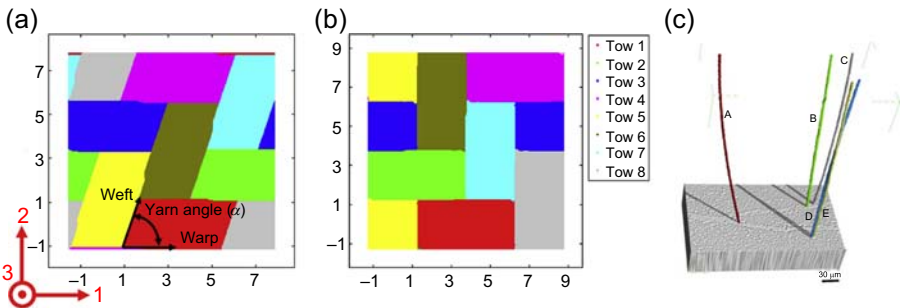


Figure 11.2 Orthogonal and nonorthogonal yarn architecture and fiber misalignment. Samples of 2×2 (a) nonorthogonal and (b) orthogonal woven prepreps with side measures of four yarns in-plane. The dimensions are mm and the yarn/tow coordinates are generated with *TexGen* [33]. (c) Fiber misalignment for five fibers in a polymer composite [6]. In these images, the resin is not shown.

Within each of these length scales, many correlated and spatially varying uncertainty sources are introduced [2]. As illustrated in Fig. 11.2(c), the high pressure and flow of the resin or draping change the *local architecture* of the fibers during the preforming process [5]. Additionally, processing variations and material imperfections cause the *fiber volume fraction* to spatially vary across the sample. These variations are particularly pronounced along the yarn paths where there is compact contact [6,7]. These macroscopic uncertainties are manifestations of many uncertainty sources that exist at the finer scales where the number and dimensionality of the uncertainty sources increase due to the delicacy of materials [8]. Moving down the scale ladder in Fig. 11.1, one can observe that the uncertainty sources are of different nature (e.g., morphological, geometrical, or property related) and spatially (within and across scales) correlated. These features render the uncertainty quantification (UQ) of a macroscopic quantity of interest extremely challenging.¹

¹ It is further noted that macroscopic uncertainty depends heavily on the quantity of interest. For example, the homogenized response in linear analyses and damage are clearly not equally sensitive to spatial microstructural variations.

Motivated by the abovementioned challenges, ever-growing research [9–11] is being conducted to rigorously couple computational mechanics models with statistical UQ and uncertainty propagation (UP) methods to provide probabilistic predictions that are in line with the observed stochasticity in materials. UQ and UP are actively pursued in various fields of science and engineering [8,10,12–26]. However, they are rarely applied to multiscale simulations because of the significant computational costs and complexities. Such simulations are applied to materials that possess a hierarchical structure where the coarse-scale behavior is greatly affected by the fine-scale details (i.e., the microstructure). They have enabled studying the effect of microstructure on many phenomena including damage evolution [27,28], fracture initiation [29], and strain localization [30–32].

We take two scales from the composite in Fig. 11.1 to illustrate the various uncertainty sources and the abovementioned challenges associated with multiscale UQ and UP. In the finite element (FE) mesh of the mesostructure in Fig. 11.3, there are over 10000 integration points (IPs, aka Gauss or material points) where each one is a realization of a representative volume element (RVE) at the next finer scale, i.e., the microscale. The response of such a hierarchical material to some external load is generally obtained via *Computational homogenization* which involves the solution of second-order elliptical partial differential equations (PDEs). In our case, these PDEs are at both scales where the boundary conditions of the microscale PDEs are determined at the mesoscale. Once the microscale PDEs are solved, the homogenized stresses and tangent moduli are sent back to the mesoscale to be used in the mesoscale PDEs. If the FE method is used in both scales to solve the boundary value problems, this method is referred to as FE^2 [34,35]. In deterministic FE^2 , all the parameters (and their evolution) at the IPs at both scales (related to, e.g., the material properties, the morphology, or the applied load) are known a priori.

If there is uncertainty, simulation parameters should be characterized statistically. For instance, in the mesoscopic RVE in Fig. 11.3, the dimensions and relative arrangement of the yarns, the fiber volume fraction, and material properties (such as Young's modulus and Poisson ratio) might vary *spatially* due to multiple factors such as manufacturing inconsistencies. These spatial variations across the IPs of the mesostructure imply that the corresponding microstructures are not identical. More importantly, these mesoscale variations are spatially correlated. For instance, the data reported in Refs. [5,6,36] demonstrate that in unidirectional (UD) fiber-reinforced

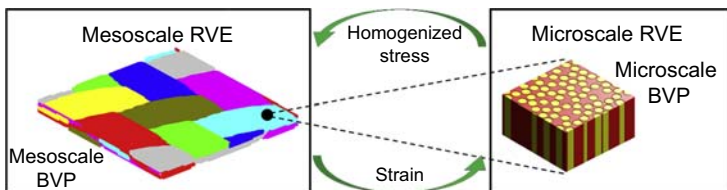


Figure 11.3 Computational homogenization in a two-scale structure. Strain is passed from the mesoscale to microscale while stress is passed in the opposite direction. The resin is hidden in the mesostructure for a better illustration (BVP stands for boundary value problem).

composites (with either metallic or polymeric matrix) not only the fiber misalignment angles and volume fraction change spatially but also these changes are negatively correlated (i.e., high volume fraction implies small misalignment angle and vice versa). Similarly, some of the properties and parameters at the microstructures might be spatially inhomogeneous. Hence, to quantify the mesoscale uncertainty, the microscale stochasticity must be *quantified*, *propagated*, and finally *coupled* with uncertainty sources at the mesoscale.

Monte Carlo (MC) sampling is a straightforward way to quantify the uncertainty of an effective coarse-scale property (e.g., Young's moduli) where many simulations are conducted to find the distributional characteristics. However, MC sampling is practically infeasible in multiscale simulations due to the (i) curse of dimensionality that arises from the number of IPs (i.e., degrees of freedom), (ii) nested nature of the uncertainty sources, and (iii) high cost of multiscale simulations. For example, in the two-scale structure in Fig. 11.3, a *single* MC sample would require (i) assigning correlated parameters (morphological, geometrical, property related, and so on) to all the IPs of the mesostructure, (ii) generating microstructures where each one is consistent with the assigned parameters to the corresponding IP in the mesoscale, and (iii) conducting a multiscale simulation via, e.g., the FE^2 method.

The computational costs of UQ and UP analyses rapidly increase as the number of scales and uncertainty sources grow. There has been some work [37–39] to enable efficient sampling techniques, but they do not fully resolve these issues and hence are inapplicable to practical cases. Since the use of multiscale materials in science and engineering is rapidly growing, there is a clear need [10,40] for efficient methods and frameworks to quantify the coarse-scale uncertainty of such materials as a function of the fine-scale uncertainties. We believe that our approach paves the path to this end by leveraging the physics of the problem at hand in addition to the statistical UQ and UP methods. With our approach, fewer simulations could be used to determine the distributional characteristics. Our goal is to devise a nonintrusive UQ and UP approach that characterizes the uncertainties via random fields (RFs) and is applicable to multiscale simulations where multiple uncertainty sources (including spatial microstructural variations) arise at different length scales. We are particularly interested in a nonintrusive approach because not only they are more general but also *opening* multiscale computer models (i.e., changing the formulations) to directly introduce uncertainty sources into them requires considerable effort.

Fibrous composites have been previously investigated to determine how much their properties and performance are sensitive to uncertainty. The focus of these works, however, has not been placed on rigorously modeling the uncertainty sources and statistically propagating their effects across multiple scales. For instance, modeling spatial variations via RFs, connecting them across different spatial scales, and investigating stochastic simulations are often neglected. Savvas et al. [41,42] studied the necessary RVE size as a function of spatial variations of fiber volume fraction and yarn architecture. Their research showed that the RVE size should increase at higher fiber volume fractions. They also concluded that the mesoscale RVE size is more affected by fiber orientation than waviness. Their further studies [20] illustrated that geometrical characteristics (i.e., the shape and arrangement of the fibers) and the

material properties (Young's moduli of the constituents) affect the homogenized response in UD composites quite significantly (with the former being more important). The variations were shown to decrease as the number of fibers and RVE size increased. Average axial and shear stiffness constituted the response in these studies.

Vanaerschot et al. [5] studied the variability in composite materials' properties and concluded that the stiffness in the mesoscale RVE is affected by the load orientation [36] and, additionally, it significantly decreases as the fiber misalignment increases. Hsiao and Daniel [43–45] experimentally and theoretically investigated the effect of fiber waviness in UD composites and demonstrated that it decreases composite's stiffness and strength under uniaxial compression loading. Komeili and Milani [2] devised a two-level factorial design at the mesoscale to study the sensitivity of orthogonal woven fabrics to the material properties and yarn geometry. They illustrated that, based on the applied load, these parameters could have a significant effect on the global response (i.e., reaction force). A similar sensitivity study based on Sobol's indices was conducted in Ref. [15] to demonstrate that the friction coefficient and yarn height significantly affect the macroscale mechanical response of interest in dry woven fabrics. In Refs. [2,15], yarn properties are spatially homogeneous and there is no fiber misalignment.

To address the shortcomings of the prior works, we employ RFs which are collections of random variables indexed in either time or space. We introduce the top-down sampling method that builds nested RFs by treating the hyperparameters of one RF as the responses of another RF. This nested structure allows to model nonstationary and C^0 (i.e., continuous but not differentiable) RFs at fine length scales (i.e., mesoscale and microscale) with a stationary and differentiable RF at the macroscale. We motivate the use of multiresponse Gaussian processes (MRGPs) to parsimoniously quantify the RFs and conduct sensitivity analyses for dimensionality reduction. The resulting approach is nonintrusive (in that the computational models need not be adapted to account for the uncertainties) and can leverage statistical techniques (such as metamodeling and dimensionality reduction) to address the considerable computational costs of multiscale simulations.

The rest of this chapter is organized as follows. Our proposed approach is introduced in Section 11.2 which is employed to quantify the macroscale uncertainty in a multiscale cured woven prepreg in Section 11.3. We conclude this chapter and provide future directions in Section 11.4.

11.2 Our approach for multiscale UQ and UP

As illustrated in Fig. 11.4, our approach for multiscale UQ and UP has two main stages: intrascale UQ and interscale UP. We start by identifying the uncertainty sources at each scale and modeling them via RFs where one RF is associated with *each* structure realization (see Section 11.2.2 for the details). We employ RFs with *sensible* (i.e., physically interpretable) parameters for three main reasons: (i) to *couple* uncertainty sources across length scales and enable their propagation from lower to higher

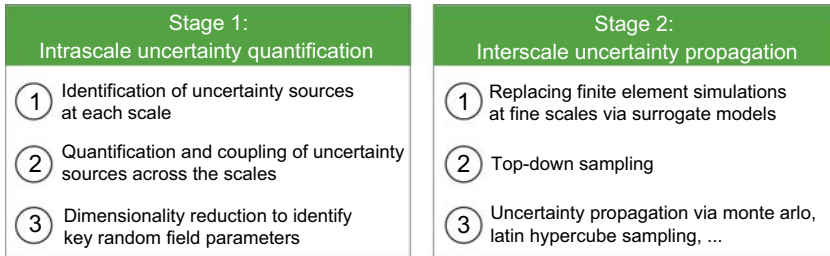


Figure 11.4 Our approach for multiscale UQ and UP. The proposed approach has two main stages. In the first stage, the various uncertainty sources across different scales are identified and modeled with RFs. In the second stage, many realizations from the multiscale material are generated via the top-down sampling approach and, subsequently, simulated to propagate the uncertainty across the scales. To address the significant computational costs of multiscale simulations, dimension reduction and metamodeling techniques are employed in the first and second stages, respectively.

scales, (ii) to connect the most important parameters of the RFs to the features of the material system and hence identify the dominant uncertainty sources in a *physically meaningful* way, and (iii) to allow for a *nonintrusive* UQ procedure by directly using the RFs' outputs in the multiscale FE simulations (instead of adapting the FE formulations for UQ and UP). Because of these reasons, we use the best linear unbiased predictor (BLUP) representation of *MRGPs*. We provide the details on MRGPs in [Section 11.2.1](#) but note here that they enable sensible characterization of uncertainty sources, are flexible and computationally efficient, and can be easily trained via available data [46,47].

At this point, the dimensionality in the UQ and UP tasks has been reduced from the number of degrees of freedom in the multiscale simulation to the few hyperparameters of the MRGP at the coarsest scale (see [Sections 11.2.1 and 11.2.2](#) for the details). However, depending on the material system and quantities of interest, generally not all the hyperparameters need to be considered in the UP process. Hence, further *dimensionality reduction* can be achieved by identifying the dominant uncertainty sources and, equivalently, the corresponding RF parameters through, e.g., *sensitivity analysis*.

The second stage of our approach starts by replacing the nested simulations at fine scales via inexpensive but accurate *metamodels* (aka surrogates or emulators) to decrease the computational costs of a single multiscale simulation from hours (or even days) to minutes. The choice of the metamodel, its inputs, and its outputs depends on the nature of the FE simulation (we elaborate on this with an example in [Section 11.3.5](#)). Finally, the uncertainty at the highest scale (e.g., macroscale in [Fig. 11.1](#)) is quantified by propagating the uncertainty from all the finer scales in the UP process. During UP, various multiscale simulations are conducted where for each simulation one realization of the spatially varying quantities is used in the multiscale material. To generate each of these realizations, we introduce the *top-down* sampling approach where realizations are assigned to the spatially varying parameters from the coarsest scale to the finest scale in the material system. We elaborate on

the details in [Section 11.3.3](#) but note that this sampling strategy enables modeling (i) nonstationary and C^0 (i.e., continuous but not differentiable) spatial variations at the fine scales and (ii) partial correlations between the various uncertainty sources within and across scales. Although the top-down sampling method can be integrated with any analytical RF, we have chosen MRGPs since they are sufficiently flexible and possess a few hyperparameters which are all physically interpretable. Additionally, other RFs can sometimes be converted into GPs upon appropriate transformations. In [Fig. 11.5](#), our approach is demonstrated for a composite with two length scales where top-down sampling is employed to determine the hyperparameters of each RF corresponding to each mesostructure.

More details on the proposed approach are provided below and in [Section 11.3](#) where it is used to propagate the microscale and mesoscale uncertainties in a cured woven fiber composite to quantify its macroscale uncertainty.

11.2.1 Multiresponse Gaussian processes for uncertainty quantification

MRGPs are widely popular in RF and surrogate modeling [[46,48–54](#)] and have been used in a wide range of applications including UQ [[48,52](#)], machine learning [[55](#)], sensitivity analyses of complex computer models [[56](#)], Bayesian optimization [[57](#)], and tractable Bayesian calibration [[58–62](#)]. For an RF with q outputs $\mathbf{y} = [y_1, \dots, y_q]^T$ and the field (e.g., spatial or temporal) inputs $\mathbf{x} = [x_1, \dots, x_d]^T$, the BLUP representation of an MRGP with *constant prior means* reads as follows:

$$\mathbf{y} \sim \mathbb{N}_q(\boldsymbol{\beta}, c(\mathbf{x}, \mathbf{x}')), \quad (11.1)$$

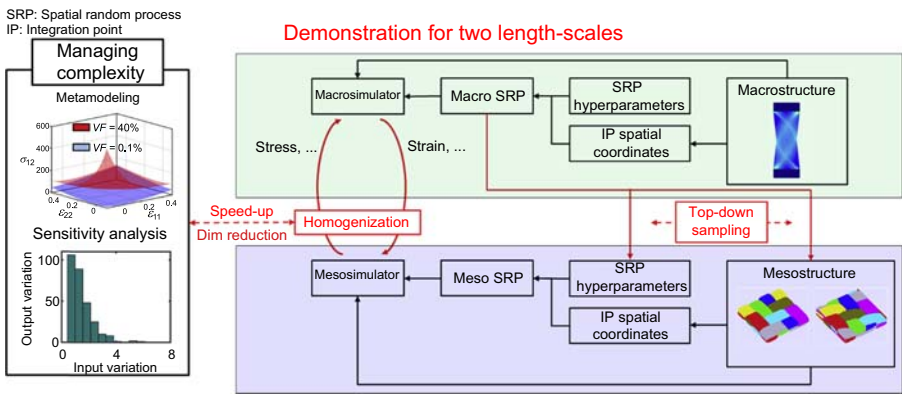


Figure 11.5 Demonstration of our approach for a two-scale structure. Spatial random processes (SRPs) are employed for generating spatial variations which are connected through the top-down sampling procedure.

where $\mathbb{N}_q$ represents a q – dimensional Gaussian process, $\boldsymbol{\beta} = [\beta_1, \dots, \beta_q]^T$ is the vector of responses' means, and $c(\mathbf{x}, \mathbf{x}')$ is a parametric function that measures the covariance between the responses at $\mathbf{x}$ and $\mathbf{x}'$. One common choice for $c(\mathbf{x}, \mathbf{x}')$ is as follows:

$$c(\mathbf{x}, \mathbf{x}') = \boldsymbol{\Sigma} \exp \left\{ \sum_{i=1}^d -10^{\omega_i} (x_i - x'_i)^2 \right\} = \boldsymbol{\Sigma} r(\mathbf{x}, \mathbf{x}'), \quad (11.2)$$

where $\boldsymbol{\Sigma}$ is a $q \times q$ symmetric positive definite matrix that captures the marginal variances and the covariances between the outputs, d is the dimensionality of the field, and $\boldsymbol{\omega} = [\omega_1, \dots, \omega_d]^T$ are the so-called roughness or scale parameters that control the smoothness of the RF. Note that the dimension of $\boldsymbol{\beta}$ and $\boldsymbol{\Sigma}$ depends on q , while that of $\boldsymbol{\omega}$ depends on d . The parameters $\boldsymbol{\beta}$, $\boldsymbol{\Sigma}$, and $\boldsymbol{\omega}$ are called the hyperparameters of an MRGP model and, collectively, enable it to model a wide range of random processes:

- The mean values of the responses over the entire input space are governed by $\boldsymbol{\beta}$.
- The general correlation between the responses (i.e., y_i and y_j , $i \neq j$) over the input space is captured by the off-diagonal elements of $\boldsymbol{\Sigma}$.
- The variations around the mean for each of the responses are controlled by the diagonal elements of $\boldsymbol{\Sigma}$.
- The smooth/rapid spatial changes of the responses across the input space are controlled by $\boldsymbol{\omega}$.

In case some experimental data are available, all the hyperparameters of an MRGP model can be estimated via, e.g., the maximum likelihood method. Otherwise, as in this work, expert or prior knowledge can be used to adjust these parameters and model a spatially varying quantity. Once these hyperparameters are determined, generating realizations from an MRGP model is achieved through a closed-form formula.

11.2.2 Top-down sampling for uncertainty propagation

To carry out one multiscale simulation, material properties must be assigned to all the IPs at all scales where the IP properties at any scale depend on an RVE at the next finer scale (this RVE itself has many IPs). Since these properties depend on the uncertainty sources (or, equivalently, on the RFs), the latter must be coupled across the scales. Recall that, due to the multiscale nature of the structure, the number of RFs significantly increases at the fine scales because we associate an RF to *each* structure realization. For instance, in the two-scale structure in Fig. 11.3, there will be $10,000 + 1$ RFs; one for the mesostructure and 10,000 for its IPs (corresponding to the microstructures). The mesoscale RF will, in essence, characterize the spatial variations of the microscale RFs.

Having used RFs whose parameters are physically sensible and can be directly linked to the uncertainty sources, this cross-scale coupling is straightforward and can be achieved with top-down sampling where the *outputs* of the MRGP at each IP of a particular scale serve as the *hyperparameters* of the MRGP of the RVE associated with that IP. This process constitutes *nested* RFs. To assign values to the IP

parameters in the entire multiscale structure, this approach starts from the coarsest or top scale and hence the name top-down sampling. In the above example, the mesoscale MRGP is first used to assign values to the mesoscale IPs which essentially assigns values to the hyperparameters of the 10,000 MRGPs at the microscale. Then, these latter MRGPs are used to assign values to the IPs of each microstructure.

While the top-down sampling method works with any parametric RF representation (e.g., PCE or KL expansion), we highly recommend employing compact representations that include a few hyperparameters. This is mainly because the number of hyperparameters at the coarse scales increases rapidly as the number of spatially varying quantities increases at the fine scales. For instance, assuming three (two) quantities change spatially in the 3D microstructure in Fig. 11.3, an MRGP with 12 (8) hyperparameters is required. To model the spatial variations of these 12 (8) hyperparameters at the mesoscale, an MRGP with 93 (47) hyperparameters is required.

Finally, we note that the top-down sampling method, in essence, discretizes a structure into mutually exclusive and collectively exhaustive sections at any length scale and, subsequently, enables using a particular RF for each section. The C^0 continuity refers to this scenario: within each section, the moments change continuously and differentiably, while across the sections they are not differentiable. In our implementation, each section corresponds to an IP.

11.3 Uncertainty quantification and propagation in cured woven fiber composites

Woven fiber composites possess a hierarchical structure where multiple sources of uncertainty exist across the scales. We now follow the steps of our approach to quantify the macroscale uncertainty in the elastic response of a cured woven composite as a function of spatial variations in seven uncertainty sources: fiber volume fraction and misalignment, matrix and fiber modulus, and yarns' geometry parameters (i.e., yarn angle, height, and spacing). As illustrated in Fig. 11.6(a), the structure is composed of four identical woven plies that are stacked in the same orientation and constitute a total thickness of 2.4 mm (the fiber orientations are indicated with light blue lines).

The geometry of these woven plies is obtained via the bias-extension simulation of woven prepreps using the nonorthogonal constitutive preforming model [63]. While the bottom of the sample is clamped, the other end is pulled by 1 mm to generate the bias tension deformation. In the macroscale simulations, 3D solid continuum elements are employed to discretize the structure. As our focus is on UQ and UP, at this point we have assumed that only elastic deformation occurs.

11.3.1 Uncertainty sources

Longitudinal fiber and matrix moduli, E_f and E_m , are the first two uncertainty sources. Given the moduli, the yarn material properties primarily depend on two parameters: fiber volume fraction (in yarn), v , and fiber misalignment. While in most previous

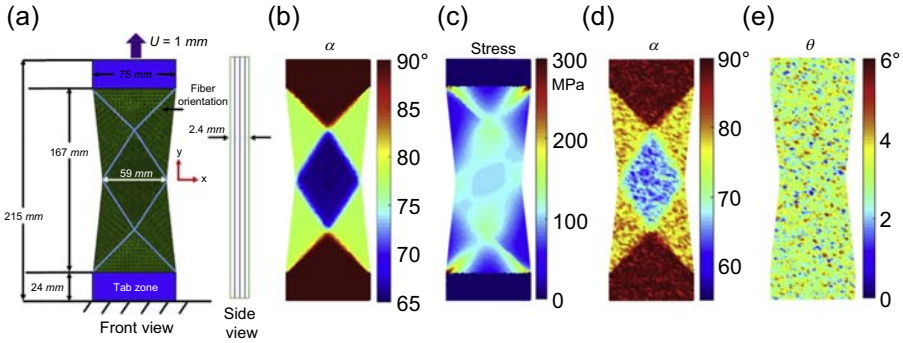


Figure 11.6 The macroscopic cured woven laminate structure studied in our work. (a) The deformed structure. The light blue lines indicate the fiber orientation. The dimensions are scaled for a clearer representation. (b) The deterministic spatial variations of yarn angle obtained from simulating a perfectly manufactured composite. (c) Von Mises stress field corresponding to Case 9 in Section 11.3.6. (d) The random spatial variations of yarn angle corresponding to one of the realizations of Case 1 in Section 11.3.6. (e) The random spatial variations of θ corresponding to one of the realizations of Case 3 in Section 11.3.6.

works ν is postulated to be spatially constant [64–66], in practice, it varies along the yarn path particularly where yarns have compact contact [6,7]. Consequently, our next uncertainty source arises from the spatial variations of ν which starts from the micro-scale and propagates to mesoscale and macroscale. In this work, we have assumed that $45\% \leq \nu \leq 65\%$ based on our material system.

During the manufacturing process, the fibers in the yarn deviate from the ideal orientation and render the cross section of the yarn heterogeneous and anisotropic. These deviations result in fiber misalignment which is different from the concept of fiber waviness in that a fiber can be perfectly waved without misalignment. As illustrated in Fig. 11.7, this misalignment can be characterized by the two angles φ and θ which measure the deviation of the fiber direction, f_i , with respect to the local orthogonal frame on the yarn cross section, g_k . Based on the available experimental data in the literature [6], in this work, we have assumed $-\pi \leq \varphi \leq \pi$ and $0^\circ \leq \theta \leq 90^\circ$. To ensure that the introduction of fiber misalignment does not change the yarn angle and is physically realistic, we enforce the sum of deviations with respect to the yarn centerline to equal zero (see section Details on the sensitivity studies at the mesoscale for implementation details).

In modeling the mesoscale woven composites, the yarn architecture is often presumed to be perfect where the yarn angle (α , the angle between the warp and the weft, see Fig. 11.2(a)) is set to 90° and the yarn height, h , and spacing, s , are fixed to their nominal values. These assumptions do not hold in practice due to the large in-plane shear deformation during preforming process and manufacturing imperfections. Hence, we also investigate the effect of the spatial variations of the woven RVE architecture (α , h , and s) on the macroscopic properties.

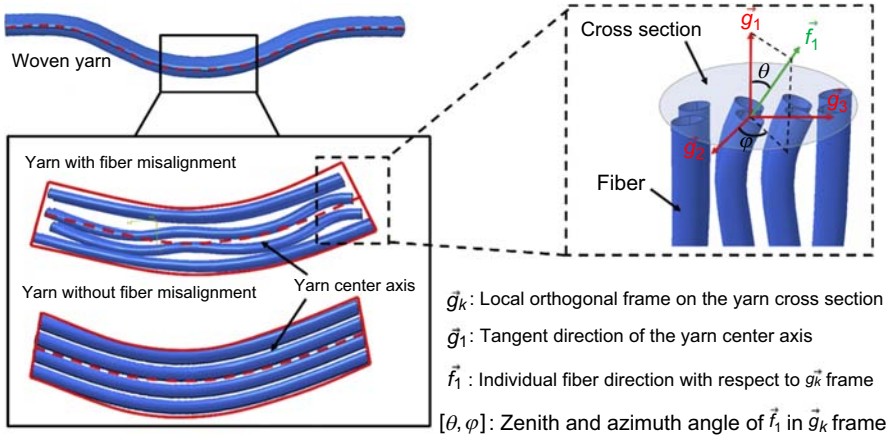


Figure 11.7 Fiber misalignment angles. The zenith and azimuth angles characterize the fiber misalignment angle with respect to the local orthogonal frame on the yarn cross section.

Lastly, we note that in our example the deterministic spatial variation of α in a perfectly manufactured composite is, as opposed to the other parameters (i.e., $[v, \varphi, \theta, h, s]$), available from the preforming process simulation [67]. This deterministic variation is used as the prior mean (β in Eq. 11.1) of spatial distribution of α , while for the other six parameters the nominal values are employed as the (spatially constant) prior mean. In all seven parameters, the posterior spatial variations are stochastic.

11.3.2 Multiscale finite element simulations

We employ the computational homogenization technique for modeling the multiscale woven sample where the material property at any length scale is calculated through the homogenization of an RVE at the lower scale. Below, we elaborate on the details of the FE simulations at each scale. It is noted that while in traditional multiscale homogenization it is assumed that macroscale and mesoscale IPs represent the same microstructure, we assign different microstructures to each IPs at each length scale.

At the microscale, the RVEs consist of $300 \times 300 \times 60$ voxels ($42 \times 42 \times 8.4 \mu\text{m}$) and the fibers have a diameter of $7 \mu\text{m}$ (see Fig. 11.8). The simulations are elastic where periodic boundary conditions (PBCs) are employed. It is assumed that the fibers and the matrix are well bonded and there are no voids. To obtain the stiffness matrix, $\mathbf{C}$, of the UD RVE, six stress-free loading states are applied (i.e., only one of the ε_{xx} , ε_{yy} , ε_{zz} , ε_{xy} , ε_{xz} , and ε_{yz} strain components are applied in each case). Since the simulations are elastic, $\mathbf{C}$ mainly depends on the volume fraction, v [68].

At the mesoscale, the open source software *TexGen* [33] is used to create the geometry and mesh for the 2×2 twill woven RVE (see Fig. 11.2(a)) with eight yarns.

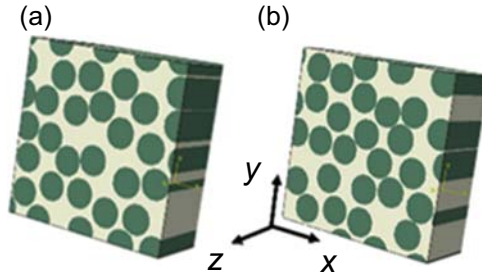


Figure 11.8 Sample UD RVEs at the microscale. Two UD RVEs with randomly distributed fibers. Both RVEs have periodic boundaries and a volume fraction, ν , of 58%. These UD RVEs correspond to mesoscale IPs and their deviation from the yarn centerline models fiber misalignment.

To generate such an RVE in *TexGen*, the yarns' paths, cross sections, and the weaving patterns must be prescribed. Yarns' paths in *TexGen* are represented by 3D spatial curves and their cross sections are defined as 2D ellipses perpendicular to the tangent of yarn centerline. The space between the yarns is filled with matrix, and voxel meshes are used to discretize the RVE where each voxel is designated to either a yarn or the matrix. To balance cost and accuracy, we have used a voxel mesh with 625,000 elements. To reduce the computation costs, PBCs are employed throughout. We note that, if PBCs are prescribed correctly, the homogenized stress–strain response does not scale with the RVE size [68].

The nominal properties of carbon fibers and epoxy resin were taken from manufacturer's data (see Table 11.1). The resin is isotropic, and its material properties are taken from pure epoxy. Yarns with well-aligned fibers are treated as transversely isotropic. With fiber misalignment, however, yarns are not transversely isotropic since the material frame across the IPs on their cross section is nonuniformly distributed. In this case, the microplane triad model proposed by Kedar et al. [69] is employed to account for fiber misalignment by defining an orthotropic microtriad, $\vec{f}_k$, for each IP of the yarn. This triad is related to the local frame, $\vec{g}_k$ (see Fig. 11.7), via the misalignment angles:

$$\vec{f}_1 = \cos(\theta) \frac{\vec{g}_1}{|\vec{g}_1|} + \sin(\theta) \cos(\varphi) \frac{\vec{g}_2}{|\vec{g}_2|} + \sin(\theta) \sin(\varphi) \frac{\vec{g}_3}{|\vec{g}_3|}, \quad (11.3)$$

Table 11.1 Fiber and matrix properties.

	E_{zz}	$E_{xx} = E_{yy}$	$\nu_{zx} = \nu_{zy}$	ν_{xy}	$G_{xz} = G_{yz}$	G_{xy}
Carbon fiber	275	19.8	0.28	0.32	29.2	5.92
Epoxy resin	3.25	3.79	0.39	0.39	1.36	1.36

The moduli (i.e., E and G) are all in GPa. See Fig. 11.8 for the definition of the coordinate system. Poisson's ratios along different directions are also provided.

$$\vec{f}_2 = -\sin(\theta) \frac{\vec{g}_1}{|\vec{g}_1|} + \cos(\theta)\cos(\varphi) \frac{\vec{g}_2}{|\vec{g}_2|} + \cos(\theta)\sin(\varphi) \frac{\vec{g}_3}{|\vec{g}_3|}, \quad (11.4)$$

$$\vec{f}_3 = \vec{f}_1 \wedge \vec{f}_2, \quad (11.5)$$

where $|\cdot|$ and $\wedge$ denote, respectively, the norm of a vector and the cross product. As for the local frame $\vec{g}_k$, it is automatically generated by *TexGen* for each IP (each voxel at the mesoscale) once the woven RVE is discretized. We note that the stiffness matrix at each yarn material point is obtained via the UD-RVE homogenization. We also note that there are three principal material directions before deformation, two of which coincide with the two yarn orientations (warp and weft, see Fig. 11.2), and the third one is perpendicular to the plane of the two yarn orientations. Hence, monoclinic material model is used to describe the material properties. In our simulation, after the deformation, we project all the stiffness constants into the orthogonal frame rather than calculating them in the nonorthogonal principal material direction (which deforms with the material). To this end, total Lagrangian formulation is used to calculate the strain and update the stress state. With this approach, the stress and strain can be accurately computed even for large strain deformations.

To link the mesoscale and macroscale, the stress–strain relations for effective elastic material properties of woven RVE are required. This relation can be written in terms of the symmetric mesoscale stiffness matrix as follows:

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{12} \\ \sigma_{13} \\ \sigma_{23} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{22} & C_{23} & C_{24} & 0 & 0 \\ & & C_{33} & C_{34} & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & Sym. & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{12} \\ 2\varepsilon_{13} \\ 2\varepsilon_{23} \end{bmatrix}, \quad (11.6)$$

where coordinate 3 is in the thickness direction of the woven RVE (see Fig. 11.2(a)). If $\alpha = 90^\circ$, coordinates 1 and 2 coincide with the warp and weft directions and the effective material behavior can be described with an orthotropic material model. If $\alpha \neq 90^\circ$, a monoclinic material model is used instead.

11.3.3 Top-down sampling, coupling, and random field modeling of uncertainty sources

To help clarify the descriptions, we first introduce some notation. We denote the three scales with numbers: $1 \rightarrow \text{Macro}$, $2 \rightarrow \text{Meso}$, and $3 \rightarrow \text{Micro}$. Superscript and subscripts denote, respectively, scales and IPs. Variables with a bar represent averaged

quantities over all the IPs at a particular scale. For instance, v_i^1 denotes the fiber volume fraction assigned to the i th IP at the macroscale. $\bar{\theta}^2 = \frac{1}{N} \sum_{i=1}^N \theta_i^2$ represents the average misalignment (zenith) angle at the mesoscale for a woven RVE.

The uncertainty sources in our composite are summarized in Table 11.2. While some sources are only defined among different structures (under spatial variations across realizations), others possess an extra degree of variation in that they also change within structures. For instance, a mesoscopic woven RVE only has one yarn angle (so it cannot spatially vary) which can be different than another woven RVE's yarn angle. However, in case of fiber volume fraction which is assigned to each mesoscale IP, the distributional characteristics (such as mean and variance) can be different between two woven RVEs. The existence of a distribution conveys that fiber volume fraction also changes across the IPs of a specific woven RVE. As motivated in Section 11.2, we use MRGPs to model all the spatial variations (other RF representations can also be used at the expense of more computations).

Assuming the eight tows in a woven RVE are statistically independent and the spatial variations within them originate from the same underlying random process [5], a total of 12 hyperparameters are required to completely characterize the spatial variations of $[\theta_i^2, \varphi_i^2, v_i^2]$ by an MRGP (see Eq. 11.1): three mean values ($\beta = [\beta_v, \beta_\varphi, \beta_\theta]^T$), six variance/covariance values for $\Sigma \left(\begin{bmatrix} \sigma_{vv}^2, \sigma_{\varphi\varphi}^2, \sigma_{\theta\theta}^2, \sigma_{v\varphi}^2, \sigma_{v\theta}^2, \sigma_{\varphi\theta}^2 \end{bmatrix} \right)$, and three roughness parameters ($\omega = [\omega_x, \omega_y, \omega_z]^T$ where xyz denotes the Cartesian coordinate system at the mesoscale). Once these parameters are specified, the spatial coordinates of the IPs in a woven RVE can be used to assign realizations of v , φ , and θ to them (see Appendix). For each IP at the macroscale, however, these 12 hyperparameters serve as some of the responses of the macroscale MRGP whose other responses correspond to $[E_{f_i}^2, E_{m_i}^2, \alpha_i^2, s_i^2, h_i^1]$. Therefore, the macroscale MRGP has a total of 173 hyperparameters (17 mean values for β , 153 unique covariance/variance values for Σ , and 3 values for $\omega = [\omega_\eta, \omega_\xi, \omega_\zeta]^T$ where $\eta\xi\zeta$ denotes the Cartesian coordinate system at the macroscale). In the top-down sampling approach, first the 173 hyperparameters of the macroscopic MRGP are prescribed. Then, this MRGP is sampled to assign 17 values to each macroscopic IP where 12 of them serve as the hyperparameters of the mesoscopic MRGPs, 3 of them are employed to construct the woven RVE, and 2 of them

Table 11.2 Uncertainty sources for one macrostructure realization.

Scale	Uncertainty sources	
	Spatial variation across realizations	Spatial variation within a realization
Micro	$\bar{v}^3, E_f, E_m$	None
Meso	$\theta_i^2, \varphi_i^2, v_i^2, E_f, E_m, \alpha^2, s^2, h^2$	$\theta_i^2, \varphi_i^2, v_i^2$
Macro	NA	$\theta_i^1, \varphi_i^1, v_i^1, E_{f_i}^1, E_{m_i}^1, \alpha_i^1, s_i^1, h_i^1$

The sources are fiber misalignment angles (θ and φ), yarn spacing and height (s and h), fiber and matrix moduli (E_f and E_m), fiber volume fraction (v), and yarn angle (α).

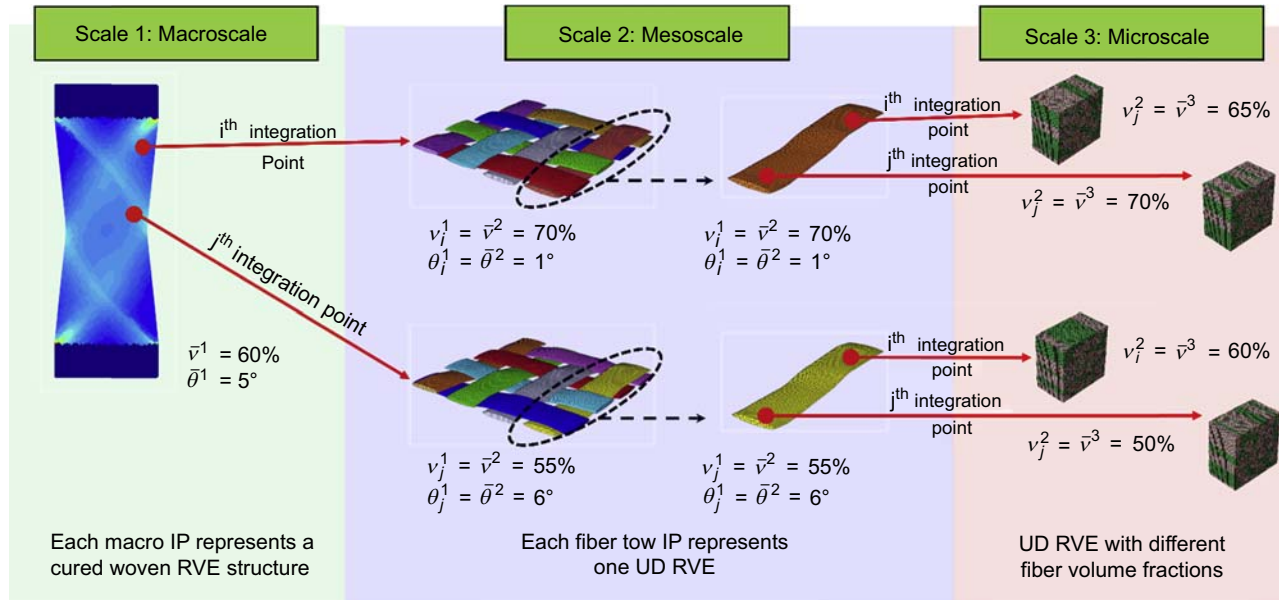


Figure 11.9 Coupling the uncertainty sources across the scales. The spatial variations of v and θ at the macroscale are connected to those at the finer scales. For brevity, the coupling is illustrated only for the average values for the two quantity (i.e., the mean of the RFs: $\beta = [\beta_v, \beta_\theta] = [\bar{v}^2, \bar{\theta}^2]$). The same method applies to other parameters of the random field (β_ϕ , Σ , and ω). The macrostructure contains 15,000 IPs. Each mesoscopic woven RVE contains 625,000 IPs where 525,000 IPs belong to the eight tows and the rest to the matrix.

to determine the fiber and matrix moduli. This process is illustrated in Fig. 11.9 where, for clarity, only two (out of the 17) hyperparameters at the mesoscale are presented.

We note that some parameters might not spatially vary according to a normal distribution. In such cases, we recommend using appropriate transformations to convert the distribution into a Gaussian one. For instance, the zenith misalignment angle has a log-normal distribution [6] and so we carry out all the computations in the log space and then revert to the original scale via exponentiation. Sample spatial variations of v^2 , ϕ^2 , and θ^2 over the woven RVE are illustrated in Fig. 11.10. Such variations are controlled by adjusting the parameters of the MRGP (see Section 11.2.1).

If transformation is not possible or the Gaussian assumption is far from reality, non-Gaussian RFs can be used in the top-sampling procedure in the expense of higher computational costs. For instance, polynomial chaos expansion, PCE [70], can be used to model the spatially varying uncertainty sources. However, one has to ensure that the prescribed bases and coefficients in the PCE correspond to reality. Another possibility is to use RF models developed for UQ of PDEs with stochastic coefficients, see for example [71–75].

11.3.4 Dimension reduction at the mesoscale via sensitivity analysis

By modeling the spatial variations via RFs, the dimensionality of the UQ and UP problem has decreased to the number of RF hyperparameters. Although this is a significant reduction, the considerable cost of multiscale simulations (even in the linear analysis) renders the UQ and UP process computationally demanding. To address this issue, we note that depending on the property of interest a subset of uncertainty sources are generally the dominant ones in physical systems. Since our composite undergoes an elastic deformation, we expect a small subset of the uncertainty sources (i.e., RF hyperparameters) to be important.

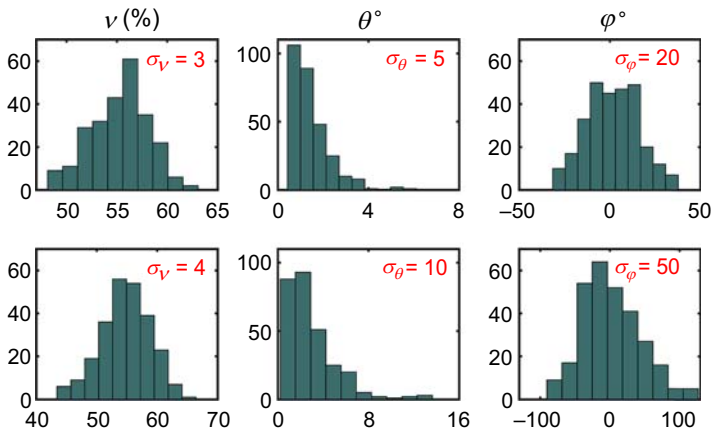


Figure 11.10 Sample spatial variations of v^2 , ϕ^2 , and θ^2 for different variances. The spatial variations belong to a randomly selected cross section of a yarn with the averages of 55%, 3, and 0°, respectively. The distribution of θ^2 is log-normal distribution.

Table 11.3 Case studies to determine the effect of fiber misalignment and its spatial variations.

Case ID	Description
1	$(1^\circ, 1, 20^2)$
2	$(1^\circ, 5, 20^2)$
3	$(1^\circ, 10, 20^2)$
4	$(3^\circ, 1, 20^2)$
5	$(3^\circ, 5, 20^2)$
6	$(3^\circ, 10, 20^2)$
7	$(5^\circ, 1, 20^2)$
8	$(5^\circ, 7, 20^2)$
9	$(5^\circ, 10, 20^2)$
10	$(1^\circ, 1, 50^2)$
11	$(1^\circ, 5, 50^2)$
12	$(1^\circ, 10, 50^2)$
13	$(3^\circ, 1, 50^2)$
14	$(3^\circ, 5, 50^2)$
15	$(3^\circ, 10, 50^2)$
16	$(5^\circ, 1, 50^2)$
17	$(5^\circ, 7, 50^2)$
18	$(5^\circ, 10, 50^2)$

The triplets in the description fields correspond to $(\bar{\theta}^2, \text{var}(\theta^2), \text{var}(\varphi^2))$.

We conducted multiscale sensitivity analyses to determine which of the 12 hyperparameters of an MRGP model are the most important ones (and must be considered in UP) based on their impact on mesoscale material response. Our studies (see Table 11.3) consisted of changing one of the hyperparameters (while keeping the rest of them fixed) and conducting 20 simulations to account for the randomness. Then, if the variations in the homogenized response (effective moduli) were negligible, the hyperparameter was deemed as insignificant and set to a constant thereafter. For brevity, we summarize the results below and include the details in the Appendix (see section [Details on the sensitivity studies at the mesoscale](#)). All the simulations in this section were conducted on a woven RVE with $\alpha = 90^\circ$.

We found that the *homogenized moduli* (see Eq. 11.6) are affected by neither the six covariance/variance values (i.e., $[\sigma_{vv}^2, \sigma_{\varphi\varphi}^2, \sigma_{\theta\theta}^2, \sigma_{v\varphi}^2, \sigma_{v\theta}^2, \sigma_{\varphi\theta}^2]$) nor the three roughness parameters $\omega = [\omega_x, \omega_y, \omega_z]^T$. In case of average values (i.e., β), the average fiber volume fraction ($\bar{v}$) and zenith angle ($\bar{\theta}$), as opposed to that of the azimuth angle, were found to considerably affect the homogenized response of a woven RVE at the

mesoscale. The effect of average values on the effective moduli is summarized in Fig. 11.11. As illustrated in Fig. 11.11(a), the moduli increase linearly as a function of average fiber volume fraction. Comparing the first nine cases in Fig. 11.11(b) with the last nine cases, it can be concluded that $\text{var}(\varphi^2)$ insignificantly affects the moduli and poison ratios. Fig. 11.11(b) also indicates that the deviations from the reference solution increase as $\bar{\theta}^2$ increases ($\bar{\theta}^2$ increases between the jumps, see Table 11.3).

It must be noted that since we are interested in the elastic response of the multiscale composite in Fig. 11.6(a), the variations of *effective* moduli were only considered in our sensitivity studies. As opposed to the effective behavior, the local behavior (i.e., stress field) of the woven RVE is quite sensitive to the spatial variations of both ν and θ (but not φ) and must be considered in nonlinear analysis, see Fig. 11.12 for the differences between stress fields in each case.

11.3.5 Replacing meso- and microscale simulations via metamodels

To further reduce the multiscale UQ and UP costs, we employ metamodels to replace the micro- and mesoscale FE simulations corresponding to each macroscale IP. In particular, the metamodel captures the macroscale spatial variations of the stiffness matrix (see Eq. 11.6) of the woven RVEs associated with the macroscale IPs as a function of yarn angle (α^2), average volume fraction ($\bar{\nu}^2$), yarn height (h) and spacing (s), average misalignment angle ($\bar{\theta}^2$), and fiber and matrix moduli (E_f and E_m). In machine learning parlance, the inputs and outputs of the metamodel are, respectively, $[\alpha^2, \bar{\nu}^2, s^2, h^2, \bar{\theta}^2, E_f, E_m]$ and the stiffness matrix $\mathbf{C}$ of a woven RVE. We note that if the mesoscale spatial variations of the fiber volume fraction and misalignment angle were found to be important in Section 11.3.4, the metamodel would have had the corresponding hyperparameters of the MRGP (e.g., $\sigma_{\nu\nu}^2$ and $\sigma_{\theta\theta}^2$) as inputs.

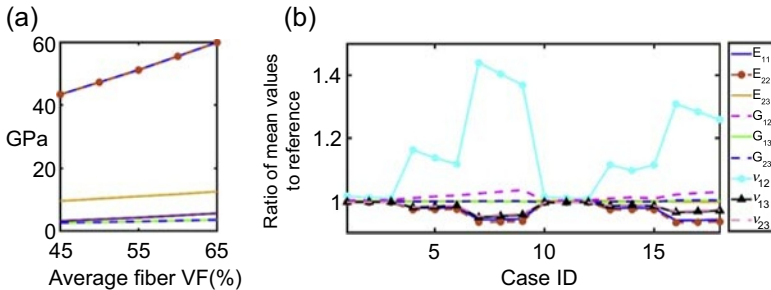


Figure 11.11 Effect of average values on the effective moduli of a woven RVE. (a) Effect of fiber volume fraction and (b) effect of misalignment. Each *point* on these figures indicates the average value over 20 simulations. See Fig. 11.2(a) for the definition of the coordinate system. The Case IDs in (b) are defined in Table 11.3. The reference solution refers to a case where there is no misalignment.

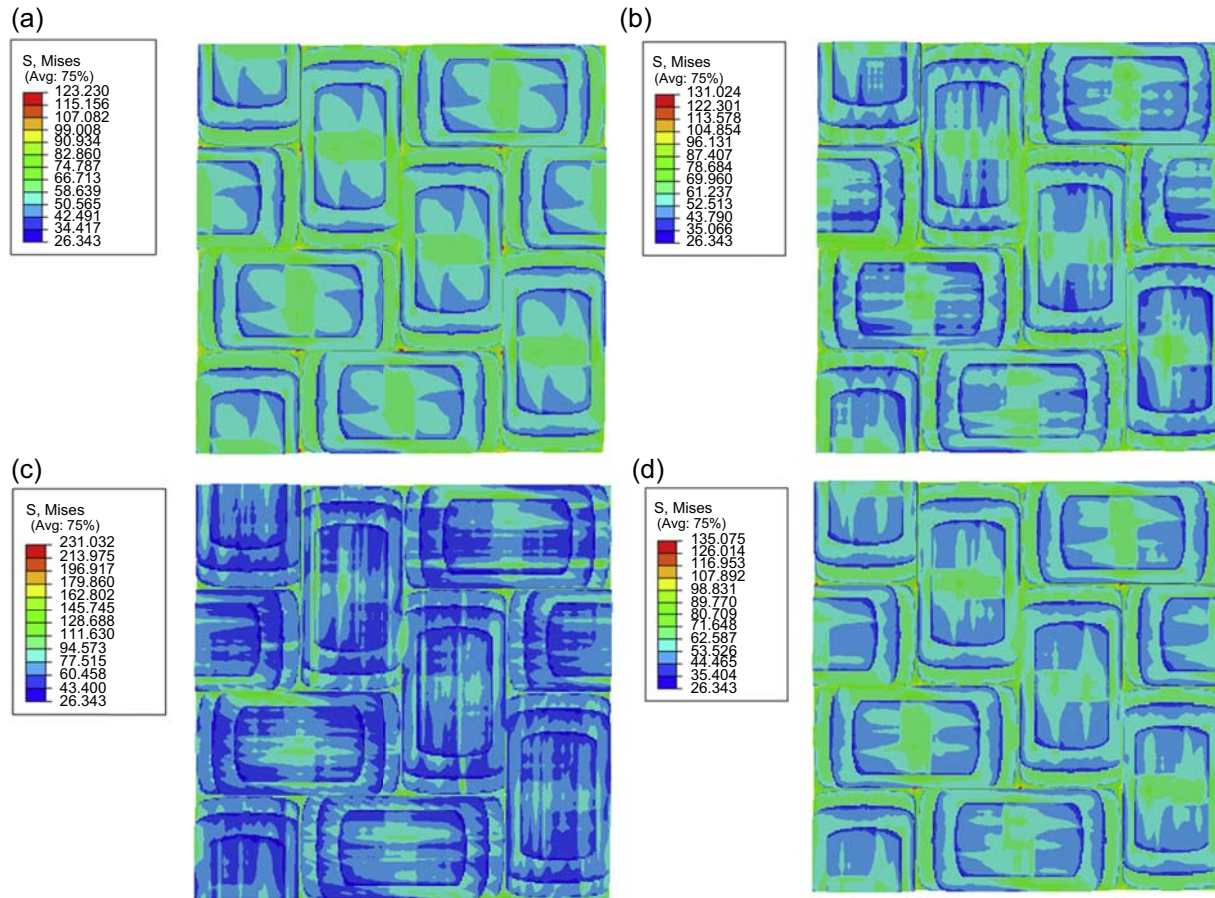


Figure 11.12 Effect of spatial variations on the stress field (MPa). Stress fields for (a) no fiber misalignment and no spatial variations in v . (b) Only spatial variations in v where $\sigma_{vv}^2 = 16\%$ and $\omega = 1$. (c) Only spatial variations in φ and θ where $\bar{\varphi} = 0^\circ$, $\bar{\theta} = 15^\circ$, $\sigma_{\varphi\varphi}^2 = 2500$, $\sigma_{\theta\theta}^2 = 2$, $\omega_\theta = 1$, and $\omega_\varphi = 1$. (d) Same settings as in (c) but with $\bar{\theta} = 2^\circ$ and $\sigma_{\varphi\varphi}^2 = 400$. In all simulations, $\bar{v} = 65\%$.

To fit the metamodel, we generated six training datasets of sizes 60, 70, ..., 110 with Sobol sequence [76,77] for $\alpha^2 \in [45^\circ, 90^\circ]$, $s^2 \in [2.2, 2.5]$ mm, $h^2 \in [0.3, 0.34]$ mm, $\bar{v}^2 \in [40\%, 70\%]$, $E_f^2 \in [150, 400]$ GPa, $E_m^2 \in [1.5, 5]$ GPa, and $\bar{\theta}^2 \in [0^\circ, 6^\circ]$. Afterward, we fitted an MRGP metamodel to each dataset. The accuracy of each model was then evaluated against a validation dataset with 30 samples via

$$e = 100 \sqrt{\frac{1}{30} \sum_{i=1}^{30} \left(1 - \frac{\hat{y}_i}{y_i} \right)^2} \% , \quad (11.7)$$

where $\hat{\mathbf{y}} = [\hat{y}_1, \dots, \hat{y}_{30}]$ and $\mathbf{y} = [y_1, \dots, y_{30}]$ are obtained from, respectively, the metamodel and FE simulations. The prediction error of each model is illustrated in Fig. 11.13 where it is evident that with roughly 100 samples all the elements of $\mathbf{C}$ can be predicted with less than 6% error.

11.3.6 Results on macroscale uncertainty

Multiple macrosimulations are conducted where θ_i^1 , v_i^1 , E_f^1 , $E_{m_i}^1$, α_i^1 , s_i^1 , and h_i^1 change spatially across the macroscale IPs. To quantify the importance of these variables' spatial variations on the macroscopic behavior, eight cases are considered. As detailed in Table 11.4, the spatial variations are changed with an MRGP at the macroscale in a controlled manner from one case to the next. Except for the last case, 20 independent macroscale simulations are conducted for each case to account for the randomness. In summary, a total of 161 macroscale simulations are conducted. The last case study serves as the reference where there is no misalignment, α_i^1 is determined via the processing simulation over the structure as illustrated in Fig. 11.6(b), and all other parameters are set to their nominal values,

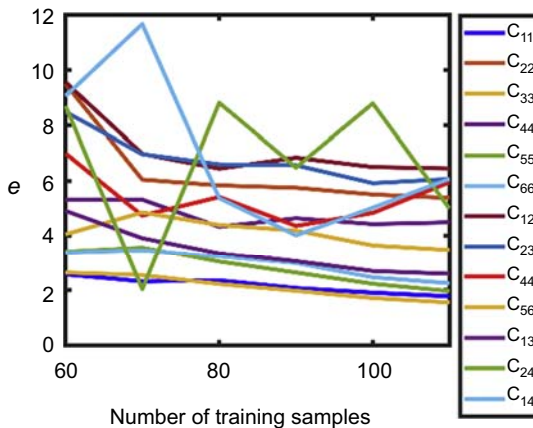


Figure 11.13 Prediction error as a function of the number of training samples. As the number of training samples increases, the accuracy of the MRGP metamodel in predicting the elements of the stiffness matrix of the mesoscale woven RVE increases.

Table 11.4 Description of the simulation settings.

	Description
Case 1	Spatial variations in α with its prior spatial distribution determined by processing simulation
Case 2	Spatial variations in fiber volume fraction with a constant prior of 55% over the structure
Case 3	Spatial variations in fiber misalignment with a constant prior of 3° over the structure
Case 4	Spatial variations in yarn spacing with a constant prior of 2.35 mm over the structure
Case 5	Spatial variations in yarn height with a constant prior of 0.32 mm over the structure
Case 6	Spatial variations in fiber modulus with a constant prior of 275 GPa over the structure
Case 7	Spatial variations in matrix modulus with a constant prior of 3.25 GPa over the structure
Case 8	Spatial variations in all parameters
Case 9	All parameters set to nominal values (α from processing simulation) and no misalignment

Nine simulation cases are considered to quantify the macroscale uncertainties and the relative importance of spatial variations. MRGPs are employed to generate random realizations in all cases. Except for Case 9 (reference simulation), all cases consist of 20 simulations to account for randomness where only one uncertainty source exists.

i.e., $v_i^1 = 55\%$, $E_{fi}^1 = 275 \text{ GPa}$, $E_{mi}^1 = 3.25 \text{ GPa}$, $s_i^1 = 2.35 \text{ mm}$, and $h_i^1 = 0.32 \text{ mm}$. In Cases 1 through 7, the effect of spatial variations is considered for one parameter at a time where the amount of variations with respect to the prior mean is controlled by the variance of the macroscale MRGP (see Eq. 11.2). In these cases, we set the variance associated with the spatially varying parameter to, respectively, 9, 25, 1, 0.05^2 , 0.01^2 , 40^2 , and 1. These variances are large enough to capture realistic spatial variations while small enough to ensure that the realized values are not outside the ranges where the mesoscale MRGP meta-model is fitted (see Section 11.3.5). Sample spatial variations for Cases 1 and 3 are demonstrated in Fig. 11.6 (b) through (e).

Since in reality the uncertainty sources coexist, in Case 8 we consider the effect of all the uncertainty sources and their correlation. Here, the individual variances (diagonals of macroscale MRGP, Σ , in Eq. 11.2) are the same as in Cases 1 through 7, while the covariances are chosen to reflect the negative correlation between the fiber volume fraction and both yarn angle and fiber misalignment. To this end, we choose $[\sigma_{\alpha v}, \sigma_{\alpha \theta}, \sigma_{v \theta}] = [-9, 3, -3]$ and set the rest of the off-diagonals of Σ to zero. We note that $\sigma_{\alpha v}$ is negative to model the increase in fiber volume fraction as the yarns get closer after preforming. $\sigma_{v \theta}$ is also negative to consider the decrease in misalignment angle in rich fiber regions [6].

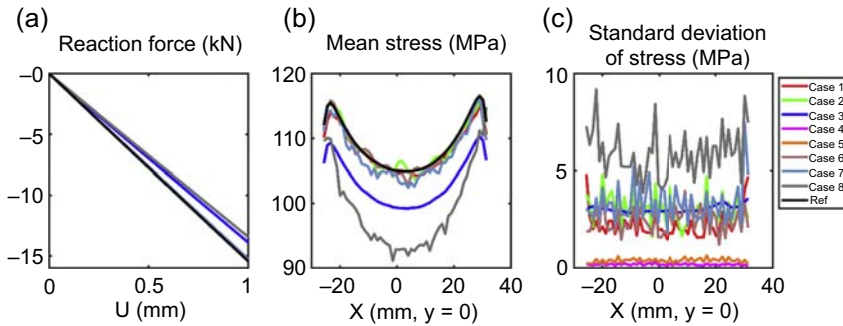


Figure 11.14 Global and local response of the macrostructure to the spatial variations. (a) Reaction force, (b) mean stress at the midsection, and (c) standard deviation of the stress field at the midsection. For Cases 1 through 8 in (b) and (c), the curves are based on 20 independent simulations. See Fig. 11.6(a) for the placement of the xy coordinate system. See Table 11.4 for the definition of the cases.

Fig. 11.14(a) compares the exerted force on the cross section of the sample for the nine cases where, for Cases 1 through 8, the force—displacement line is averaged over the 20 multiscale simulations. The results suggest that in the presence of fiber misalignment, the structure weakens and hence the reaction force decreases. This weakening is exacerbated in the presence of other uncertainty sources. In particular, while in the reference case the maximum reaction force (magnitude) is 15.4 kN, in Cases 3 and 8 it is 14 and 13.5 kN, respectively. These results indicate that (i) fiber misalignment must be accounted for in the simulation of composites even if one is primarily interested in the global response in linear analyses. (ii) The interaction among various uncertainty sources should be considered: once all the uncertainty sources are accounted for, the structure is more noticeably weakened with a 12.3% reduction in reaction force. (iii) The insensitivity to the spatial variations of some parameters can be explained by the fact that in linear analyses the global response is mainly affected by the averaged properties. Since we only introduce spatial variations (we do not change the parameter averages over the structure² except for fiber misalignment), the results intuitively make sense.

To illustrate the effect of spatial variations on local behavior, we compare the average and standard deviation of the von Mises stress field over the midsection of the structure in Fig. 11.14(b,c), respectively. We choose the midsection over the entire structure for analyzing the strain field since an explicit solver is employed in our multiscale FE simulations where artificial stress concentrations might occur at the boundaries of the structure. The curves in these two figures are obtained by analyzing the 20 simulations corresponding to each case. Similar to

² For instance, the average yarn angle over the entire macrostructure is roughly 78 degrees, see Fig. 11.6(b). Upon introducing spatial variations as shown in Fig. 11.6(d), this average is not changed.

Fig. 11.14(a,b) demonstrates that the structure weakens in the presence of fiber misalignment as the mean stress over the midsection is lower than that of the reference structure (Case 9). It is evident that the most realistic case where all the uncertainty sources are present results in the weakest structure. More interestingly, this weakening is not uniform over the midsection and is the largest at the middle where the reduction is roughly 12.3%.

The highest variations among the simulations of a specific case are observed in Case 8, where all the parameters change spatially and correlatedly, see Fig. 11.14(c). Cases 2, 3, and 7 are next in line with Cases 2 and 7 having more fluctuations among the IPs (note that each point along the x axis corresponds to an IP in the midsection). Finally, Cases 4 and 5, which correspond to the simulations where the yarn spacing and height change, have the least amount of variations. This is expected since the stiffness matrix of a woven RVE (obtained via the mesoscale MRGP metamodel) is also insignificantly sensitive to these parameters. We highlight, however, that we have considered a relatively small range of variations for these two parameters. Their effect will be more prominent if these ranges are increased.

11.4 Conclusion and future works

Limited advancement has been made in integrating statistical UQ and UP methods with multiscale simulations. Herein, we have introduced an approach for multiscale UQ and UP that models the uncertainty sources with MRGPs and employs statistical techniques (such as metamodeling and sensitivity analyses) to address the computational costs. Our choice of RF enables manageable UQ by directly relating the hyperparameters of the MRGP to the physical uncertainty sources. It also allows coupling the uncertainty sources across the spatial scales and builds nested RFs that can model nonstationary and C^0 (i.e., continuous but not differentiable) fields at the fine scale. These nested RFs were built through the top-down sampling scheme where the hyperparameters of MRGP models at the mesoscale are determined at the macroscale via a single (and separate) MRGP model.

We applied our approach to quantify the macroscale uncertainty in the linear analysis of a cured woven composite due to spatial variations of yarn angle, fiber volume fraction, fiber misalignment, local yarn height and spacing, fiber modulus, and matrix modulus. We chose composites because they possess a hierarchical structure and are ubiquitously employed in aerospace, construction, and transportation industries. Computational homogenization was used to conduct the multiscale simulations where a monoclinic material model was employed to allow for modeling nonorthogonal woven RVE samples which exhibit different behavior spatially. We also modeled fiber misalignment in mesoscale cured woven RVE analyses by implementing a microplane triad model. Our results indicate that the effect of uncertainty sources on the materials' response at the macroscale, especially the stress field, could be significant. In

particular, it was demonstrated that the spatial variations weaken the composite especially when they are considered together. To the best of our knowledge, these effects have not been previously studied elsewhere.

Our microscale and mesoscale RVEs were sufficiently large and so more uncertainty would have been observed in the responses had we chosen smaller RVEs. With smaller RVEs, the sensitivity of the homogenized moduli and stresses to RF parameters (e.g., roughness parameters) will increase. Additionally, we focused on the first and second moments of the response (i.e., the stress field) for macroscale UQ. Higher moments should clearly be considered to quantify the uncertainty more rigorously. Our choice of MRGPs implies a normality assumption which might not hold in other applications where the distributions are heavily skewed or appropriate transformations are not readily available. In such cases, other RF representations can be integrated with the top-down sampling approach at the expense of more computations. We plan to gather experimental images from various structures at different spatial scales to further demonstrate the applications of our approach. For instance, if there are n images available at the mesoscale (each at a particular spatial location), we can learn n MRGPs at the mesoscale and, subsequently, learn a macroscale MRGP that explains how the hyperparameters of the mesoscale MRGPs vary spatially.

Appendix

Details on the sensitivity studies at the mesoscale

In [Section 11.3.4](#), it was illustrated that only the average values of fiber volume fraction and zenith angle (one component of the misalignment angle) affected the homogenized response of a woven RVE at the mesoscale. These two parameters are controlled by the corresponding mean values of the MRGP that models the mesoscale spatial variations (i.e., β_v and β_θ). The other parameters of the MRGP model (i.e., β_ϕ , σ_{vv}^2 , $\sigma_{\phi\phi}^2$, $\sigma_{\theta\theta}^2$, $\sigma_{v\phi}^2$, $\sigma_{v\theta}^2$, $\sigma_{\phi\theta}^2$, ω_x , ω_y , and ω_z) were found to affect the homogenized response insignificantly through sensitivity studies.

In our sensitivity studies, we investigated the uncertainty sources one by one. That is, all the hyperparameters of the MRGP model were fixed except for those controlling one uncertainty source. For instance, to investigate the effect of fiber volume fraction and its spatial variations, β_v and σ_{vv}^2 were changed while the rest of the MRGP hyperparameters were fixed. For each combination of β_v and σ_{vv}^2 , then, 30 independent samples were generated from the MRGP model to account for the inherent randomness. Next, the variability of the effective moduli of the woven RVE among these simulations was quantified. If the variability was significant, the parameter was deemed as important. Otherwise, it was set as a constant and, subsequently, not considered in the metamodeling stage in [Section 11.3.5](#) (because it would not change in the multiscale simulations). Below, we demonstrate one of the cases where the significance of local fiber volume fraction is investigated.

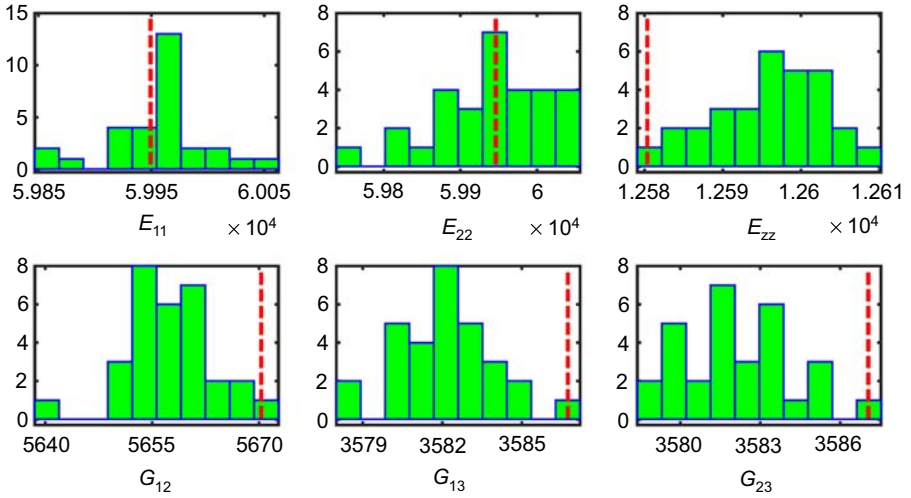


Figure 11.15 Variation of moduli (MPa) in a woven RVE due to spatial variations of fiber volume fraction (v). The effective moduli change due to the variations in the local fiber volume fraction. The changes are, however, insignificant. Herein, $\beta_v = 65\%$ and $\sigma_{vv}^2 = 16\%$. Since the latter parameters are nonzero, 30 simulations were conducted to quantify the effect of variations. The *dashed red lines* correspond to the moduli when $\sigma_{vv}^2 = 0$.

The average value and spatial variations of v are controlled via β_v and σ_v^2 , respectively. Hence, we fixed the other parameters and took 30 random and independent realizations from the mesoscale MRGP model for each combination of β_v and σ_v^2 . The considered values for β_v and σ_v^2 are, respectively, $[45, 50, 55, 60, 65]\%$ and $[9, 16]\%$. In this case, the rest of the hyperparameters (i.e., β_θ , β_ϕ , $\sigma_{\phi\phi}^2$, $\sigma_{\theta\theta}^2$, $\sigma_{v\phi}^2$, $\sigma_{v\theta}^2$, $\sigma_{\phi\theta}^2$) were set to zero to have the variability be only a function of spatial variations on v . Fig. 11.15 summarizes the results of 30 mesoscale simulations where $\beta_v = 65\%$ and $\sigma_v^2 = 16\%$. The dashed red line corresponds to the moduli of a woven RVE with $\sigma_v^2 = 0\%$ (i.e., with no spatial variations). As it can be observed, the spatial variations do not significantly affect the homogenized response of a woven RVE, and hence, one can only consider the average fiber volume fraction. Such analyses were conducted for various combinations and the results are summarized in Fig. 11.11 for the three parameters v , θ , and ϕ . In the cases where θ and ϕ changed, the simulated annealing algorithm was used to ensure that $\sum_{i=1}^N \sin(\theta_i^2) \cos(\phi_i^2) = 0$ and $\sum_{i=1}^N \sin(\theta_i^2) \sin(\phi_i^2) = 0$ at each yarn cross section to avoid changing the yarn angle due to fiber misalignment (N denotes the number of IPs on the yarn cross section).

We note that, in our simulations we chose realistic ranges for all the parameters to resemble experimental data (see, for example, Ref. [6]). With very large roughness parameters (i.e., ω in Eq. 11.2), fiber VF can change significantly between any two adjacent IPs (in yarn, and *not* across yarn matrix, the latter is permissible) which is not physically meaningful.

Conditional distribution

If $\mathbf{X} = [X_1, \dots, X_n]^T$ and $\mathbf{Y} = [Y_1, \dots, Y_m]^T$ are jointly Gaussian,

$$\begin{bmatrix} \mathbf{Y} \\ \mathbf{X} \end{bmatrix} \sim \mathcal{N}_{m+n} \left(\begin{bmatrix} \boldsymbol{\mu}_Y \\ \boldsymbol{\mu}_X \end{bmatrix}, \begin{bmatrix} \boldsymbol{\Sigma}_{YY} & \boldsymbol{\Sigma}_{YX} \\ \boldsymbol{\Sigma}_{XY} & \boldsymbol{\Sigma}_{XX} \end{bmatrix} \right), \quad (11.8)$$

where $\mathcal{N}_{m+n}$ denotes the multivariate normal distribution, $\boldsymbol{\mu}_Y = E[\mathbf{Y}]$, $\boldsymbol{\mu}_X = E[\mathbf{X}]$, $\boldsymbol{\Sigma}_{YY} = \text{Cov}(\mathbf{Y}, \mathbf{Y})$, $\boldsymbol{\Sigma}_{XX} = \text{Cov}(\mathbf{X}, \mathbf{X})$, $\boldsymbol{\Sigma}_{YX} = \boldsymbol{\Sigma}_{XY}^T = \text{Cov}(\mathbf{Y}, \mathbf{X}) = E[(\mathbf{X} - \boldsymbol{\mu}_X)(\mathbf{Y} - \boldsymbol{\mu}_Y)^T]$, and $E[\cdot]$ denotes the expectation operator. The conditional distribution of $\mathbf{Y}$ given $\mathbf{X}$ is

$$\mathbf{Y}|\mathbf{X} \sim \mathcal{N}_m(\boldsymbol{\mu}_Y + \boldsymbol{\Sigma}_{YX}\boldsymbol{\Sigma}_{XX}^{-1}(\mathbf{X} - \boldsymbol{\mu}_X), \boldsymbol{\Sigma}_{YY} - \boldsymbol{\Sigma}_{YX}\boldsymbol{\Sigma}_{XX}^{-1}\boldsymbol{\Sigma}_{YX}^T), \quad (11.9)$$

In our example, $\mathbf{Y} = [v, \boldsymbol{\theta}]$ and $\mathbf{X} = \boldsymbol{\alpha}$.

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Modeling non-Gaussian random fields of material properties in multiscale mechanics of materials

12

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12.1 Introduction

Uncertainty quantification is a predominant ingredient of predictive science and engineering. Since the seminal work from Ghanem and Spanos [1], many developments were proposed regarding the mathematical representation, identification, and propagation of model form and parametric uncertainties in computational models (see Ref. [2] for state-of-the-art reviews; see also [3–5]). All these aspects are of paramount importance in the development of numerical tools for robust design and high-fidelity simulations. In general, probabilistic modeling must be envisioned and addressed as a multifaceted problem in which issues associated with mathematical consistency, robust sampling, identification constraints, and validation strategy are deeply intertwined.

In a multiscale setup, variability can arise from microstructural randomness when the separation of scales is not achieved [6] and/or from various types of uncertainties related to imperfect processing conditions at the manufacturing stage for example. This variability impacts the fidelity of simulations conducted at the scale under consideration and can propagate and mitigate over coarser scales. While the propagation of such material uncertainties has attracted much attention for the design and assessment of robust stochastic solvers [2], the development of appropriate, physics-based, and identifiable stochastic models of random fields remains quite unexplored—especially within nonlinear frameworks. The construction of such models must ensure that *all* mathematical requirements (necessary to prove the existence of unique solutions to the associated stochastic boundary value problem [SBVP], for example) and relevant physical constraints (associated with some symmetry properties for tensor-valued coefficients for instance) are satisfied (see, e.g., Refs. [7,8]) for the analysis of stochastic (elliptic) partial differential equations with scalar-valued and tensor-valued coefficients, respectively. As physical properties generally take values in bounded (or semibounded) sets, Gaussian models are not mathematically admissible [9,10] (although they may fit some limited data-based estimations reasonably well, typically on a finite set of first-order and second-order marginal probability distributions), and one is therefore left with the construction of stochastic models for non-Gaussian random fields. It should be noticed that boundedness from below is also typically

required in the analysis of SBVPs. The selection of a model then depends on both the application of interest and intended purpose, and quality assessment may subsequently be performed by using any relevant validation metric. This methodological chapter aims at advancing a probabilistic modeling framework for non-Gaussian random fields, relevant to multiscale solid mechanics and materials science. In the context stated above, discussions about uncertainty propagation and model validation are outside the scope of this work.

This chapter is organized as follows. The overall methodology is introduced and illustrated on a simple problem in [Section 12.2](#). The probabilistic modeling of non-Gaussian, matrix-valued random fields is then addressed in [Section 12.3](#). In particular, stochastic representations for elasticity tensors with any material symmetry are presented. The case of nonlinear constitutive models is finally presented in [Section 12.4](#).

The notations in [Table 12.1](#) will be used throughout this chapter.

12.2 Methodology and elementary example

12.2.1 Definition of scales

Consider a quantity of interest that is a positive scalar, modeled at a given scale by the random field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$, defined on a probability space $(\Theta, \mathcal{T}, \mathcal{P})$, and indexed by a bounded domain Ω in $\mathbb{R}^d$. For simplicity, assume that the material is made of two connected phases at the microscopic scale, each occupying a domain Ω_i , $i \in \{1, 2\}$, such that $\Omega = \bigcup_{i=1}^2 \Omega_i$ and $\Omega_1 \cap \Omega_2 = \emptyset$; see the far left panel in [Fig. 12.1](#).

At the microscopic scale $\mathcal{S}^{\text{micro}}$, the properties of the constitutive phases are assumed piecewise constant and may be either deterministic or stochastic. For the former case, the field can thus be written as

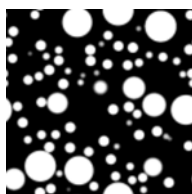
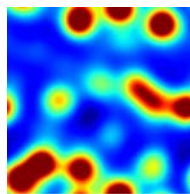
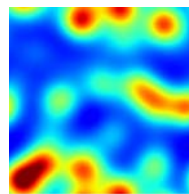
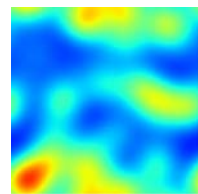
$$Z(\mathbf{x}) = \sum_{i=1}^2 \mathbb{1}_{\Omega_i}(\mathbf{x}) z_i, \quad \mathbf{x} \in \Omega, \quad (12.1)$$

where z_i denotes the (deterministic) value of the physical quantity of interest in phase Ω_i . The modeling of $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ is then equivalent to the modeling of the characteristic random field $\{\mathbb{1}_{\Omega_i}(\mathbf{x}), \mathbf{x} \in \Omega\}$ (as $\mathbb{1}_{\Omega_2}(\mathbf{x}) = 1 - \mathbb{1}_{\Omega_1}(\mathbf{x})$ in Ω), which can be achieved by means of random structure models including, for instance, point processes and random sets [[12, 13](#)].

At coarser scales, the nature of $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ changes due to upscaling and lack of scale separation, from a piece-constant field to a field exhibiting filtered variations over Ω . This phenomenon is illustrated in [Fig. 12.1](#), where the samples at the mesoscales $\mathcal{S}_1^{\text{meso}}$, $\mathcal{S}_2^{\text{meso}}$, and $\mathcal{S}_3^{\text{meso}}$, while smoother than their microscopic counterparts, still contain some signature of unresolved physics. In this chapter, we consider the modeling of $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ at any given microscopic scale. In particular, the case of random fields defined concurrently at several mesoscales (which is relevant to specific classes of materials, such as woven composites) is not addressed (see Ref. [[14](#)] for an

Table 12.1 Main notations.

$a, \mathbf{a}, [\mathbf{A}]$	Deterministic scalar, vector and matrix
$A, \mathbf{A}, [\mathbf{A}]$	Random scalar, vector and matrix
$\llbracket \mathbf{A} \rrbracket$	Fourth-order deterministic tensor
c	Normalization constant (with line-dependent values)
$[\mathbf{C}]$	Elasticity random matrix
$[\mathbf{F}]$	Deformation gradient
$\mathcal{H}$	Nonlinear measurable mapping (transport map)
$[\mathbf{I}_n]$	Identity matrix of rank n
$[\mathbf{T}]$	First Piola–Kirchhoff stress tensor
w	Deterministic strain energy function
W	Stochastic strain energy function
Z	Generic scalar random variable
Ξ	Vector-valued Gaussian random variable
$[\sigma]$	Cauchy stress tensor
φ	Deformation map
Ω	Bounded domain in $\mathbb{R}^d$
$\mathbb{M}_3(\mathbb{R})$	Set of (3×3) real matrices with determinant equal to 1
$\mathbb{S}_n^{++}(\mathbb{R})$	Set of $(n \times n)$ positive-definite symmetric real matrices
$\mathbb{S}_6^{\text{sym}}(\mathbb{R})$	Set of (6×6) elasticity matrices with given material symmetry
$\langle \cdot, \cdot \rangle$	Euclidean inner product, $\langle \mathbf{a}, \mathbf{b} \rangle = \sum_{i=1}^n a_i b_i$
$\ \cdot \ $	Euclidean norm, $\ \mathbf{a} \ = \langle \mathbf{a}, \mathbf{a} \rangle^{1/2}$
$\text{Cof}(\cdot)$	Cofactor matrix
$\text{Tr}(\cdot)$	Trace of a matrix, $\text{Tr}([\mathbf{A}]) = \sum_{i=1}^n A_{ii}$
$\ \cdot \ _F$	Frobenius norm of $[\mathbf{A}]$, $\ [\mathbf{A}]\ _F = \text{Tr}([\mathbf{A}]^T [\mathbf{A}])$
E	Mathematical expectation

Scale S^{micro} Scale S_1^{meso} Scale S_2^{meso} Scale S_3^{meso} **Figure 12.1** One sample of a random medium at different scales, ranging from the microscopic to coarser, mesoscopic scales (from left to right) [11].

example). From the perspectives of uncertainty quantification and stochastic multi-scale mechanics, $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ is then traditionally fed as the random coefficient into a system of stochastic partial differential equations. As indicated previously, the field is consequently required to satisfy basic properties arising from the mathematical analysis of this system (i.e., to ensure the existence and uniqueness of solutions). These properties will be discussed more extensively later. At this stage, the random field is assumed to be of second order:

$$E\{Z(\mathbf{x})^2\} < +\infty, \quad \forall \mathbf{x} \in \Omega. \quad (12.2)$$

12.2.2 On the representation of random fields

General representations of random fields can be obtained through integral representation theorems or Karhunen–Loève (KL) and polynomial chaos expansions; see, e.g., Refs. [2,15], for details.

Assume, for instance, that $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ is a mean square continuous second-order random field and denote by C_Z its continuous covariance function:

$$C_Z(\mathbf{x}, \mathbf{x}') = E\{(Z(\mathbf{x}) - m_Z(\mathbf{x}))(Z(\mathbf{x}') - m_Z(\mathbf{x}'))\}, \quad \forall (\mathbf{x}, \mathbf{x}') \in \Omega \times \Omega, \quad (12.3)$$

where $\mathbf{x} \mapsto m_Z(\mathbf{x}) = E\{Z(\mathbf{x})\}$ is the mean function of the random field. In this paragraph, Ω is assumed to be compact. The random field of interest can then be represented as

$$Z(\mathbf{x}) = m_Z(\mathbf{x}) + \sum_{i=1}^{+\infty} \sqrt{\lambda_i} \phi_i(\mathbf{x}) \eta_i, \quad \forall \mathbf{x} \in \Omega, \quad (12.4)$$

where $\{(\lambda_i, \phi_i)\}_{i \geq 1}$ is the set of pairs of eigenvalues (ordered as a nonincreasing sequence) and eigenfunctions satisfying the integral equation

$$\int_{\Omega} C_Z(\mathbf{x}, \mathbf{x}') \phi(\mathbf{x}') d\mathbf{x}' = \lambda \phi(\mathbf{x}), \quad \forall \mathbf{x} \in \Omega, \quad (12.5)$$

with $d\mathbf{x}' = dx'_1 \cdots dx'_d$ the Lebesgue measure in $\mathbb{R}^d$, and $\{\eta_i\}_{i \geq 1}$ are random variables defined as

$$\eta_i = \frac{1}{\sqrt{\lambda_i}} \int_{\Omega} (Z(\mathbf{x}) - m_Z(\mathbf{x})) \phi_i(\mathbf{x}) d\mathbf{x}. \quad (12.6)$$

These random variables are, by construction, centered such that $E\{\eta_i \eta_j\} = \delta_{ij}$, with δ the Kronecker delta. Eq. (12.4) corresponds to the KL expansion of the random field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ and shows that the latter can, indeed, be represented by a countable

family of random variables (which are the reduced or KL random variables $\{\eta_i\}_{i \geq 1}$). In practice, the KL expansion can be truncated at order N_{KL} ,

$$Z^{(N_{KL})}(\mathbf{x}) = m_Z(\mathbf{x}) + \sum_{i=1}^{N_{KL}} \sqrt{\lambda_i} \phi_i(\mathbf{x}) \eta_i, \quad \forall \mathbf{x} \in \Omega, \quad (12.7)$$

with $Z^{(N_{KL})} \xrightarrow{N_{KL} \rightarrow +\infty} Z$ in the mean square sense and can thus be employed to perform a statistical reduction of the random field. The order of truncation N_{KL} must be deduced from a convergence analysis: in general, N_{KL} becomes larger for random fields that are weakly correlated over Ω (i.e., when the covariance function exhibits a fast decay). In practice, solving the integral equation given by Eq. (12.5) can be problematic for large-scale three-dimensional domains and may require the recourse to ad hoc numerical strategies (see, e.g., Ref. [16] and the references therein).

Despite its apparent simplicity, Eq. (12.7) hides a few major difficulties when identification aspects come into the picture (that is, when the characteristics of the random field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ are not assumed a priori). First, the use of the KL expansion necessitates the estimation of the covariance function C_Z , which requires a rich database (in terms of both available samples and full-field measurements) that is rarely, if ever, available. Second, the probability measure of the random vector $\boldsymbol{\eta} = (\eta_1, \dots, \eta_{N_{KL}})$ is generally unknown (unless the expanded field is Gaussian, in which case $\boldsymbol{\eta}$ is a Gaussian random vector with statistically independent components) and must be defined. A possible way to handle this problem is to subsequently describe $\boldsymbol{\eta}$ through a polynomial chaos expansion [17,18]. Truncating the expansion after N_{pce} terms yields

$$\boldsymbol{\eta}^{(N_{pce})} = \sum_{j=0}^{N_{pce}-1} \mathbf{y}^{(j)} \Psi_j(\boldsymbol{\Xi}), \quad (12.8)$$

where the random variable $\boldsymbol{\Xi}$ is defined by a probability measure $P_{\boldsymbol{\Xi}}(d\boldsymbol{\xi})$ with support $\mathcal{S}_{\boldsymbol{\Xi}} \subseteq \mathbb{R}^{N_g}$ (with $N_g \ll N_{KL}$ in general), and $\{\Psi_j\}_{j=0}^{N_{pce}-1}$ is a set of multivariate polynomials that are orthogonal with respect to $P_{\boldsymbol{\Xi}}(d\boldsymbol{\xi})$. The number of terms N_{pce} (or equivalently, the order of the expansion) must be determined from a suitable convergence analysis. A choice commonly made in model identification is to take $P_{\boldsymbol{\Xi}}(d\boldsymbol{\xi})$ as the standard Gaussian probability measure, in which case $\{\Psi_j\}_{j \geq 0}$ are multivariate Hermite polynomials. In this setting, the identification task is passed on to the identification of the coefficients $\mathbf{y}^{(0)}, \dots, \mathbf{y}^{(N_{pce}-1)}$, which is usually cast as a statistical inverse problem [19,20]. Substituting Eq. (12.8) into Eq. (12.7), the chaos expansion of the field is finally obtained as

$$Z^{(N_{KL}, N_{pce})}(\mathbf{x}) = m_Z(\mathbf{x}) + \sum_{j=0}^{N_{pce}} Z_{N_{KL}}^{(j)}(\mathbf{x}) \Psi_j(\boldsymbol{\Xi}), \quad (12.9)$$

with

$$Z_{N_{KL}}^{(j)}(\mathbf{x}) = \sum_{i=1}^{N_{KL}} \sqrt{\lambda_i} \phi_i(\mathbf{x}) y_i^{(j)}, \quad \forall \mathbf{x} \in \Omega. \quad (12.10)$$

While the two random field representations given by Eqs. (12.7) and (12.9) are very general, they necessitate solving statistical inverse problems that are severely ill-posed and potentially high-dimensional. In addition, most physical quantities satisfy, e.g., boundedness constraints that may require a specific treatment—in the form of an algebraic regularization, for instance. For Z strictly positive almost surely, a simple remedy consists in defining $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ as

$$Z(\mathbf{x}) = \exp\{Y(\mathbf{x})\}, \quad \forall \mathbf{x} \in \Omega, \quad (12.11)$$

with $\{Y(\mathbf{x}), \mathbf{x} \in \Omega\}$ an auxiliary random field to be defined. The transformation above readily ensures that $Z(\mathbf{x}) > 0$ for all $\mathbf{x}$ in Ω . However, the exponential of any second-order random field is not, in general, a second-order random field [8]. It follows that the random field $\{Y(\mathbf{x}), \mathbf{x} \in \Omega\}$ must, in turn, be defined with caution, so that $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ inherits this fundamental property. At this point, it should be noticed that KL and chaos expansions are, of course, easily applicable when no random field identification based on small datasets is sought. They are routinely used for the development and analysis of stochastic solvers (in this case, the random field model is fully prescribed as a modeling assumption) (see Ref. [2]).

Following this discussion, the problem that will be attacked in the rest of this chapter is not to construct a representation for any second-order random field, for a given multiscale framework. The alternative strategy pursued hereinafter aims at bridging the gap between experiments and advanced modeling tools for uncertainty quantification and consists in constructing subclasses of random fields that are

- 1 admissible, in the sense that they satisfy all mathematical requirements that make the associated SBVP well posed (see Refs. [9,21]);
- 2 consistent with physics-guided constraints, such as constraints related to anisotropy (this point being central in multiscale analysis [22]);
- 3 defined by a limited number of model parameters controlling key properties of the fields, such as the fluctuation level and spatial correlation lengths.

These subclasses are especially relevant to model stochastic physical quantities based on limited experimental data. Adopting the terminology proposed in Ref. [19], such models will be referred to as *algebraic models* in the sequel. They can be used per se or can ultimately be combined with more general representations, if need be [19,20]. The case where samples of the field can be synthesized through the upscaling of microscopic models is not discussed hereinafter (see, e.g., Refs. [23–27]): in this situation, there is virtually no data limitation (at the expense of performing extensive multiscale computations though), and the representations introduced above, as well as other types of fully parametric representations, can be used.

12.2.3 Information-theoretic description of random fields

To gain a first insight into stochastic modeling issues for algebraic models, let us address the construction of a model for $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$. Assume that the random field takes its values in $\mathbb{R}_{>0}$ (this field could represent a diffusion or elastic coefficient) so that the random field is non-Gaussian. A standard way to introduce non-Gaussianity is to express the field as

$$Z(\mathbf{x}) = \mathcal{H}(\Xi(\mathbf{x}), \mathbf{x}), \quad \forall \mathbf{x} \in \Omega, \quad (12.12)$$

where $\mathcal{H}$ is a measurable nonlinear mapping and $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ is a normalized stationary Gaussian field in $\mathbb{R}^d$. Non-Gaussian random fields defined as in Eq. (12.12) are sometimes referred to as translation random fields in the literature [28] (see Remark 12.1). Here, the dependence of $\mathcal{H}$ on location $\mathbf{x}$ is reported to highlight the fact that certain types of nonstationary fields can also be modeled. For the sake of simplicity, and without loss of generality, we assume below that $\mathcal{H}$ is independent of $\mathbf{x}$, and we thus write $Z(\mathbf{x}) = \mathcal{H}(\Xi(\mathbf{x}))$. Eq. (12.12) is parameterized by the mapping $\mathcal{H}$ and the correlation function R_Ξ defining the underlying Gaussian field $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$:

$$R_\Xi(\boldsymbol{\tau}) = E\{\Xi(\mathbf{x} + \boldsymbol{\tau})\Xi(\mathbf{x})\}, \quad \forall \boldsymbol{\tau} \in \mathbb{R}^d, \quad (12.13)$$

where $\boldsymbol{\tau}$ is the so-called lag (or separation) vector. The correlation function plays a very important role, both practically (from the standpoint of random media modeling) and theoretically. In particular, it is related to key probabilistic features exhibited by $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$, including continuity and differentiability properties [15], and may reflect, for instance, the isotropy of the underlying random media. Note that, in general, properties of the non-Gaussian field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ cannot be theoretically inferred from those exhibited by the above Gaussian field, due to the nonlinearity of the transformation in Eq. (12.12). However, some properties can still be deduced when $\mathcal{H}$ is a continuous mapping.

In this chapter, information theory [29,30] is invoked to construct suitable probabilistic representations using the principle of maximum entropy (MaxEnt). This approach was proven very efficient in a variety of applications, including nuclear physics [31], structural dynamics [32] (see Chapter 8 in Ref. [2] and the references therein for an extensive review), and materials modeling (see Refs. [9,33–39] for contributions in linear elasticity and [40–44] for stochastic modeling in nonlinear elasticity), to name a few. By construction, it also allows one to reduce the modeling bias, hence making the obtained models good candidates as prior models within a Bayesian framework (see Refs. [19,20] for a discussion in linear elasticity). The idea is to construct $\mathcal{H}$ such that

$$Z(\mathbf{x}) \sim P_{\text{MaxEnt}}(dz), \quad \forall \mathbf{x} \text{ fixed in } \Omega, \quad (12.14)$$

where the notation $\sim$ means “is distributed according to” and P_{MaxEnt} is the MaxEnt probability measure, obtained through the maximization of Shannon entropy [45,46] under the constraint equation

$$E\{\mathbf{g}(Z(\mathbf{x}))\} = \underline{\mathbf{g}}, \quad (12.15)$$

where $\mathbf{g}$ is a mapping with values in $\mathbb{R}^{N_c}$, and $\underline{\mathbf{g}}$ is a given vector in $\mathbb{R}^{N_c}$. The definition of $\mathbf{g}$ reflects the information available on $Z(\mathbf{x})$: if the first- and second-order moments of $Z(\mathbf{x})$ are known ($N_c = 2$), for instance, then $\mathbf{g}$ is the mapping $z \mapsto \mathbf{g}(z) = (z, z^2)$. Indeed, Eq. (12.15) integrates two types of constraints. The first set of constraints is related to minimal mathematical requirements: these constraints define properties that make the model admissible. The second type of information is associated with additional, moment-type information that is prescribed to provide some modeling flexibility. This set may add modeling bias as more (nonminimal) information is accounted for. It should be kept in mind that adding too many constraints leads to an overparameterization of the stochastic model, incompatible with identifiability constraints. In addition, the definition of appropriate flexibility is application-dependent and should be assessed on the basis of intended purpose only. In general, models with high flexibility may be required to predict local quantities of interest at the scale where randomness is introduced, while properly catching a restricted number of key characteristics, such as the fluctuation level and the correlation lengths, is typically sufficient to remain predictive at coarser scales. This latter point was demonstrated in Ref. [11], where the use of a non-Gaussian model matching second-order statistics enabled the prediction of the macroscopic properties with a very good accuracy.

Once the information constraints have been identified, then the probability density function is obtained as the solution of the following optimization problem:

$$\arg \max_{\mathcal{C}_{ad}} Ent\{f\} \quad (12.16)$$

where $Ent\{f\}$ is the Shannon entropy of the probability density function f with support $\mathcal{S}_Z$ defined as

$$Ent\{f\} = - \int_{\mathcal{S}_Z} f(z) \log(f(z)) dz, \quad (12.17)$$

and $\mathcal{C}_{ad}$ is the set of probability density functions satisfying the constraint equation (see Eq. 12.15). The above functional optimization problem can be solved by the method of Lagrange multipliers and the solution takes the form

$$f_{Z(\mathbf{x})}(z) = \mathbb{1}_{\mathcal{S}_Z}(z) c \exp\{ - \langle \boldsymbol{\lambda}, \mathbf{g}(z) \rangle \}, \quad (12.18)$$

where $\mathbb{1}_{\mathcal{S}_Z}$ is the characteristic function of $\mathcal{S}_Z$ ($\mathcal{S}_Z = \mathbb{R}_{>0}$ in this section), c is the normalization constant, $\boldsymbol{\lambda}$ is a vector-valued Lagrange multiplier to be calibrated (see,

e.g., Ref. [47], for the case of matrix-valued fields), and $\langle \cdot, \cdot \rangle$ denotes the Euclidean inner product. The mapping $\mathcal{H}$ is then constructed such that

$$Z(\mathbf{x}) \sim f_{Z(\mathbf{x})}(z)dz, \quad (12.19)$$

with $\mathbf{x}$ fixed in Ω . A fundamental aspect of this construction is that Eq. (12.12) completely defines the full system of marginal distributions of $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$.

Remark 12.1. In the retained modeling framework, the family of first-order marginal probability distributions is used to construct the nonlinear mapping $\mathcal{H}$. If required, any desired match in terms of correlation structure must thus be investigated by performing some optimization-based updating procedure on the correlation function R_{Ξ} . This can be achieved by first expanding the latter on its basis of eigenfunctions (following Mercer's theorem),

$$R_{\Xi}(\mathbf{x}, \mathbf{x}') \approx \sum_{i=1}^{N_{KL}} \lambda_i \phi_i(\mathbf{x}) \phi_i(\mathbf{x}'), \quad \forall (\mathbf{x}, \mathbf{x}') \in \Omega \times \Omega, \quad (12.20)$$

and by subsequently updating the eigenvalues $\{\lambda_i\}_{i=1}^{N_{KL}} \mapsto \{\lambda_i^{new}\}_{i=1}^{N_{KL}}$ to minimize the distance to a target correlation function. An “optimal” correlation function is then obtained as

$$R_{\Xi}^{new}(\mathbf{x}, \mathbf{x}') = \sum_{i=1}^{N_{KL}} \lambda_i^{new} \phi_i(\mathbf{x}) \phi_i(\mathbf{x}'), \quad \forall (\mathbf{x}, \mathbf{x}') \in \Omega \times \Omega. \quad (12.21)$$

This approach is slightly different from the one integrating information on the correlation structure in the definition of $\mathcal{H}$. Such a construction is, in general, more complex and naturally involves compatibility-type restrictions (see Ref. [48]).

12.2.4 Getting started with a toy problem

Before addressing the general case of constrained matrix-valued non-Gaussian random fields, let us illustrate the overall methodology by modeling the scalar-valued random field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ considered in the previous section. We thus have $\mathcal{S}_Z = \mathbb{R}_{>0}$ and assume that the mean value of the field is known:

$$E\{Z(\mathbf{x})\} = \underline{z}, \quad \forall \mathbf{x} \in \Omega. \quad (12.22)$$

To ensure a repulsion near the origin 0 in $\mathbb{R}$, a repulsive constraint is considered as

$$E\{\log(Z(\mathbf{x}))\} = \chi, \quad |\chi| < +\infty. \quad (12.23)$$

The choice of the natural logarithm in Eq. (12.23) stems from the fact that it ensures the strongest decrease near 0^+ (as compared to any polynomial term) and allows us to prove the existence (i.e., the finiteness) of the second-order moments for $Z(\mathbf{x})$ and $Z(\mathbf{x})^{-1}$. The constraint Eq. (12.15) then holds with $\mathbf{g}(z) = (\log(z), z)$ and $\underline{\mathbf{g}} = (\chi, \underline{z})$, and the MaxEnt solution (12.18) takes the simple form

$$f_{Z(\mathbf{x})}(z) = \mathbb{1}_{\mathbb{R}_{>0}}(z) c \exp\{-\langle \lambda, \mathbf{g}(z) \rangle\}, \quad \forall z \in \mathbb{R}, \quad (12.24)$$

where $\lambda_1 \in (-\infty, 1)$ and $\lambda_2 \in \mathbb{R}_{>0}$, due to integrability requirements. Note that these multipliers do not depend on location here because the right-hand sides in Eqs. (12.22) and (12.23) do not depend on $\mathbf{x}$. Given the expression of $\mathbf{g}$, it follows that $f_{Z(\mathbf{x})}$ equivalently reads as

$$f_{Z(\mathbf{x})}(z) = \mathbb{1}_{\mathbb{R}_{>0}}(z) c z^{-\lambda_1} \exp\{-\lambda_2 z\}, \quad (12.25)$$

which shows, upon close inspection, that $Z(\mathbf{x})$ (recall, again, that $\mathbf{x}$ is fixed here) is distributed according to a Gamma Law with shape and scale parameters given by $(1 - \lambda_1)$ and $1/\lambda_2$, respectively. Based on this result, the mapping $\mathcal{H}$ can be defined through a simple inverse transformation:

$$\mathcal{H} = F_{\mathcal{G}_{(1-\lambda_1, 1/\lambda_2)}}^{-1} \circ F_{\mathcal{N}_{(0,1)}}, \quad (12.26)$$

in which $F_{\mathcal{G}_{(1-\lambda_1, 1/\lambda_2)}}^{-1}$ is the inverse cumulative distribution function of the Gamma Law with parameters $(1 - \lambda_1)$ and $1/\lambda_2$, $F_{\mathcal{N}_{(0,1)}}$ is the cumulative distribution function of the standard Gaussian law, and symbol $\circ$ denotes the operator of function composition. To obtain a physics-based parameterization of the model, it is convenient to express the Lagrange multipliers λ_1 and λ_2 as functions of the mean value $\underline{z}$ and coefficient of variation of $Z(\mathbf{x})$, denoted by δ_Z :

$$\lambda_1 = 1 - \frac{1}{\delta_Z^2}, \quad \lambda_2 = \frac{1}{\underline{z} \delta_Z^2}. \quad (12.27)$$

While a measure of the statistical fluctuations is not directly integrated in the MaxEnt formalism (through a constraint on the second-order moment), it should be noticed that the model can still be parametrized in terms of the mean value and coefficient of variation. However, it is worth mentioning that the constraint given by Eq. (12.23) is stronger than a variance constraint that would lead to the restriction of a Gaussian model to $\mathbb{R}_{>0}^+$. Finally, it should be noticed that the mapping cannot always be expressed in the simple form given in Eq. (12.26). For most general applications where the transport map is unknown, the use of a Rosenblatt transform [49] or a transformation based on stochastic differential equations [50] can be invoked alternatively.

Two sample paths of the underlying Gaussian random field $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ and non-Gaussian random field $\{Z(\mathbf{x}), \mathbf{x} \in \Omega\}$ are shown for a one-dimensional problem

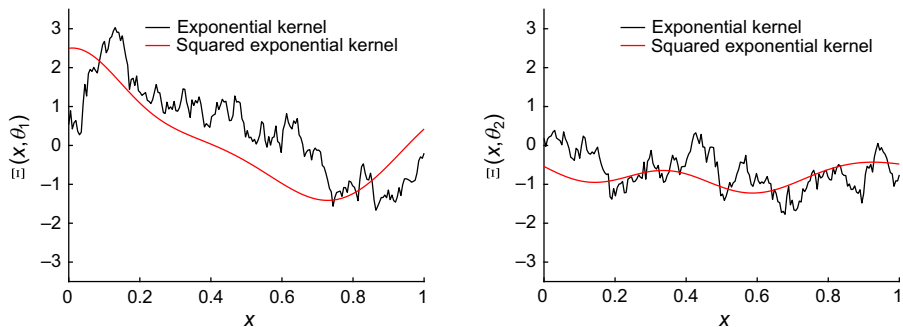


Figure 12.2 Two sample paths of the Gaussian random field $\{\Xi(x), x \in [0, 1]\}$, for the exponential (black) and squared exponential (red) correlation functions.

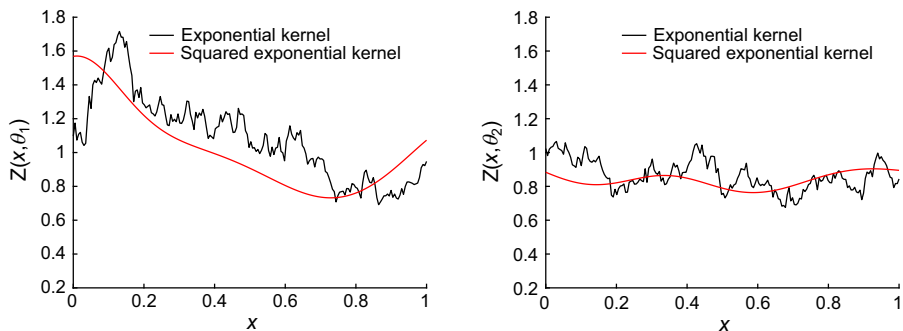


Figure 12.3 Two sample paths of the non-Gaussian random field $\{Z(x), x \in [0, 1]\}$, for the exponential (black) and squared exponential (red) correlation functions, with $\underline{z} = 1$ and $\delta_Z = 0.2$.

and two choices of correlation function R_{Ξ} in Figs. 12.2 and 12.3. In these simulations, we take $\Omega = [0, 1]$ and the spatial correlation length is set to 0.25 in both cases. Parameters of the non-Gaussian field are given by $\underline{z} = 1$ and $\delta_Z = 0.2$.

While the spatial correlation length is the same in all cases, the impact of the correlation function on sample path smoothness is clearly illustrated. In fact, the Gaussian random field is mean square continuous but not mean square differentiable for the exponential correlation function [15,51], which leads to realizations with a stronger roughness (especially when compared to samples obtained using the squared exponential function, for which the random field is mean square continuous and infinitely mean square differentiable).

This basic example shows how important the selection of an appropriate correlation kernel is and that its definition must be addressed very carefully to obtain meaningful results. Some effects of the nonlinear transformation $\mathcal{H}$ mapping the Gaussian random field to the non-Gaussian field can be observed by comparing Figs. 12.2 and 12.3. As expected, given the retained hyperparameters, the fluctuations for the non-Gaussian field are more contained and shifted upward. However, it should be emphasized at this point that the effect of the mapping $\mathcal{H}$ is much deeper because it does modify, by construction, the entire system of marginal probability distribution of the random field.

In the next section, we will use the methodology introduced in this section to address the more complex case of matrix-valued random fields with values in constrained spaces, arising from the consideration of material symmetries. These models are relevant to the modeling of stochastic coefficients in elliptic linear operators, such as elasticity and diffusion tensors. The former is selected as a prototypical case in the following. For the sake of completeness regarding the case of elasticity fields, note that the theoretical construction of general spectral representations for any second-order elasticity tensor random fields was addressed in Ref. [52].

12.3 Application to matrix-valued non-Gaussian random fields in linear elasticity

12.3.1 Preliminaries

Let $\{[C(\mathbf{x})], \mathbf{x} \in \Omega\}$ denote the random field of interest, representing the elasticity of the material. Throughout this part, a standard matrix formalism is adopted, following the modified Voigt notation for elasticity tensors [53]. The random field then takes its values in $\mathbb{S}_6^{\text{sym}}(\mathbb{R}) \subseteq \mathbb{S}_6^{++}(\mathbb{R})$, where $\mathbb{S}_6^{++}(\mathbb{R})$ is the set of all 6×6 real symmetric positive definite matrices and $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$ is defined as

$$\mathbb{S}_6^{\text{sym}}(\mathbb{R}) = \left\{ [A] \in \mathbb{S}_6^{++}(\mathbb{R}) : [Q]^T [A] [Q] = [A], \quad \forall [Q] \in \mathcal{G}_{\text{sym}} \right\}, \quad (12.28)$$

wherein $\mathcal{G}_{\text{sym}} \subseteq \text{SO}(3)$ defines the symmetry group of the material. Let $\mathbf{x} \mapsto [\underline{C}(\mathbf{x})]$ be the $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$ -valued mean function of the random field:

$$[\underline{C}(\mathbf{x})] = E\{[C(\mathbf{x})]\}, \quad \forall \mathbf{x} \in \Omega. \quad (12.29)$$

Assume that the mean function satisfies a uniform ellipticity condition:

$$\exists \underline{k}_0 > 0, \quad \langle \mathbf{z}, [\underline{C}(\mathbf{x})] \mathbf{z} \rangle > \underline{k}_0 \|\mathbf{z}\|^2, \quad \forall \mathbf{z} \in \mathbb{R}^6, \quad (12.30)$$

with $\|\cdot\|$ the Euclidean norm.

To proceed with the construction of the stochastic model [54], the set of mathematical requirements must be specified first (see the discussion in Section 12.2.3). The well-posedness of the SBVP imposes, in particular, that the random field $\{[C(\mathbf{x})], \mathbf{x} \in \Omega\}$ must be of second order, that is,

$$E\left\{ \|[C(\mathbf{x})]\|_F^2 \right\} < +\infty, \quad \forall \mathbf{x} \in \Omega, \quad (12.31)$$

in which $\|\cdot\|_F$ denotes the Frobenius norm, and such that the bilinear form related to the SBVP is continuous and elliptic.

As proven in Ref. [9], the last constraint requires the existence of a lower bound for the elasticity field and that $\{[C(\mathbf{x})]^{-1}, \mathbf{x} \in \Omega\}$ be of second order as well. To

accommodate these constraints, it is assumed that the random field satisfies the mild boundedness property

$$0 < \frac{\varepsilon}{1 + \varepsilon} [\underline{C}(\mathbf{x})] < [C(\mathbf{x})], \quad \forall \mathbf{x} \in \Omega \quad (12.32)$$

almost surely, where $0 < \varepsilon \ll 1$ is an arbitrary small parameter. It is next convenient to introduce a regularized form of the field [8], given by

$$[C(\mathbf{x})] = \frac{1}{1 + \varepsilon} [\underline{C}(\mathbf{x})]^{1/2} (\varepsilon [I_6] + [M(\mathbf{x})]) [\underline{C}(\mathbf{x})]^{1/2}, \quad \forall \mathbf{x} \in \Omega, \quad (12.33)$$

where $\{[M(\mathbf{x})], \mathbf{x} \in \Omega\}$ denotes an auxiliary $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$ -valued random field. Note that Eq. (12.33) defines a one-to-one correspondence between $[C(\mathbf{x})]$ and $[M(\mathbf{x})]$, because $[\underline{C}(\mathbf{x})]^{1/2}$ is almost surely invertible by construction. The state space for the random field $\{[M(\mathbf{x})], \mathbf{x} \in \Omega\}$ readily follows from its algebraic definition and Eq. (12.32). It can then be shown that the field satisfies the uniform ellipticity property

$$\langle \mathbf{z}, [C(\mathbf{x})] \mathbf{z} \rangle \geq \varepsilon_0 \mathbf{z}^2, \quad \forall \mathbf{z} \in \mathbb{R}^6, \quad (12.34)$$

in which the constant ε_0 is given by

$$\varepsilon_0 = \frac{k_0 \varepsilon}{1 + \varepsilon}. \quad (12.35)$$

Note that by construction, the random field $\{[M(\mathbf{x})], \mathbf{x} \in \Omega\}$ is such that

$$E\{[M(\mathbf{x})]\} = [I_6], \quad \forall \mathbf{x} \in \Omega. \quad (12.36)$$

In practice, the stochastic modeling step can thus be performed on the random field $\{[M(\mathbf{x})], \mathbf{x} \in \Omega\}$, which uniquely defines $\{[C(\mathbf{x})], \mathbf{x} \in \Omega\}$ through Eq. (12.33). This construction is specifically discussed in the next section.

12.3.2 Setting up the MaxEnt formulation

Following the discussion in Section 12.2.3, the random field $\{[M(\mathbf{x})], \mathbf{x} \in \Omega\}$ is defined as

$$[M(\mathbf{x})] = \mathcal{H}(\Xi(\mathbf{x})), \quad \forall \mathbf{x} \in \Omega, \quad (12.37)$$

where $\mathcal{H}$ is a nonlinear mapping that will be determined through the MaxEnt approach, and $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ is now a $\mathbb{R}^n$ -valued homogeneous Gaussian random field with normalized, statistically independent components, each defined by a correlation function $R_{\Xi_k}(\boldsymbol{\tau}) = E\{\Xi_k(\mathbf{x} + \boldsymbol{\tau}) \Xi_k(\mathbf{x})\}$, $\forall \boldsymbol{\tau} \in \mathbb{R}^d$. Here, n denotes the dimension of the

matrix set $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$, with $2 \leq n \leq 21$ ($n = 2$ corresponds to isotropic materials and $n = 21$ to triclinic materials).

One way to approach the MaxEnt problem is to consider the constraints

$$E\{[\mathbf{M}(\mathbf{x})]\} = [\mathbf{I}_6], \quad \forall \mathbf{x} \in \Omega, \quad (12.38)$$

and

$$E\{\log(\det([\mathbf{M}(\mathbf{x})]))\} = \chi, \quad -\infty < \chi < 0, \quad (12.39)$$

where the latter is, here again, introduced as a repulsive term. At this point, the fact that $[\mathbf{M}(\mathbf{x})]$ is $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$ -valued can be used to reformulate the construction in a more convenient form. More precisely, the random matrix $[\mathbf{M}(\mathbf{x})]$ ($\mathbf{x}$ being fixed) can be expanded as

$$[\mathbf{M}(\mathbf{x})] = \sum_{i=1}^n M_i(\mathbf{x}) [E^{(i)}], \quad (12.40)$$

where $\{[E^{(i)}]\}_{i=1}^n$ is the Walpole basis of the matrix set $\mathbb{S}_6^{\text{sym}}(\mathbb{R})$ [55], and the random vector of coefficients $\{\mathbf{M}(\mathbf{x}), \mathbf{x} \in \Omega\}$ takes its values in

$$\mathcal{S}^{\text{sym}} = \left\{ \mathbf{m} \in \mathbb{R}^n \left| \sum_{i=1}^n m_i [E^{(i)}] > 0 \right. \right\}. \quad (12.41)$$

The definition of this basis involves, in part, orthogonal tensors that form an algebra isomorphic to that of $N_W \times N_W$ matrices, where N_W depends on the material symmetry under consideration [55]. This particular structure allows for the definition of a symbolic representation (which is referred to as the Walpole array representation in Ref. [56]) for any elasticity tensor $[\mathbf{M}] \in \mathbb{S}_6^{\text{sym}}(\mathbb{R})$, reported below for a few symmetry classes (see Ref. [55] for other material symmetries).

- Isotropic material ($n = 2$):

$$[\mathbf{M}] = \{M_1, M_2\}. \quad (12.42)$$

- Cubic material ($n = 3$):

$$[\mathbf{M}] = \{M_1, M_2, M_3\}. \quad (12.43)$$

- Transversely isotropic material ($n = 5$):

$$[\mathbf{M}] = \left\{ [N^{(1)}], M_4, M_5 \right\}, \quad (12.44)$$

with

$$\left[N^{(1)} \right] = \begin{bmatrix} M_1 & M_3 \\ M_3 & M_2 \end{bmatrix}.$$

- Tetragonal system ($n = 7$):

$$[M] = \left\{ \left[N^{(1)} \right], \left[N^{(2)} \right], M_7 \right\}, \quad (12.45)$$

with

$$\left[N^{(1)} \right] = \begin{bmatrix} M_1 & M_3 \\ M_3 & M_2 \end{bmatrix}, \quad \left[N^{(2)} \right] = \begin{bmatrix} M_4 & M_6 \\ M_6 & M_5 \end{bmatrix}.$$

The properties of the Walpole basis make algebraic manipulations on elasticity tensors straightforward. Elevating a transversely isotropic tensor to any power can be performed, for instance, as

$$[M]^k = \left\{ \left[N^{(1)} \right]^k, M_4^k, M_5^k \right\}, \quad \forall k \in \mathbb{Z}, \quad (12.46)$$

where the positive definiteness of $[M]$ implies the positive-definiteness (and thus, the invertibility) of $\left[N^{(1)} \right]$, M_4 and M_5 (and vice versa). Taking advantage of these properties, the constraint [Eqs. \(12.38\) and \(12.39\)](#) can be rewritten on the elements of the symbolic decomposition [\[54\]](#). The constraint on the mean value gives

$$E \left\{ \left[N^{(i)}(\mathbf{x}) \right] \right\} = [I_{N_W}], \quad 1 \leq i \leq \mathcal{I}, \quad (12.47)$$

where the number $\mathcal{I}$ of matrix-valued elements is symmetry-dependent (and ranges from 0, for the isotropic and cubic classes, to 2), and

$$E \{ M_j(\mathbf{x}) \} = 1, \quad \mathcal{J}_0 \leq j \leq n, \quad (12.48)$$

for any $\mathbf{x}$ in Ω , with $\mathcal{J}_0 = 1 + N_W(N_W + 1)\mathcal{I}/2$. The repulsive constraint given by [Eq. \(12.39\)](#) yields

$$E \left\{ \log \left(\det \left(\left[N^{(i)}(\mathbf{x}) \right] \right) \right) \right\} = \chi_i, \quad -\infty < \chi_i < 0, \quad 1 \leq i \leq \mathcal{I} \quad (12.49)$$

and

$$E \{ \log(M_j(\mathbf{x})) \} = \chi_j, \quad -\infty < \chi_j < 0, \quad \mathcal{J}_0 \leq j \leq n. \quad (12.50)$$

As Eqs. (12.47)–(12.50) do not contain cross information on the random variables involved, the MaxEnt approach implies that the random elements in the Walpole representation are, indeed, statistically independent. The probability density function of each random matrix $[N^{(i)}(\mathbf{x})]$, $1 \leq i \leq \mathcal{I}$, is first obtained by considering Eqs. 12.47–12.49 (see Ref. [32] for technical details). The result reads as

$$p_{[N^{(i)}(\mathbf{x})]}([N]) = \mathbb{1}_{\mathbb{S}_{N_W}^{++}(\mathbb{R})}([N]) c(\det([N]))^{\alpha_i} \exp\left(-\frac{(N_W + 1)}{2\delta_{[N^{(i)}]}^2} \text{Tr}([N])\right), \quad (12.51)$$

where α_i is defined as

$$\alpha_i = \frac{(N_W + 1)(1 - \delta_{[N^{(i)}]}^2)}{2\delta_{[N^{(i)}]}^2} \quad (12.52)$$

and $\delta_{[N^{(i)}]}$ is the dispersion parameter given by

$$\delta_{[N^{(i)}]} = \left\{ \frac{1}{N_W} E\left\{ \left\| [N^{(i)}(\mathbf{x})] - [I_{N_W}] \right\|_F^2 \right\} \right\}^{1/2}, \quad (12.53)$$

This parameter is such that

$$0 < \delta_{[N^{(i)}]} < \sqrt{\frac{N_W + 1}{N_W + 5}}. \quad (12.54)$$

Regarding the scalar-valued random elements, it can readily be observed that the constraint Eqs. (12.48) and (12.50) are similar to those already introduced in (12.22) and (12.23). Consequently, it can be deduced that

$$M_j(\mathbf{x}) \sim \mathcal{G}\left(\delta_{M_j}^{-2}, \delta_{M_j}^2\right), \quad \mathcal{J}_0 \leq j \leq n, \quad (12.55)$$

for any $\mathbf{x}$ fixed in Ω , where δ_{M_j} is the coefficient of variation of $M_j(\mathbf{x})$. The next step in the modeling approach is to express the random variables defined by the probability density functions (12.51) and (12.55) as functions of Gaussian variables and to substitute the latter with the random variables corresponding to a Gaussian field taken at location $\mathbf{x}$. This point is addressed in the next section.

12.3.3 Defining the non-Gaussian random field

Let $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ be a $\mathbb{R}^n$ -valued, homogeneous, and normalized Gaussian random field with statistically independent components, defined by a set of correlation functions $\{R_{\Xi_k}\}_{k=1}^n$. For any $\mathbf{x}$ in Ω , we introduce the subvector partitioning

$$\Xi(\mathbf{x}) = \left(\Xi^{(1)}(\mathbf{x})^T, \dots, \Xi^{(\mathcal{I})}(\mathbf{x})^T, \Xi_{\mathcal{J}_0}(\mathbf{x}), \dots, \Xi_n(\mathbf{x}) \right), \quad (12.56)$$

where the first $\mathcal{I}$ vectors are $\mathbb{R}^{N_W(N_W+1)/2}$ Gaussian random vectors and the remaining terms are scalar Gaussian random variables. This structure allows us to define a series of independent mappings, following the convention

$$\Xi^{(i)}(\mathbf{x}) \mapsto [\mathbf{N}^{(i)}(\mathbf{x})], \quad 1 \leq i \leq \mathcal{I} \quad (12.57)$$

and

$$\Xi_j(\mathbf{x}) \mapsto M_j(\mathbf{x}), \quad \mathcal{J}_0 \leq j \leq n. \quad (12.58)$$

In particular, and following the construction presented in Ref. [9], each random matrix $[\mathbf{N}^{(i)}(\mathbf{x})]$, $1 \leq i \leq \mathcal{I}$, can be decomposed as

$$[\mathbf{N}^{(i)}(\mathbf{x})] = [\mathbf{H}^{(i)}(\mathbf{x})]^T [\mathbf{H}^{(i)}(\mathbf{x})], \quad (12.59)$$

where $[\mathbf{H}^{(i)}(\mathbf{x})]$ is an upper triangular random matrix with components defined as

$$[\mathbf{H}^{(i)}(\mathbf{x})]_{k\ell} = \frac{\delta_{[\mathbf{N}^{(i)}]}}{\sqrt{N_W + 1}} \Xi_{\beta(k,\ell)}^{(i)}(\mathbf{x}) \quad (12.60)$$

for $1 \leq k < \ell \leq N_W$, and as

$$[\mathbf{H}^{(i)}(\mathbf{x})]_{\ell\ell} = \frac{\delta_{[\mathbf{N}^{(i)}]}}{\sqrt{N_W + 1}} \sqrt{2F_{\mathcal{G}(\gamma_\ell^{(i)},1)}^{-1} \left(F_{\mathcal{N}(0,1)} \left(\Xi_{\beta(\ell,\ell)}^{(i)}(\mathbf{x}) \right) \right)} \quad (12.61)$$

for $1 \leq \ell \leq N_W$ (where the notations introduced in Eq. 12.26 are used). In the two equations above, $\beta(k,\ell)$ and $\gamma_\ell^{(i)}$ are given by

$$\beta(k,\ell) = k + \frac{\ell(\ell-1)}{2}, \quad \gamma_\ell^{(i)} = \frac{N_W + 1}{2\delta_{[\mathbf{N}^{(i)}]}^2} + \frac{1-\ell}{2}. \quad (12.62)$$

The random fields $\{M_j(\mathbf{x}), \mathbf{x} \in \Omega\}$, $\mathcal{J}_0 \leq j \leq n$, can easily be defined using the results from Section 12.2.4:

$$M_j(\mathbf{x}) = F_{\mathcal{G}(\delta_{M_j}^{-2}, \delta_{M_j}^2)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_j(\mathbf{x})) \right), \quad \forall \mathbf{x} \in \Omega. \quad (12.63)$$

The combination of Eqs. (12.59)–(12.61) and Eq. (12.63) completely defines the mappings introduced in Eqs. (12.57 and 12.58) and hence the mapping $\mathcal{H}$ (see Eq. 12.37) and the random field model for $\{[\mathbf{M}(\mathbf{x})], \mathbf{x} \in \Omega\}$.

The non-Gaussian random field model presented in this section enables the efficient simulation of tensor-valued elasticity fields for any material symmetry of interest. Every drawn sample is, by construction, consistent with the theory of linear elasticity, and the model ensures that the SBVP is well posed. In addition, it is worth noticing that

in the presented framework, the entire elasticity tensor is randomized: this is in contrast with formulations where a few moduli are made stochastic while others are kept deterministic. In practice, the random field model is parametrized by

- the correlation functions $\{R_{\Xi_k}\}_{k=1}^n$ defining the n statistically independent components of the Gaussian field $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$;
- the mean function $\mathbf{x} \mapsto [\underline{C}(\mathbf{x})]$ of the elasticity field; and
- the sets of parameters $\{\delta_{[N^{(i)}]}\}_{i=1}^T$ and $\{\delta_{M_j}\}_{j=\mathcal{J}_0}^n$ controlling the statistical fluctuations of the random elements in the Walpole representation.

Contributions related to the experimental identification of an algebraic probabilistic model in two-dimensional elasticity can be found in Refs. [57,58], while identification results based on numerical (multiscale) experiments can be found in, e.g., Refs. [11,33,34,39,59]. Finally, discussions about validation of information-theoretic, non-Gaussian random field models can be found for various types of metrics and quantities of interest in Refs. [11,59–61].

12.3.4 Application to transversely isotropic materials

12.3.4.1 Formulation

In this section, we deploy the proposed modeling framework to model an elasticity tensor field exhibiting transverse isotropy almost surely, at any point of the domain. Let $\mathbf{n}$ be the unit vector defining the axis of transverse isotropy, and introduce the second-order tensors $[P]$ and $[Q]$ given by

$$[P] = \mathbf{n} \otimes \mathbf{n}, \quad [Q] = [I_3] - [P], \quad (12.64)$$

where the symbol $\otimes$ denotes tensor product. In this case, the basis introduced in Eq. (12.40) is obtained by using an appropriate matrix representation of the following fourth-order tensors [55]:

$$\begin{aligned} \llbracket E^{(1)} \rrbracket &= [P] \otimes [P], \quad \llbracket E^{(2)} \rrbracket = ([Q] \otimes [Q])/2, \\ \llbracket E^{(3)} \rrbracket &= ([P] \otimes [Q] + [Q] \otimes [P])/\sqrt{2}, \\ \llbracket E^{(4)} \rrbracket &= [Q] \boxtimes [Q] - ([Q] \otimes [Q])/2, \quad \llbracket E^{(5)} \rrbracket = [P] \boxtimes [Q] + [Q] \boxtimes [P], \end{aligned} \quad (12.65)$$

where $\boxtimes$ is the symmetrized tensor product. The random elasticity matrix $[\mathbf{C}(\mathbf{x})] = \sum_{i=1}^5 C_i(\mathbf{x})[E_i]$ can then be written in symbolic form as

$$[\mathbf{C}(\mathbf{x})] = \{[\mathbf{D}(\mathbf{x})], C_4(\mathbf{x}), C_5(\mathbf{x})\}, \quad (12.66)$$

with

$$[\mathbf{D}(\mathbf{x})] = \begin{bmatrix} C_1(\mathbf{x}) & C_3(\mathbf{x}) \\ C_3(\mathbf{x}) & C_2(\mathbf{x}) \end{bmatrix}. \quad (12.67)$$

For $\mathbf{n} = (0, 0, 1)$, the elasticity matrix in Voigt notation reads as

$$[\mathbf{C}(\mathbf{x})] = \begin{bmatrix} \frac{C_2(\mathbf{x}) + C_4(\mathbf{x})}{2} & \frac{C_2(\mathbf{x}) - C_4(\mathbf{x})}{2} & \frac{C_3(\mathbf{x})}{\sqrt{2}} & 0 & 0 & 0 \\ \frac{C_2(\mathbf{x}) - C_4(\mathbf{x})}{2} & \frac{C_2(\mathbf{x}) + C_4(\mathbf{x})}{2} & \frac{C_3(\mathbf{x})}{\sqrt{2}} & 0 & 0 & 0 \\ \frac{C_3(\mathbf{x})}{\sqrt{2}} & \frac{C_3(\mathbf{x})}{\sqrt{2}} & C_1(\mathbf{x}) & 0 & 0 & 0 \\ 0 & 0 & 0 & C_5(\mathbf{x}) & 0 & 0 \\ 0 & 0 & 0 & 0 & C_5(\mathbf{x}) & 0 \\ 0 & 0 & 0 & 0 & 0 & C_4(\mathbf{x}) \end{bmatrix}.$$

The mean matrix $[\underline{\mathbf{C}}(\mathbf{x})]$ can similarly be decomposed as

$$[\underline{\mathbf{C}}(\mathbf{x})] = \{[\underline{\mathbf{D}}(\mathbf{x})], \underline{C}_4(\mathbf{x}), \underline{C}_5(\mathbf{x})\}, \quad (12.68)$$

with

$$[\underline{\mathbf{D}}(\mathbf{x})] = \begin{bmatrix} \underline{C}_1(\mathbf{x}) & \underline{C}_3(\mathbf{x}) \\ \underline{C}_3(\mathbf{x}) & \underline{C}_2(\mathbf{x}) \end{bmatrix} \quad (12.69)$$

and $\underline{C}_i(\mathbf{x}) = E\{C_i(\mathbf{x})\}$ for $1 \leq i \leq 5$. The random matrix $[\mathbf{M}(\mathbf{x})]$ can then be written in symbolic form as

$$[\mathbf{M}(\mathbf{x})] = \left\{ \begin{bmatrix} M_1(\mathbf{x}) & M_3(\mathbf{x}) \\ M_3(\mathbf{x}) & M_2(\mathbf{x}) \end{bmatrix}, M_4(\mathbf{x}), M_5(\mathbf{x}) \right\}, \quad (12.70)$$

so that

$$[\mathbf{N}^{(1)}(\mathbf{x})] = \begin{bmatrix} M_1(\mathbf{x}) & M_3(\mathbf{x}) \\ M_3(\mathbf{x}) & M_2(\mathbf{x}) \end{bmatrix}. \quad (12.71)$$

From the definition in Eq. (12.33) and the properties of the basis, it follows that

$$[\mathbf{D}(\mathbf{x})] = \frac{1}{1 + \varepsilon} [\underline{\mathbf{D}}(\mathbf{x})]^{1/2} \left(\varepsilon [I_2] + [\mathbf{N}^{(1)}(\mathbf{x})] \right) [\underline{\mathbf{D}}(\mathbf{x})]^{1/2}, \quad (12.72)$$

$$C_4(\mathbf{x}) = \frac{1}{1 + \varepsilon} \underline{C}_4(\mathbf{x}) (\varepsilon + M_4(\mathbf{x})), \quad (12.73)$$

and

$$C_5(\mathbf{x}) = \frac{1}{1 + \varepsilon} C_5(\mathbf{x})(\varepsilon + M_5(\mathbf{x})). \quad (12.74)$$

The combination of Eqs. (12.72–12.74) with Eq. (12.66) completely defines the elasticity tensor random field $\{\mathbf{C}(\mathbf{x}), \mathbf{x} \in \Omega\}$.

Let us now turn to the explicit definition of the random fields $\{[\mathbf{N}^{(1)}(\mathbf{x})], \mathbf{x} \in \Omega\}$, $\{M_4(\mathbf{x}), \mathbf{x} \in \Omega\}$, and $\{M_5(\mathbf{x}), \mathbf{x} \in \Omega\}$. In the present case, we have $I = 1$ and $N_W = 2$ and $\mathcal{J}_0 = 1 + N_W(N_W + 1)I/2 = 4$. The underlying Gaussian field introduced at the beginning of Section 12.3.3 (see Eq. 12.56) is then taken as

$$\Xi(\mathbf{x}) = \left(\Xi^{(1)}(\mathbf{x})^T, \Xi_4(\mathbf{x}), \Xi_5(\mathbf{x}) \right), \quad (12.75)$$

with $\Xi^{(1)}(\mathbf{x})^T = (\Xi_1(\mathbf{x}), \Xi_2(\mathbf{x}), \Xi_3(\mathbf{x}))^T$. Remember that by construction, the random fields $\{\Xi_i(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ and $\{\Xi_j(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ are statistically independent for $i \neq j$. The mapping $\Xi^{(1)}(\mathbf{x}) \mapsto [\mathbf{N}^{(1)}(\mathbf{x})]$ (see Eq. 12.57) is defined by using Eqs. 12.59–12.62. Specifically, one has $[\mathbf{N}^{(1)}(\mathbf{x})] = [\mathbf{H}^{(1)}(\mathbf{x})]^T [\mathbf{H}^{(1)}(\mathbf{x})]$, where $[\mathbf{H}^{(1)}(\mathbf{x})]$ is an upper-triangular 2×2 matrix such that

$$[\mathbf{H}^{(1)}(\mathbf{x})]_{11} = \frac{\delta_{[\mathbf{N}^{(1)}]}}{\sqrt{3}} \sqrt{2F_{\mathcal{G}(\gamma_1^{(1)}, 1)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_1(\mathbf{x})) \right)} \quad (12.76)$$

$$[\mathbf{H}^{(1)}(\mathbf{x})]_{22} = \frac{\delta_{[\mathbf{N}^{(1)}]}}{\sqrt{3}} \sqrt{2F_{\mathcal{G}(\gamma_2^{(1)}, 1)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_3(\mathbf{x})) \right)} \quad (12.77)$$

and

$$[\mathbf{H}^{(1)}(\mathbf{x})]_{12} = \frac{\delta_{[\mathbf{N}^{(1)}]}}{\sqrt{3}} \Xi_2(\mathbf{x}), \quad (12.78)$$

with

$$\gamma_1^{(1)} = \frac{3}{2\delta_{[\mathbf{N}^{(1)}]}^2}, \quad \gamma_2^{(1)} = \frac{3}{2\delta_{[\mathbf{N}^{(1)}]}^2} - \frac{1}{2}. \quad (12.79)$$

Recall that in the equations above, $\delta_{[\mathbf{N}^{(1)}]}$ is a model parameter controlling the level of statistical fluctuations of the random matrix $[\mathbf{N}^{(1)}(\mathbf{x})]$ such that

$0 < \delta_{[N^{(1)}(\mathbf{x})]} < \sqrt{3/7} \approx 0.6547$ (see Eq. 12.54). The mappings $\Xi_4(\mathbf{x}) \mapsto M_4(\mathbf{x})$ and $\Xi_5(\mathbf{x}) \mapsto M_5(\mathbf{x})$ (see Eq. 12.58) are finally obtained from Eq. (12.63):

$$M_4(\mathbf{x}) = F_{\mathcal{G}(\delta_{M_4}^{-2}, \delta_{M_4}^2)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_4(\mathbf{x})) \right), \quad \forall \mathbf{x} \in \Omega, \quad (12.80)$$

$$M_5(\mathbf{x}) = F_{\mathcal{G}(\delta_{M_5}^{-2}, \delta_{M_5}^2)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_5(\mathbf{x})) \right), \quad \forall \mathbf{x} \in \Omega, \quad (12.81)$$

where δ_{M_4} and δ_{M_5} are the coefficients of variation of $M_4(\mathbf{x})$ and $M_5(\mathbf{x})$, respectively. In practice, a realization of the non-Gaussian elasticity random field $\{[\mathbf{C}(\mathbf{x})], \mathbf{x} \in \Omega\}$ can be obtained by first drawing realizations of the Gaussian random field $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ over a set of points (typically, the integration points of a finite element mesh), using any appropriate algorithm, and then by using the equations above, from Eqs. (12.66)–(12.81), to compute the corresponding realization of the elastic parameters.

12.3.4.2 Two-dimensional numerical illustration

To illustrate the formulation, we consider the simulation of the elasticity random field model defined in Section 12.3.4.1. The mean model is chosen constant and is defined by using standard values for a unidirectional carbon–epoxy composite:

$$[\underline{\mathbf{C}}] = \begin{pmatrix} 10.0735 & 0.5497 & 2.9745 & 0 & 0 & 0 \\ & 10.0735 & 2.9745 & 0 & 0 & 0 \\ & & 182.6657 & 0 & 0 & 0 \\ & & & 14 & 0 & 0 \\ \text{Sym.} & & & & 14 & 0 \\ & & & & & 9.5238 \end{pmatrix}. \quad (12.82)$$

This mean value exhibits transverse isotropy with respect to $\mathbf{n} = (0, 0, 1)$. The mean values of the coefficients on the Walpole basis are given by

$$\underline{C}_1 = 182.6657, \underline{C}_2 = 10.6232, \underline{C}_3 = 4.2066, \underline{C}_4 = 9.5238, \underline{C}_5 = 14. \quad (12.83)$$

We take $\Omega = [-0.5, 0.5] \times [-0.5, 0.5]$, and the domain is discretized with 3652 linear triangular finite elements (1907 nodes); see Fig. 12.4.

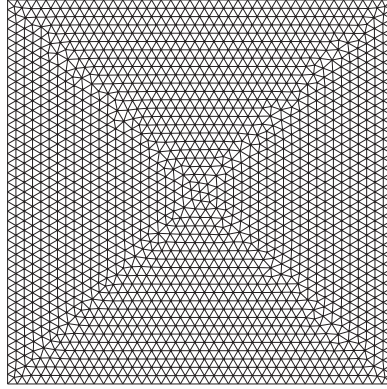


Figure 12.4 Finite element mesh of domain Ω .

The simulation of the random field at the nodes can then be performed as follows. First, the correlation functions for all Gaussian random fields $\{\Xi_k(\mathbf{x}), \mathbf{x} \in \Omega\}$, $1 \leq k \leq 5$, are assumed similar (for simplicity) and given by (squared exponential kernel)

$$R_{\Xi_k}(\boldsymbol{\tau}) = \exp\{-\tau_1^2 / (2\mathcal{L}_1^2)\} \times \exp\{-\tau_2^2 / (2\mathcal{L}_2^2)\}, \quad (12.84)$$

where τ_i is the lag distance and $\mathcal{L}_i$ is a parameter controlling the correlation range along $\mathbf{e}^i$, $1 \leq i \leq 2$, with $\mathbf{e}^1 = (1, 0)$ and $\mathbf{e}^2 = (0, 1)$. By definition, the spatial correlation length along $\mathbf{e}^i$ is equal to $\mathcal{L}_i \sqrt{\pi/2}$. The simulation of the Gaussian fields can be conducted through a variety of techniques, including the use of a spectral representation [62–64], factorization-based techniques [65,66], or the approach based on (fractional) stochastic partial differential equations proposed in Ref. [67]. A factorization method is chosen hereinafter, and the realizations for the independent components of $\{\Xi(\mathbf{x}), \mathbf{x} \in \Omega\}$ are shown in Fig. 12.5.

The realizations of $\{\Xi_1(\mathbf{x}), \mathbf{x} \in \Omega\}$, $\{\Xi_2(\mathbf{x}), \mathbf{x} \in \Omega\}$, and $\{\Xi_3(\mathbf{x}), \mathbf{x} \in \Omega\}$ are next used to compute the realization of $\{[\mathbf{H}^{(1)}(\mathbf{x})], \mathbf{x} \in \Omega\}$ by using Eqs. (12.76–12.78), and this realization is subsequently used to compute the realization of $\{[\mathbf{N}^{(1)}(\mathbf{x})], \mathbf{x} \in \Omega\}$ (see Eq. 12.59). The realizations of $\{\Xi_4(\mathbf{x}), \mathbf{x} \in \Omega\}$ and $\{\Xi_5(\mathbf{x}), \mathbf{x} \in \Omega\}$ are then fed into Eqs. (12.80 and 12.81) to obtain the realizations of $\{M_4(\mathbf{x}), \mathbf{x} \in \Omega\}$ and $\{M_5(\mathbf{x}), \mathbf{x} \in \Omega\}$. These realizations are shown in Fig. 12.6.

The realizations of the components of the elasticity tensor random field on the Walpole basis can finally be generated by using Eqs. (12.72), (12.73), and (12.74). The realizations of some components of $\{[\mathbf{C}(\mathbf{x})], \mathbf{x} \in \Omega\}$ are shown in Fig. 12.7 for $\varepsilon = 10^{-6}$.

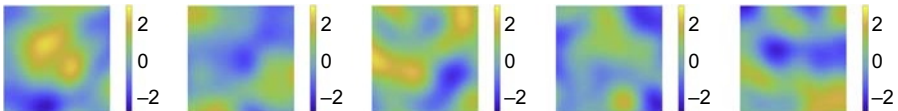


Figure 12.5 Realizations of the components of the Gaussian random field $\{\Xi(\mathbf{x}), \mathbf{x} \in \Omega\}$.

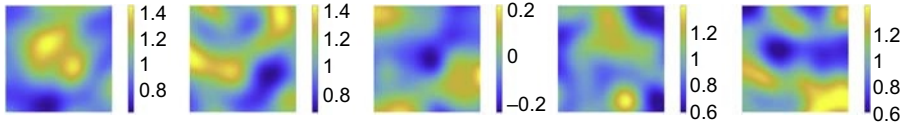


Figure 12.6 Realizations of the random fields $\{[N^{(1)}(\mathbf{x})]_{11}, \mathbf{x} \in \Omega\}$, $\{[N^{(1)}(\mathbf{x})]_{22}, \mathbf{x} \in \Omega\}$, $\{[N^{(1)}(\mathbf{x})]_{12}, \mathbf{x} \in \Omega\}$, $\{M_4(\mathbf{x}), \mathbf{x} \in \Omega\}$, and $\{M_5(\mathbf{x}), \mathbf{x} \in \Omega\}$ (from left to right), associated with the realizations of the Gaussian field shown in Fig. 12.5.

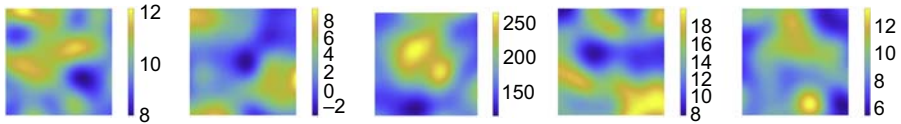


Figure 12.7 Realizations of the random fields $\{[C(\mathbf{x})]_{11}, \mathbf{x} \in \Omega\}$, $\{[C(\mathbf{x})]_{13}, \mathbf{x} \in \Omega\}$, $\{[C(\mathbf{x})]_{33}, \mathbf{x} \in \Omega\}$, $\{[C(\mathbf{x})]_{44}, \mathbf{x} \in \Omega\}$, and $\{[C(\mathbf{x})]_{66}, \mathbf{x} \in \Omega\}$ (from left to right).

Notice how the elastic coefficients fluctuate smoothly around the mean value given by Eq. (12.82), due in part to the choice of a squared exponential covariance function for the underlying Gaussian fields. Such samples can be used to perform some uncertainty propagation by using any appropriate stochastic solvers (see Ref. [2] for a review).

12.4 Application to vector-valued non-Gaussian random fields in nonlinear elasticity

12.4.1 Background

We now turn to the randomization of nonlinear constitutive models and specifically focus on hyperelastic behaviors. In contrast to linear elasticity, for which probabilistic representations can be derived for any underlying structure of the elasticity operator (that is, for all types of symmetry), the case of nonlinear elasticity cannot be addressed in an exhaustive manner, given the large variety of (deterministic) models available in the literature. Consequently, this section is not devoted to the construction of non-Gaussian stochastic models for all types of strain energy functions (which are also referred to as potentials in the sequel). Alternatively, it aims at developing the modeling approach on a specific class of models, associated with isotropic and incompressible materials (to facilitate technical exposure). Interested readers are referred to Refs. [40–42] for details and various extensions (see also [43]) and can straightforwardly extend the presented results to any strain energy functions of interest. An application to stochastic nonlinear homogenization is specifically presented in Ref. [41], while discussions about inverse identification and validation can be found in Refs. [44,68].

Let Ω denote the reference configuration in $\mathbb{R}^d$, with generic point $\mathbf{x}$. The body under consideration is assumed to undergo a deformation map $\boldsymbol{\varphi}$, and we denote by

$[F]$ the associated deformation gradient: $[F]_{ij} = \partial \varphi_i / \partial x_j$. As indicated above, it is assumed for simplicity that the body exhibits an isotropic incompressible hyperelastic response, characterized by a frame invariant strain energy function w . The (deterministic) constitutive model to be randomized is given by

$$[T] = \frac{\partial w([F])}{\partial [F]} - \lambda [F]^{-T}, \quad \forall [F] \in \mathbb{M}_3(\mathbb{R}), \quad (12.85)$$

where $[T]$ is the first Piola–Kirchhoff stress tensor and λ is the Lagrange multiplier arising from the incompressibility condition, $\det([F]) = 1$. The above constitutive law can also be expressed using the Cauchy stress tensor $[\sigma]$ as

$$[\sigma] = \frac{\partial w([F])}{\partial [F]} [F]^T - \lambda [I_3]. \quad (12.86)$$

12.4.2 Setting up the MaxEnt formulation

As for the linear elastic case detailed in [Section 12.3](#), the first step of the methodology consists in identifying mathematical requirements for the strain energy function. These requirements are essentially raised by existence theorems for nonlinear boundary value problems. Following Refs. [\[69,70\]](#), the boundary value problem of three-dimensional finite elasticity admits at least one solution if w is polyconvex and satisfies the coercivity property

$$\exists c_0 > 0, c_1 \in \mathbb{R} \left| w([F]) \geq c_0 \left(\| [F] \|_F^2 + \| \text{Cof}([F]) \|_F^{\frac{3}{2}} \right) + c_1, \quad (12.87) \right.$$

where the notation $\text{Cof}([F])$ denotes the cofactor matrix of $[F]$. It should be noticed that the above properties are sufficient but not necessary and that other types of constraints could equivalently be accounted for.

To derive explicit results, it is relevant at this point to select a form for the strain energy function. Given its widespread adoption in both numerical modeling and experimental analysis, the class of Ogden potentials is selected as a prototypical class of strain energy functions [\[71\]](#). Any potential in this class writes

$$\begin{aligned} w([F]) = & \sum_{i=1}^m p_i \left(\text{Tr} \left(([F]^T [F])^{\eta_i/2} \right) - 3 \right) \\ & + \sum_{j=m+1}^{m+n} p_j \left(\text{Tr} \left((\text{Cof}([F]^T [F]))^{\eta_j/2} \right) - 3 \right), \end{aligned} \quad (12.88)$$

where $\{p_i\}_{i=1}^{m+n}$ and $\{\eta_i\}_{i=1}^{m+n}$ are model parameters. Note that the popular Mooney–Rivlin model is obtained by setting $m = n = 1$ and $\eta_1 = \eta_2 = 2$ and thus reads as

$$w^{mr}([F]) = p_1 \left(\| [F] \|_F^2 - 3 \right) + p_2 \left(\| \text{Cof}([F]) \|_F^2 - 3 \right). \quad (12.89)$$

It can then be shown (see, e.g., Ref. [70]) that the strain energy function w defined by Eq. (12.88) satisfies the admissibility requirements if

$$p_k > 0, \quad 1 \leq k \leq m+n, \quad (12.90)$$

and

$$\eta_1 \geq 2, \quad \eta_{m+1} \geq \frac{3}{2}, \quad \eta_1 \geq \dots \geq \eta_m \geq 1, \quad \eta_{m+1} \geq \dots \geq \eta_{m+n} \geq 1. \quad (12.91)$$

These inequalities constitute a first set of constraints; the stochastic model must accommodate in the almost sure sense. Another constraint stems from the so-called consistency condition at small strains, obtained by linearizing the strain energy function near the reference configuration (that is, at $[F] = [I_3]$). In the case under consideration, this condition is given by

$$2\mu = \sum_{k=1}^{m+n} p_k \eta_k^2, \quad (12.92)$$

where μ denotes the shear modulus of the (isotropic) material.

Let W be the stochastic stored energy function corresponding to a proper randomization of the Ogden potential given by Eq. (12.88). Let $\mathbf{P} = (P_1, \dots, P_{m+n})$ be the random variable corresponding to the probabilistic modeling of the vector $\mathbf{p} = (p_1, \dots, p_{m+n})$, and assume that the exponents $\{\eta_i\}_{i=1}^{m+n}$ are deterministic and such that the inequalities in Eq. (12.91) hold. It should be noticed that the randomization of these exponents does not raise any additional difficulties and can easily be performed in the proposed framework. The relevance of this choice is, however, application-dependent, and stochastic models with deterministic exponents were proven very efficient in, e.g., Ref. [68] (see Remark 12.3).

The stochastic Ogden strain energy function then writes

$$\begin{aligned} W([F]) = & \sum_{i=1}^m P_i \left(\text{Tr} \left(([F]^T [F])^{\eta_i/2} \right) - 3 \right) \\ & + \sum_{j=m+1}^{m+n} P_j \left(\text{Tr} \left(\text{Cof} \left(([F]^T [F])^{\eta_j/2} \right) - 3 \right), \end{aligned} \quad (12.93)$$

and the consistency at small strains implies that

$$2G = \sum_{k=1}^{m+n} P_k \eta_k^2, \quad (12.94)$$

where G is the stochastic shear modulus. Several strategies can be pursued to impose the equality constraint (12.94). One possibility is to define the stochastic shear

modulus through Eq. (12.94), in which case the model is developed on $\mathbf{P}$ and the only constraints to be fed into the MaxEnt principle are those related to Eq. (12.90). It can thus be anticipated, in view of the discussion in Section 12.3, that the components of the random vector $\mathbf{P}$ would be statistically independent from one another. An alternative approach consists in modeling the random shear modulus, with the aim to rely on small strain information to perform model calibration for instance. This choice imposes, in turn, to select an arbitrary component in $\mathbf{P}$, say P_{m+n} , for instance, and to define it algebraically, through Eq. (12.94). This modeling approach is pursued hereinafter.

Let $\tilde{\mathbf{P}}$ be the random vector obtained by removing the component P_{m+n} in $\mathbf{P}$: $\tilde{\mathbf{P}} = (P_1, \dots, P_{m+n-1})$. Let us introduce the decomposition

$$\tilde{f}_{\mathbf{P},G}(\mathbf{p}, \mu) = f_G(\mu) \tilde{f}_{\mathbf{P}|G=\mu}(\mathbf{p}; \mu), \quad (12.95)$$

where f_G is the probability density function of the random shear modulus G and $\tilde{f}_{\mathbf{P}|G=\mu}$ is the conditional probability density function of $\tilde{\mathbf{P}}$ given $G = \mu$. As G is an elastic constant, we proceed as in the section devoted to linearized elasticity. The constraints related to the stochastic shear modulus are then written as

$$E\{G\} = \underline{g} \quad (12.96)$$

and

$$E\{\log(G)\} = \chi, \quad |\chi| < +\infty. \quad (12.97)$$

so that

$$G \sim \mathcal{G}(\delta_G^{-2}, \underline{g}\delta_G^2), \quad (12.98)$$

where $\underline{g}$ and δ_G are the mean and coefficient of variation of G . To derive the model for the conditional probability density function $\tilde{f}_{\mathbf{P}|G=\mu}$, it is convenient to introduce an auxiliary random variable $\mathbf{U} = (U_1, \dots, U_{m+n-1})$ such that

$$(\tilde{P}_k | G = \mu) = \frac{2\mu}{\eta_k^2} U_k, \quad 1 \leq k \leq m+n-1. \quad (12.99)$$

Given the inequality constraints raised by the polyconvexity requirement, it follows that the random variable $\mathbf{U}$ takes its values in the set

$$\mathcal{S}_{\mathbf{U}} = \left\{ \mathbf{u} \in \mathbb{R}_{>0}^{m+n-1} \left| 1 - \sum_{k=1}^{m+n-1} u_k > 0 \right. \right\}. \quad (12.100)$$

This definition of the admissible set $\mathcal{S}_U$ leads us to introduce the constraints

$$E\{\log(U_k)\} = \chi_k, \quad |\chi_k| < +\infty, \quad 1 \leq k \leq m+n-1, \quad (12.101)$$

and

$$E\left\{\log\left(1 - \sum_{k=1}^{m+n-1} u_k\right)\right\} = \chi_{m+n}, \quad |\chi_{m+n}| < +\infty, \quad (12.102)$$

which, again, ensure that the MaxEnt-induced probability measure *appropriately* vanishes at the boundary of $\mathcal{S}_U$. It can be deduced that the probability density function p_U reads as

$$p_U(\mathbf{u}) = 1_{\mathcal{S}_U}(\mathbf{u}) c \prod_{k=1}^{m+n-1} u_k^{\lambda_k-1} \left(1 - \sum_{k=1}^{m+n-1} u_k\right)^{\lambda_{m+n}-1}, \quad (12.103)$$

which shows that $\mathbf{U}$ follows a Dirichlet type I distribution with parameters $\{\lambda_i > 0\}_{i=1}^{m+n}$. In practice, the statistically independent random variables G and $\mathbf{U}$ are sampled, and Eq. (12.99) (together with the small-strain consistency condition) is used to obtain realizations of the model parameters defining the stochastic strain energy function.

Remark 12.2. For $m = n = 1$ and $\eta_1 = \eta_2 = 2$, the Ogden strain energy function corresponds to the Mooney–Rivlin model. In this case, the stochastic strain energy function writes as

$$W([F]) = P_1 \left(\| [F] \|_F^2 - 3 \right) + P_2 \left(\| \text{Cof}([F]) \|_F^2 - 3 \right), \quad (12.104)$$

and the consistency condition at small strains reads as $G = 2(P_1 + P_2)$. In this case, one has

$$(P_1 | G = \mu) = \frac{\mu}{2} U, \quad (12.105)$$

in which the random variable U follows a beta distribution parametrized by (α, β) , with $\alpha > 0$ and $\beta > 0$ (note that the choice $\alpha > 1$ and $\beta > 1$ makes the distribution unimodal).

Remark 12.3. The stochastic model presented in this section was used in Ref. [68] to represent non-Gaussian constitutive models for soft biological tissues (at fixed strain rates). A simple yet very efficient strategy for model calibration was proposed, and simulation results were gauged against experimental data (compression tests) for a variety of tissues, such as the brain, liver, and spinal cord matter. A comparison

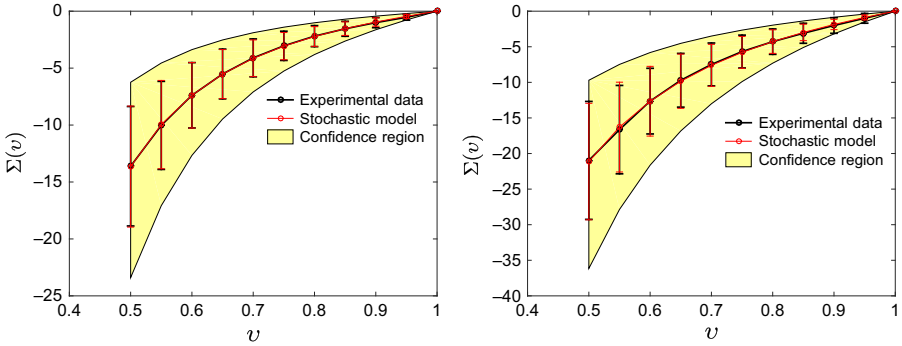


Figure 12.8 Experimental results and predictions obtained with the non-Gaussian model ($m = n = 1$) for gray matter (left panel) and white matter (right panel), obtained at a given strain rate $\dot{\epsilon} = 5 \text{ [s}^{-1}\text{]}$ [68].

between the experimental data (in the form of mean and standard deviation of the first Piola–Kirchhoff stress, as a function of the principal stretch) and model predictions (in the form of mean, standard deviation, and 95% confidence region) can be found for brain tissues in Fig. 12.8. It is seen that the first-order stochastic Ogden potential allows the experimental variability to be accurately reproduced.

12.4.3 Defining random field models for strain energy functions

Let us finally address the case of spatially dependent, nonlinear behaviors. In this case, the methodology for modeling non-Gaussian fields, introduced in Section 2.3, can be followed. For ease of explanation, only results relying upon the derivations from Section 4.2 (relevant to isotropic, incompressible materials) are reported below. The interested reader is referred to Ref. [42] for theoretical results and a forward propagation analysis associated with anisotropic strain energy functions.

Let $\{W_\varepsilon(\mathbf{x}), \mathbf{x} \in \Omega\}$ be the random field corresponding to a regularized form of the strain energy function:

$$W_\varepsilon(\mathbf{x}, [F]) = \frac{1}{1 + \varepsilon} (W(\mathbf{x}, [F]) + E\{W(\mathbf{x}, [F])\}), \quad \forall \mathbf{x} \in \Omega, \quad (12.106)$$

where ε is a small positive parameter, W is the stochastic potential (at location $\mathbf{x}$) defined as

$$\begin{aligned} W(\mathbf{x}, [F]) = & \sum_{i=1}^m P_i(\mathbf{x}) \left(\text{Tr} \left(([F]^T [F])^{\eta_i/2} \right) - 3 \right) \\ & + \sum_{j=m+1}^{m+n} P_j(\mathbf{x}) \left(\text{Tr} \left(\text{Cof}([F]^T [F])^{\eta_j/2} \right) - 3 \right), \end{aligned} \quad (12.107)$$

with $\{\mathbf{P}(\mathbf{x}) = (P_1(\mathbf{x}), \dots, P_{m+n}(\mathbf{x})), \mathbf{x} \in \Omega\}$ the $\mathbb{R}_{>0}^{m+n}$ -valued non-Gaussian random field of model parameters, and the exponents $\{\eta_i\}_{i=1}^{m+n}$ are assumed to satisfy the inequality constraints given by Eq. (12.91) (note that the dependence of $[F]$ on $\mathbf{x}$ is not made explicit in the equations above, for notational convenience). It is further assumed at this point that the mean function of the random field $\{\mathbf{P}(\mathbf{x}), \mathbf{x} \in \Omega\}$ is independent of $\mathbf{x}$, that is

$$E\{P_k(\mathbf{x})\} = \underline{p}_k > 0, \quad \forall \mathbf{x} \in \Omega, \quad 1 \leq k \leq m+n, \quad (12.108)$$

and that the mean strain energy function $\mathbf{x} \mapsto \underline{w}(\mathbf{x}, [F]) = E\{W(\mathbf{x}, [F])\}$ satisfies a uniform coercivity property. The regularized strain energy function can be written as

$$\begin{aligned} W_\varepsilon(\mathbf{x}, [F]) = & \sum_{i=1}^m P_{\varepsilon i}(\mathbf{x}) \left(\text{Tr} \left(([F]^T [F])^{\eta_i/2} \right) - 3 \right) \\ & + \sum_{j=m+1}^{m+n} P_{\varepsilon j}(\mathbf{x}) \left(\text{Tr} \left(\text{Cof}([F]^T [F])^{\eta_j/2} \right) - 3 \right), \end{aligned} \quad (12.109)$$

with

$$P_{\varepsilon i}(\mathbf{x}) = \frac{1}{1 + \varepsilon} (P_i(\mathbf{x}) + \varepsilon \underline{p}_i), \quad \forall \mathbf{x} \in \Omega, \quad (12.110)$$

by construction, $1 \leq i \leq m+n$. It can be deduced that

$$P_{\varepsilon i}(\mathbf{x}) > \frac{\varepsilon}{1 + \varepsilon} \underline{p}_i > 0, \quad \forall \mathbf{x} \in \Omega. \quad (12.111)$$

Following the discussion in the previous sections, this construction makes the associated nonlinear boundary value problem well posed. The construction of a non-Gaussian model for the random field of parameters can then be achieved by combining the methodology detailed in Section 2.3 with the results obtained in Section 4.2. Let $\{G(\mathbf{x}), \mathbf{x} \in \Omega\}$ denote the random field of shear modulus, such that (see Eq. 12.94)

$$2G(\mathbf{x}) = \sum_{k=1}^{m+n} P_k(\mathbf{x}) \eta_k^2, \quad \forall \mathbf{x} \in \Omega. \quad (12.112)$$

Following the results derived in Section 4.2 (and assuming that the constraint equations on $G(\mathbf{x})$ are given by Eqs. (12.96) and (12.97)), it can be deduced that

$$G(\mathbf{x}) \sim \mathcal{G}(\delta_G^{-2}, \underline{g} \delta_G^2), \quad (12.113)$$

for any $\mathbf{x}$ fixed in Ω , where the mean value $\underline{g}$ satisfies

$$\underline{g} = \frac{1}{2} \sum_{k=1}^{m+n} p_k \eta_k^2 \quad (12.114)$$

and δ_G is the coefficient of variation of $G(\mathbf{x})$. Similarly, let $\{\mathbf{U}(\mathbf{x}), \mathbf{x} \in \Omega\}$ be the random field with values in

$$\mathcal{S}_U = \left\{ \mathbf{u} \in \mathbb{R}_{>0}^{m+n-1} \left| 1 - \sum_{k=1}^{m+n-1} u_k > 0 \right. \right\}, \quad (12.115)$$

such that $\mathbf{U}(\mathbf{x})$ satisfies Eqs. (12.101) and (12.102). It follows from the information-theoretic approach that

$$\mathbf{U}(\mathbf{x}) \sim \mathcal{D}(\lambda_1, \dots, \lambda_{m+n}) \quad (12.116)$$

for any $\mathbf{x}$ fixed in Ω , in which $\mathcal{D}(\lambda_1, \dots, \lambda_{m+n})$ denotes the Dirichlet type I probability distribution with parameters $\{\lambda_i > 0\}_{i=1}^{m+n}$. To completely define the non-Gaussian random fields $\{G(\mathbf{x}), \mathbf{x} \in \Omega\}$ and $\{\mathbf{U}(\mathbf{x}), \mathbf{x} \in \Omega\}$, let $\{\Xi(\mathbf{x}), \mathbf{x} \in \mathbb{R}^d\}$ be a $\mathbb{R}^{m+n+1}$ -valued, homogeneous Gaussian random field with statistically independent normalized components and denote by $\{R_{\Xi_k}\}_{k=1}^{m+n+1}$ the associated set of correlation functions. Following the methodology detailed throughout this chapter, we then let

$$G(\mathbf{x}) = F^{-1}_{\mathcal{G}(\delta_G^{-2}, \underline{g}\delta_G^2)} \left(F_{\mathcal{N}(0,1)}(\Xi_{m+n+1}(\mathbf{x})) \right). \quad (12.117)$$

The random field $\{\mathbf{U}(\mathbf{x}), \mathbf{x} \in \Omega\}$ can next be defined by using of the relation between the Dirichlet type I distribution and the Gamma distribution (see Section 4, Chapter 11 in Ref. [72]). More specifically, we introduce the random fields $\{Y_i(\mathbf{x}), \mathbf{x} \in \Omega\}_{i=1}^{m+n}$ such that

$$Y_i(\mathbf{x}) = F_{\mathcal{G}(\lambda_i, 1)}^{-1} \left(F_{\mathcal{N}(0,1)}(\Xi_i(\mathbf{x})) \right), \quad 1 \leq i \leq m+n. \quad (12.118)$$

It can then be shown that the components of $\{\mathbf{U}(\mathbf{x}), \mathbf{x} \in \Omega\}$ can be defined as

$$U_i(\mathbf{x}) = \frac{Y_i(\mathbf{x})}{\sum_{j=1}^{m+n} Y_j(\mathbf{x})}, \quad \forall \mathbf{x} \in \Omega, \quad (12.119)$$

for $1 \leq i \leq m+n-1$. The combination of Eqs. (12.117)–(12.119) defines the nonlinear mapping $\mathcal{H}$.

In practice, a realization of the strain energy random field can be drawn as follows:

- (i) Generate a realization $\mathbf{x} \mapsto \mu(\mathbf{x})$ of $\{G(\mathbf{x}), \mathbf{x} \in \Omega\}$, using Eq. (12.117).
- (ii) Generate a realization $\mathbf{x} \mapsto \mathbf{u}(\mathbf{x})$ of $\{\mathbf{U}(\mathbf{x}), \mathbf{x} \in \Omega\}$, using Eq. (12.119).
- (iii) Compute the associated realization $\mathbf{x} \mapsto \mathbf{p}(\mathbf{x})$ of $\{\mathbf{P}(\mathbf{x}), \mathbf{x} \in \Omega\}$ through

$$p_k(\mathbf{x}) = \frac{2\mu(\mathbf{x})u_k(\mathbf{x})}{\eta_k^2}, \quad 1 \leq k \leq m+n-1 \quad (12.120)$$

and

$$p_{m+n}(\mathbf{x}) = \frac{2\mu(\mathbf{x})}{\eta_{m+n}^2} \left(1 - \sum_{k=1}^{m+n-1} u_k(\mathbf{x}) \right) \quad (12.121)$$

for all $\mathbf{x}$ in Ω .

- (iv) Compute the associated realizations $\{\mathbf{x} \mapsto p_{\varepsilon_k}(\mathbf{x})\}_{k=1}^{m+n}$ of the random fields $\{p_{\varepsilon_k}(\mathbf{x}), \mathbf{x} \in \Omega\}_{k=1}^{m+n}$ using

$$p_{\varepsilon_k}(\mathbf{x}) = \frac{1}{1 + \varepsilon} (p_k(\mathbf{x}) + \varepsilon p_k), \quad \forall \mathbf{x} \in \Omega, \quad 1 \leq k \leq m+n. \quad (12.122)$$

- (v) Define the associated realization $\mathbf{x} \mapsto w_\varepsilon(\mathbf{x})$ of $\{W_\varepsilon(\mathbf{x}), \mathbf{x} \in \Omega\}$ using

$$\begin{aligned} w_\varepsilon(\mathbf{x}, [F]) &= \sum_{i=1}^m p_{\varepsilon_i}(\mathbf{x}) \left(\text{Tr} \left(([F]^T [F])^{\eta_i/2} \right) - 3 \right) \\ &\quad + \sum_{j=m+1}^{m+n} p_{\varepsilon_j}(\mathbf{x}) \left(\text{Tr} \left(\text{Cof}([F]^T [F])^{\eta_j/2} \right) - 3 \right). \end{aligned} \quad (12.123)$$

Note that the steps (i)–(ii) require the generation of realizations for Gaussian random fields.

12.5 Conclusion

Uncertainty quantification for multiscale analysis requires the construction of admissible probabilistic models for random variables and random fields. In this chapter, a methodology for constructing information-theoretic stochastic models for non-Gaussian random fields has been presented. These models specifically ensure that all mathematical requirements on the fields under consideration are fulfilled and can accommodate additional, physics-guided constraints (related to anisotropy specification, for instance).

By *voluntarily* limiting the amount of information that is fed into the entropy maximization, a low-dimensional parametrization can be achieved. This feature makes these models attractive for the identification of constitutive laws, even when experimental data remain scarce. The reduction of the modeling bias also makes such models relevant within Bayesian frameworks, for which they constitute classes of objective prior models.

The overall approach was first developed by considering the modeling of non-Gaussian tensor-valued random fields exhibiting any material symmetries—ranging from isotropic to triclinic systems. These results can be applied to perform the forward propagation of uncertainties across relevant scales, as well as to solve underdetermined statistical inverse problems. The approach can also be used, in a straightforward manner, to represent matrix-valued diffusion fields (to solve, e.g., direct or inverse problems involving groundwater flows with uncertainties). The modeling of spatially dependent strain energy functions was then addressed. Detailed results were provided for isotropic, incompressible Ogden-type materials. This class of strain energy function random fields allows the variability exhibited by engineered polymeric composites and soft biological tissues to be modeled.

Acknowledgments

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Fractal dimension indicator for damage detection in uncertain composites

13

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13.1 Introduction

Fiber-reinforced laminated composite structures are extensively used in many engineering applications. The main advantage of composite materials over other conventional materials is the ability to be engineered according to the design requirements. Proper tailoring of composites enhances their specific stiffness, strength, fracture toughness, etc. However, composite structures are susceptible to damage. Commonly seen damage modes in composite structures are matrix cracks, delamination, debonding, and fiber breakage/pull out [1]. Matrix cracking is often the first defect that occurs in a composite laminate subjected to a quasistatic or cyclic tensile load and low velocity impact [2,3]. Matrix cracks cause degradation of mechanical properties of the composite structure. Matrix cracks trigger other damage mechanisms such as delamination, debonding, and fiber breakage [4]. Therefore, it is important to detect matrix cracks in composite structures to prevent the development of matrix cracking—initiated damage. Research has also shown that a multiscale approach is useful to model damage in composites [5]. The damage variables such as matrix crack size can then be related to a mesoscale stiffness law. In this chapter, we demonstrate the application of fractal dimension (FD) for damage detection in composites. This method amplifies the changes in the structural response caused due to damage. While FD is often used for biomedical signals related to human health, its use for monitoring structural health is new and has enormous possibilities.

Several methods have been used to detect damage in composite structures. For small damage involving matrix cracks and delamination, nondestructive techniques (NDTs) are often used. Popular NDTs are ultrasonic, acoustic emission, eddy current, X-ray, thermography, etc. Implementation of these conventional NDTs is time consuming, costly, and requires a rough estimate of damage location in the case of a large structure such as an aircraft wing or helicopter/wind turbine rotor blade. Vibration-based methods are well developed for damage detection of composite structures [6,7]. Damage in the structure affects the dynamic characteristics such as natural frequencies, mode shapes, and damping factors. Changes in these parameters can be used for extracting damage information [8–10]. Vibration-based methods have been

considered for damage detection of structures with smart materials, which can be used to excite the structure to measure the dynamic responses. But in the case of large structures like an aircraft wing or a bridge, it is difficult to excite the structure to measure the frequencies and mode shapes. In such cases, a damage detection method based on static response is highly preferable compared to vibration-based methods. Static deflection measurements are easier to obtain with higher levels of accuracy.

In the literature, damage detection based on static response has received less attention. Hjelmstad and Shin [11] proposed a damage detection method based on a parametric estimation scheme. Parametric estimation is done by minimizing the error between static displacements of the damaged structure and undamaged structure. Bakhtiari-Nejad et al. [12] also used a similar concept for detecting damage by minimizing the difference between the static load vector of the undamaged and damaged structure. Caddemi and Morassi [13] considered an inverse problem based on nonlinear optimization for crack detection in beams. Yam et al. [14] proposed damage indices based on out-of-plane static deflection and its slope and curvature. Damage detection is carried out by investigating the changes in these parameters of intact and damaged cases. Ghrib et al. [15] proposed the equilibrium gap concept and data-discrepancy functional-based methods for damage detection in beams using static deflection. They found that these methods are able to detect concentrated and distributed damage in beams. Amiri et al. [16] proposed a method to detect damage in shear frames using static deflection based on diagonalization of the stiffness matrix. The concept behind these methods involves solving an inverse problem by minimizing the error between measured and predicted displacements. Here, the baseline parameter values should be known for model-based prediction. This approach is computationally complex and uncertainties in baseline values will affect the accuracy of damage detection. Alternative methods are required to effectively detect damage information from the static response data without using baseline values. A damage in the structure introduces localized anomalies into the static deflection shape. Such anomalies can be amplified and extracted by using novel methods such as wavelets [17,18] and FD. Andreaus et al. used displacement transducers and a laser sensor to measure static deflection at selected points in a structure [19]. Digital photographs of cracked beams were analyzed using the wavelet transform. The proposed damage detection method could be implemented on algorithms running on a personal computer and using pictures from a commercial digital camera. The location of the damage was indicated by the peak of the wavelet transform. However, wavelet transforms are relatively complicated signal processing methods and FD can represent a simpler approach for solving the damage detection problem. It should be pointed out that static response of a structure can be more sensitive to modeling inaccuracies compared to dynamic characteristics. However, some of the methods such as those presented in this chapter can be directly implemented using measured data for the damaged and undamaged structure. The predictions from computational models are used in this chapter to illustrate the damage detection method.

Fractals represent a natural approach for detection of anomalies in Euclidean curves. The mathematical theory of fractals was first developed by Mandelbrot [20]. He defines that “fractal dimension is an index for characterizing fractal patterns or sets by quantifying their complexity as a ratio of the change in detail to the change in scale.” FDs were first used as an index to characterize complicated geometrical forms for which the details were more important than the overall picture. For typical sets with ordinary geometric figures, the theoretical FD is identical to the set’s topological or Euclidean dimension. For a set of points, both the Euclidean and FD is zero. For a set of lines, the dimension is one. For a set of surfaces and volumes, the dimensions are two and three, respectively. However, for fractal sets where the geometry is complicated and the details matter more than the whole, the FD can become noninteger. Thus, it is a fractional dimension. Mathematically speaking, a set for which the theoretical FD exceeds the topological dimension is said to have fractal geometry. Physical phenomenon such as turbulence, coastlines, river networks, and human physiology has been characterized using FDs. There are several mathematical approaches for calculating the FD, which will be introduced later in this chapter. However, FD concept moved from the realm of mathematics to applications once it was realized that it could be applied to complicated time series of data which were analogous to complicated geometric figures.

Inspired by the concept of Mandelbrot [20], Katz [21] developed a method to calculate the FD and this method is often used in the biological sciences. The FD acts as an amplifier of changes in the data time series. Thus, it can be used to indicate the presence of a fault in the system. Human health monitoring leads to the collection of many signals to evaluate the condition of different organs in the body. In biomedical fields, FD is used to detect transient changes in biomedical waveforms such as electroencephalograms [22–24] and medical image analysis [25]. Colomer et al. applied FD approach for damage detection in the retina [26]. Typically, researchers in the biomedical fields use experimental sampled data to calculate the FD. A natural application of FD would be in the area of structural damage detection where time series or signals of undamaged and damaged structures are often available through sensor measurements. However, in the field of structural damage detection, not much attention was given to the concept of FD and methods based on derivatives such as curvature have been used to find the location of sharp changes in signal response which may indicate the presence of damage.

Selected researchers have explored the effectiveness of FD for application in structural damage detection. Hadjileontiadis et al. [27] developed an FD-based crack detector to detect cracks in beams. In this study [27], Katz’s FD algorithm is applied to the fundamental vibration mode shape. The location of the crack is calculated by the sudden change in the value of FD and the size of crack is determined by the FD measure. Hadjileontiadis et al. [27] also found that the FD-based crack detector is robust against measurement noise. Hadjileontiadis and Douka [28] extended the FD-based damage detection to two-dimensional structures such as plates. Qiao et al. [29] used generalized fractal dimension (GFD), a modified version of the Katz’s method, for delamination detection in composite plates. In this study [29], FD

method is applied to the mode shape curvature of the damaged plate to detect the damage location. Shi et al. [30] applied FD method on the deflection profile of a beam with damage. Huang et al. used Higuchi's FD to quantify the time frequency characteristics of local free vibration data obtained from structures and perform damage identification [31]. A steel beam and a bridge were considered in this study. Damage detection methods must be robust to not only measurement uncertainty but also to uncertainty in the structure caused by random material properties. This aspect becomes important when the damage detection algorithm is deployed across many samples of a structure [32]. Some research has addressed damage detection in composites using modal methods in the presence of uncertainty [33]. However, they considered uniformly distributed randomness in the composite plate.

Composite structures are manufactured through multistage complex processes. These processes can easily lead to variations in elastic properties and density of composite laminates [34]. The scatter in material properties depends on variation in microlevel properties (elastic properties of fiber and matrix) and variation in fabrication processes (fiber volume ratio, misalignment of ply orientation, fiber waviness, interlamina voids, porosity of the matrix, incomplete curing of resin, variation in ply thickness). These will result in structural elements with uncertainties in material properties and geometry [35]. These uncertainties are generally spatially distributed in nature.

In the literature, only a few experimental studies have quantified the uncertainties in composite materials. From experiments conducted on unidirectional carbon/epoxy samples, Jeong and Sheno [36] found that COV of composite elastic material properties E_1 , E_2 , G_{12} , ν_{12} , tensile strength, and compressive strength are 4.61%, 3.95%, 3.14%, 5.95%, 14.27%, and 13.5%, respectively. Variation in fiber mass/unit area and fiber straightness influence the structural properties of the laminate and variation in resin content can lead to spatial variation in material properties and geometric distortions. Experimental studies conducted by Yurgartis [37] show that the variation in fiber angle in the prepreg and laminate is $\pm 3^\circ$ of the mean fiber direction and the standard deviation of the distribution varies between 0.693 and 1.936° . Mehrez et al. [38] conducted an experimental study to identify the spatial variation of composite material properties and proposed probabilistic modeling methods to model the random field from a limited number of experiments [39]. Carbillet et al. [40] studied the effect of spatial variability of geometry, loading, and material parameters of composite plate on failure probability. The study found that probability of failure increased by a factor of four when spatial variability of geometry, loading, and material parameters are considered. It is clear that spatial variability can have a significant effect on the performance of composite structure.

In this chapter, numerical simulation is used to illustrate the effect of spatial variation of material property in damage detection of composite plate using FD. Finite element method is used to model cantilevered composite plate with damage. Matrix cracks are used as damage since matrix cracks are the first damage mechanism often seen in composite and are also amenable to multiscale analysis. Matrix crack model developed by Adolfsson and Gudmundson [41] is integrated in the finite element model. FD-based damage detection method is used to detect localized matrix cracks

in a composite plate. Robustness of the damage detection method is studied by considering spatial variation in material properties of composite laminate. Spatial variation of the composite material properties is represented by two-dimensional Gaussian homogeneous random field. Karhunen–Loeve (KL) expansion is used to generate a discrete random field for probabilistic analysis. This chapter is an extended and updated version of research done in Ref. [42].

13.2 Formulation

A brief outline of the finite element model of the composite plate with matrix cracks is provided in this section. This is followed by a discussion on the FD measure and on the modeling of spatial uncertainty.

13.2.1 Finite element model of composite plate

Finite element model of composite plate is developed using classical laminated plate theory. The displacement field is

$$u(x, y, z) = u_0(x, y) - z \frac{\partial w_0}{\partial x} \quad (13.1)$$

$$v(x, y, z) = v_0(x, y) - z \frac{\partial w_0}{\partial y} \quad (13.2)$$

$$w(x, y, z) = w_0(x, y) \quad (13.3)$$

where u , v , and w are the displacement components in the x , y , and z directions, respectively, and u_0 , v_0 , and w_0 are the midplane displacements. The rectangular nonconforming plate bending element with four nodes and five degrees of freedom per node is used for developing the finite element model for the smart composite plate. The strains associated with the displacements are

$$\{\varepsilon\} = \{\varepsilon^{(0)}\} - z \{\varepsilon^{(1)}\} \quad (13.4)$$

where

$$\begin{aligned} \{\varepsilon\} &= \{\varepsilon_x \quad \varepsilon_y \quad \gamma_{xy}\}^T \\ \{\varepsilon^{(0)}\} &= \left\{ \frac{\partial u_0}{\partial x} \quad \frac{\partial v_0}{\partial y} \quad \frac{\partial u_0}{\partial y} + \frac{\partial v_0}{\partial x} \right\}^T \\ \{\varepsilon^{(1)}\} &= \left\{ \frac{\partial^2 w_0}{\partial x^2} \quad \frac{\partial^2 w_0}{\partial y^2} \quad 2 \frac{\partial^2 w_0}{\partial x \partial y} \right\}^T \end{aligned} \quad (13.5)$$

Strain displacement relation can be written in terms of nodal degrees of freedom

$$\{\varepsilon\} = [B]\{u^e\} \quad (13.6)$$

Stress strain relation can be written as

$$\{\sigma\} = [\bar{Q}]\{\varepsilon\} \quad (13.7)$$

where $\bar{Q}$ is the plane stress reduced elastic tensor. Using the principle of virtual displacements, equilibrium equation can be represented as

$$\int_V \sigma_{ij} \delta \varepsilon_{ij} dV = \int_S f_i^S \delta u_i^S dS \quad (13.8)$$

where f_i^S is the external surface force acting on the surface S . The final finite element equilibrium equation can be written as

$$KU = F \quad (13.9)$$

where K is the stiffness matrix, F is the force vector, and U is the nodal degrees of freedom vector. Detailed derivation of Eq. (13.9) is given in Ref. [43].

13.2.2 Matrix crack modeling

Matrix cracking in the composite laminate is inserted through the extension (**A**), extension-bending (**B**), and bending (**D**) stiffness matrices. These are transverse matrix cracks. The stiffness matrices for the presence of matrix cracks $\mathbf{A}^{(c)}$, $\mathbf{B}^{(c)}$, and $\mathbf{D}^{(c)}$ are obtained by subtracting the damage matrices $\Delta\mathbf{A}$, $\Delta\mathbf{B}$, and $\Delta\mathbf{D}$ from the stiffness matrices **A**, **B**, and **D** of the virgin laminate.

$$\mathbf{A}^{(c)} = \mathbf{A} - \Delta\mathbf{A} \quad (13.10)$$

$$\mathbf{B}^{(c)} = \mathbf{B} - \Delta\mathbf{B} \quad (13.11)$$

$$\mathbf{D}^{(c)} = \mathbf{D} - \Delta\mathbf{D} \quad (13.12)$$

These stiffness matrices reduce with increasing crack density. The dimensionless crack density ρ^k for the ply k is defined by

$$\rho^k = \frac{t^k}{s^k} \quad (13.13)$$

Here s^k is the average crack spacing and t^k is the thickness of ply k .

The **A**, **B**, and **D** matrices are defined in terms of the lamina stiffnesses for the undamaged laminate and are given by

$$\mathbf{A} = \sum_{k=1}^N t^k \mathbf{Q}^k \quad (13.14)$$

$$\mathbf{B} = \sum_{k=1}^N t^k z^k \mathbf{Q}^k \quad (13.15)$$

$$\mathbf{D} = \sum_{k=1}^N t^k \left[(z^k)^2 + \frac{(t^k)^2}{12} \right] \mathbf{Q}^k \quad (13.16)$$

where the midplane position z^k and thickness t^k of ply k is introduced as

$$z^k = \frac{h^k + h^{k-1}}{2} \quad \text{and} \quad t_k = h^k - h^{k-1} \quad (13.17)$$

and N is the number of lamina. Also, $\mathbf{Q}^k$ is the plane stress matrix of ply k , and h^{k-1} and h^k are the lower and upper coordinates of ply k .

Gudmundson and Zang [44] related the strain increment produced by an array of cracks to the local crack face displacement. The changes in stiffness matrices can be written as

$$\Delta \mathbf{A} = \sum_{k=1}^N \sum_{l=1}^N \sqrt{t^k \rho^k t^l \rho^l} \mathbf{C}_{EE}^{kl} \quad (13.18)$$

$$\Delta \mathbf{B} = \sum_{k=1}^N \sum_{l=1}^N \sqrt{t^k \rho^k t^l \rho^l} \left(z^l \mathbf{C}_{EE}^{kl} \right) \quad (13.19)$$

$$\Delta \mathbf{D} = \sum_{k=1}^N \sum_{l=1}^N \sqrt{t^k \rho^k t^l \rho^l} \left(z^k z^l \mathbf{C}_{EE}^{kl} + \frac{t^k t^l}{4} \mathbf{C}_{BB}^{kl} \right) \quad (13.20)$$

where the matrix **C** takes account of the elastic properties and crack orientation relative to applied stress and can be written as

$$C_m^{kl} = \mathbf{Q}^k (\mathbf{N}^k)^T \boldsymbol{\beta}_m^{kl} \mathbf{N}^l \mathbf{Q}^l \quad m = EE, BB \quad (13.21)$$

where EE and BB denote pure extension and bending, respectively. The matrix $\mathbf{N}^k$ is defined from the constant unit normal vectors $\mathbf{n}^k$ for crack surfaces of ply k and can be written as

$$\mathbf{N}^k = \begin{bmatrix} \mathbf{n}_1^k & 0 & \mathbf{n}_2^k \\ 0 & \mathbf{n}_2^k & \mathbf{n}_1^k \end{bmatrix} \quad (13.22)$$

Thus, damage matrices are proportional to the crack density and crack displacement vector β_m^{km} . Adolfsson and Gudmundson [41] obtained crack opening displacement matrix assuming that the different modes of cracks opening displacements and tractions are independent and can be written as

$$\beta_m^{kl} = \begin{bmatrix} \beta_{11(m)}^{kl} & 0 \\ 0 & \beta_{22(m)}^{kl} \end{bmatrix} \quad m = EE, BB \quad (13.23)$$

The assumption given above suggests that there will be no coupling between the crack opening displacements of different plies, hence

$$\beta^{kl} = 0 \quad \text{for all } k \neq l \quad (13.24)$$

The components of β^{kk} are derived using the relation between the stress intensity factors and energy release rate. The β_{11} components relate to crack face displacement in Mode III antiplane strain. β_{22} relates to Mode I crack opening and can only be evaluated numerically by a series expression. The resulting components of the β^{kk} matrices are as given below:

$$\beta_{11(E E)}^{kk} = \frac{\pi}{2} \gamma_1^k \frac{8}{(\pi \rho^k)^2} \ln \left[\cosh \left(\frac{\pi \rho^k}{2} \right) \right] \quad (13.25)$$

$$\beta_{22(E E)}^{kk} = \frac{\pi}{2} \gamma_2^k \sum_{j=1}^{10} \frac{a_j}{(1 + \rho^k)^j} \quad (13.26)$$

for the components connected with pure extension (EE) and

$$\beta_{11(B B)}^{kk} = \frac{\pi}{16} \gamma_2^k \sum_{j=1}^{10} \frac{b_j}{(1 + \rho^k)^j} \quad (13.27)$$

$$\beta_{22(B B)}^{kk} = \frac{\pi}{16} \gamma_2^k \sum_{j=1}^{10} \frac{c_j}{(1 + \rho^k)^j} \quad (13.28)$$

for the components which must be added to take bending (*BB*) into account.

The quantities γ_1^k and γ_2^k are defined from the materials properties of ply k as

$$\gamma_1^k = \frac{1}{2G_{LT}^k} \quad (13.29)$$

$$\gamma_2^k = \frac{1 - \mu_{LT}^k \mu_{TL}^k}{E_T^k} \quad (13.30)$$

Here E_T , μ_{LT} , μ_{TL} , and G_{LT} represent the transverse Young's modulus, two Poisson ratios, and shear modulus for the composite ply k . The curve fit parameters a_j , b_j , and c_j are given in Ref. [44]. The results of the components connected to pure extension were obtained from Ref. [44] and the components required to be added to take bending into account are obtained from Ref. [41] using the least squares fit to the results from numerical integration.

13.2.3 Fractal dimension

The topological dimension, useful for measuring the dimension of familiar geometric objects, is not useful for measuring the dimensions of fractals. Instead, the Hausdorff dimension can be used, which is defined as follows. A typical signal can be divided into smaller sections of length m . Using the self-similarity feature of fractals, which basically indicates that the geometry is similar at different length scales, it is possible to obtain the number of self-similar parts S forming the original signal if we magnify the original signal by a factor n . The relationship is given by a power law in terms of S , n , and the Hausdorff dimension D as

$$S = n^D \quad (13.31)$$

The Hausdorff dimension is then defined as

$$D = \frac{\log S}{\log n} \quad (13.32)$$

Here n is known as the magnification factor. The FD can be considered to measure the rate of increase in detail in the signal as the magnification increases. It is therefore a measure of local signal complexity. For a signal of lower complexity, the FD is close to one, and for a more complex signal, it is closer to two. One can see from the definition that it is difficult to choose the appropriate length of each subsection of the signal, i.e., the selection of m can be difficult.

Katz addressed this issue by defining the FD in a manner similar to the Hausdorff dimension. The FD was defined as

$$D = \frac{\log L}{\log d} \quad (13.33)$$

Here L is the total length of the signal and d is the Euclidean distance between the first point in the series and the point most distant from the first point. A close observation of this definition shows this to be the Hausdorff dimension defined in the earlier equation and by selecting d as the furthest distance, Katz chose the largest magnification to calculate the FD. However, the FD calculated using this approach becomes dependant on the units of measurement used. Katz introduced a normalization to address this issue by using,

$$FD = \frac{\log L/\bar{a}}{\log d/\bar{a}} \quad (13.34)$$

where $\bar{a}$ represents the average number of steps in the series. Now, since $n = L/\bar{a}$, we get the FD of a curve defined by a sequence of points as [21]

$$FD = \frac{\log(n)}{\log(n) + \log\left(\frac{d}{L}\right)} \quad (13.35)$$

where $d = \max \text{dist}(1, i)$ is the diameter estimated as the distance between the first point of the sequence and the i th point of the sequence that provides the farthest distance and L is the total length of the curve of the sum of the distance between successive points. The number of steps in the curve is $n = L/\bar{a}$, where $\bar{a}$ is the average step or average distance between successive points. Qiao et al. [29] used the GFD for delamination detection in a composite plate. Eq. (13.35) is modified by introducing a scale parameter inspired from the wavelet transformation. Qiao et al. mention that “Compared to the mode shape itself, the irregularity caused by the damage on the deformation mode shape is local and smaller, and we can filter the sharp peak value of FD introduced by the mode shape itself while keeping one for the local damage through choosing a proper scale factor s .” For example for higher mode shapes, the FD of a healthy mode shape shows peak due to change in curvature. At that time, FD can give a false prediction. To avoid this problem, a proper scale factor must be used. We have used a scale factor of 100 for a normalized deflection curve. The deflection curve was normalized as the vertical displacement was very less compared to the X and Y dimension. Thus, it becomes possible to amplify the damage detection ability using a scale factor of 100 on a normalized curve rather than directly applying FD on an actual deflection curve.

$$GFD_s(x_i) = \frac{\log(n)}{\log(n) + \log\left(\frac{d_s(x_i, M)}{L_s(x_i, M)}\right)} \quad (13.36)$$

$$L_s(x_i, M) = \sum_{j=1}^M \sqrt{(y(x_{i+j}) - y(x_{i+j-1}))^2 + s^2(x_{i+j} - x_{i+j-1})^2} \quad (13.37)$$

$$d_s(x_i, M) = \max_{1 \leq j \leq M} \sqrt{(y(x_{i+j}) - y(x_i))^2 + s^2(x_{i+j} - x_i)^2} \quad (13.38)$$

where s is the scale parameter.

FD scheme is constructed by employing a sliding window of M -sample length applied to the deflection curve. The sliding window is shifted along the curve. The FD parameter is calculated using Eq. (13.36) and the value of the estimated FD is assigned to the midpoint of sliding window. In this way, point-to-point values of the estimated FD of a curve are obtained. We have used a sliding window size of four in this chapter. This means that the sliding window consists of four elements. For example, for beam elements, four elements consist of five nodes. The FD is calculated based on the X and Z dimensions and assigned the FD value for the middle node of the sliding window.

For the analysis of 2D structures, such as plates, the FD operator is applied to succeeding horizontal or vertical 1D slices of the 2D deflection data $w(x, y)$ [28].

$$FD^H(i) = GFD\{w(i, 1:L)\}, \quad i = 1, \dots, L \quad (13.39)$$

$$FD^V(i) = GFD\{w(1:L, i)\}, \quad i = 1, \dots, L \quad (13.40)$$

The estimated FD^H and FD^V matrices provide a means for scanning the plate for existence of matrix cracks.

13.2.4 Spatial uncertainty in material property

Spatial variation of the composite material properties is represented by a two-dimensional Gaussian homogeneous random field. Random variables in a random field are spatially correlated. The degree of correlation between nearby random variables can be specified by a covariance function. Exponential model-based covariance function is widely used in uncertainty analysis of composite structures [34,45] and it can be represented as

$$C_{ij} = C_0 \exp\left[-\left|\frac{x_{ij}}{l}\right|\right] \quad i, j = 1, \dots, n \quad (13.41)$$

where C_0 is the variance, x_{ij} is the distance between points x_i and x_j , and l is the correlation length of the field. Here continuous random field is discretized according to the finite element mesh, resulting in n dependent random variables.

A discrete random field can be represented using KL expansion [46]. A discrete random field $k(x, \theta)$ of length n can be represented using KL expansion in the form

$$k(x, \theta) = \bar{k}(x) + \sum_{i=1}^{r \leq n} \sqrt{\lambda_i} \phi_i(x) \zeta_i(\theta) \quad (13.42)$$

where $\bar{k}$ denotes the mean of k , ζ_i are the uncorrelated standard normal (zero mean and unit variance) random variables, and λ_i and ϕ_i are the eigenvalues and eigenvectors of the covariance matrix, respectively. The eigenvalue problem can be expressed as

$$C\phi_i = \lambda_i\phi_i \quad (13.43)$$

Solution of the eigenvalue problem gives n eigensolutions. But only r eigenvectors are considered in *KL* expansion (shown in Eq. 13.42). The number of eigenvectors required in *KL* expansion depends on the eigenvalues. Eigenvectors corresponding to the smaller eigenvalues compared to the largest eigenvalue are neglected in the *KL* expansion. The criterion to find the number of modes (r) in *KL* expansion can be represented as [47]

$$\frac{\sum_{i=1}^r \lambda_i}{\sum_{i=1}^n \lambda_i} \geq 0.9 \quad (13.44)$$

Here an eigenvalue energy-like criteria is used and the 0.9 in the equation indicates that the energy threshold is set to 90%.

13.3 Numerical results

A finite element model of the damaged composite plate structure is formulated by integrating the matrix crack model into the plate analysis as discussed in Section 13.2.1. Fig. 13.1 shows a laminated composite cantilever plate of dimension 200 mm $\times$ 200 mm. The stacking sequence of the composite laminate is $[\theta / -\theta / \theta / -\theta]$ and $\theta = 45^\circ$. The total thickness of the composite plate is 1 mm and each layer has the same thickness (0.25 mm). The material properties of composite materials are taken from reference [48]. The finite element mesh consists of 1600 rectangular plate bending elements with four nodes and five degrees of freedom per node. A uniform distributed load of 100 N/m² is applied in the negative z direction and static analysis is conducted. Fig. 13.2 shows the static deflection of undamaged plate under a uniform load of 100 N/m².

13.3.1 Localized damage detection based on fractal dimension–based approach

To study the effect of localized damage on the static response of a composite plate, area A shown in Fig. 13.1 is considered as the region with matrix crack density $\rho = 4$ [49]. This level of matrix crack density corresponds to matrix crack saturation for the

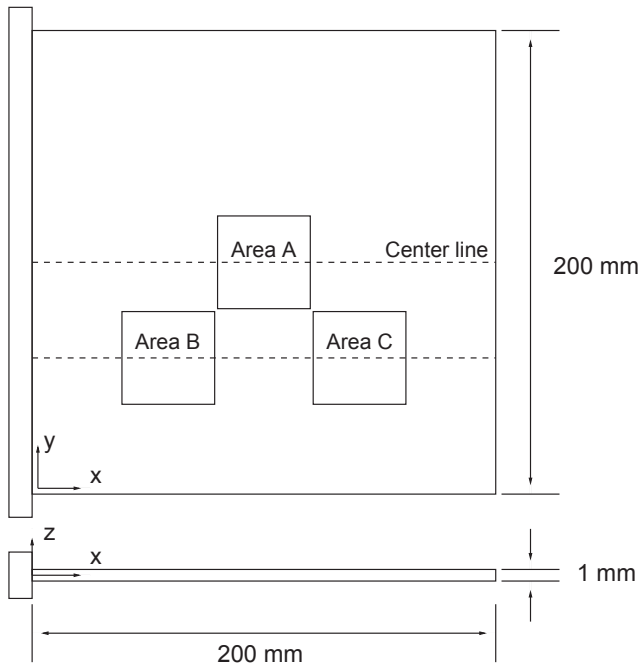


Figure 13.1 Cantilevered composite plate.

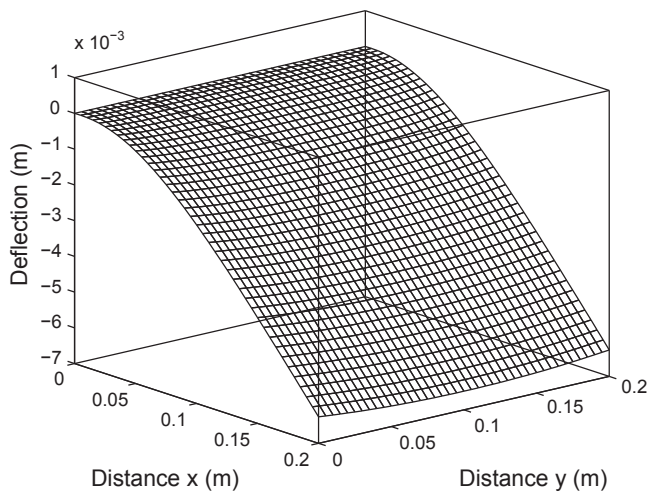


Figure 13.2 Static deflection of undamaged composite plate under a uniform load of 100 N/m^2 .

given structure which also marks the onset of delamination and fiber breakage. Matrix cracks effect the composite plate stiffness matrices and the net result of this degradation in localized stiffness can be seen in the change of deflection of the structure. For a helicopter rotor blade modeled as a beam structure, the stiffness

reduction in the flexural stiffness is about 6%–12% and in the torsion stiffness is about 25%–30% at matrix crack saturation. The area A is 4% of the total plate area (200 mm $\times$ 200 mm). Static analysis is performed for this damaged case and Fig. 13.3 shows the center line deflection of undamaged and damaged case. Here center line deflection refers to the deflection $w(x, y = 100 \text{ mm})$ shown in Fig. 13.1. It is clear from Fig. 13.3 that there is almost no visible change in static deflection curve when a small localized damage is considered. So it is practically difficult to detect the presence of damage by comparing the difference in static deflection of damaged and undamaged structure. Some signal processing amplification is needed to extract the damage location from the deflection curve.

The static deflection $w(x, y)$ of composite plate is processed using three different approaches:

1. Calculate FD of the deflection curve.
2. Calculate curvature of the deflection curve.
3. Calculate the FD of curvature value calculated in the second approach.

Eq. (13.39) is used to calculate the FD of the deflection curve and FD^H is referred as FD in the following results. The curvature is the second-order spatial derivative ($\partial^2 w / \partial x^2$) and is calculated using the central difference method. These three methods are applied to the static deflection for damaged and undamaged case. Fig. 13.4 shows the three-dimensional plots of these three approaches for undamaged and damaged case. In this case, the damage is located at the area A shown in Fig. 13.1. Fig. 13.4(a), (c) and (e) represent the undamaged case and Fig. 13.4(b), (d) and (f)

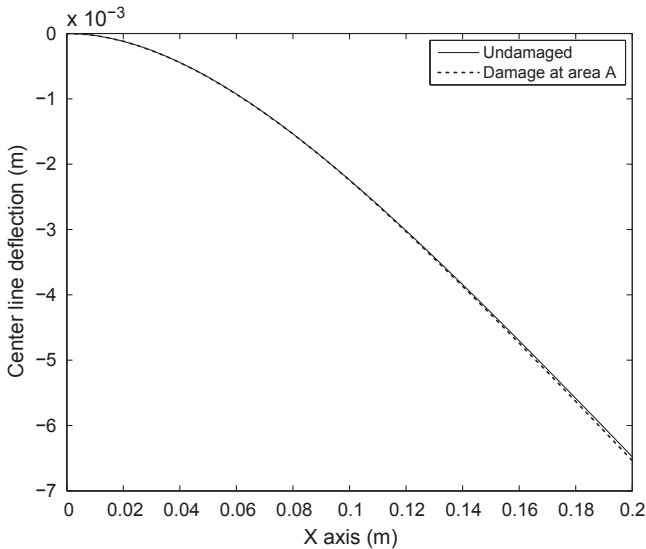


Figure 13.3 Center line deflection of undamaged and damaged (damage at area A) plate under a uniform load of 100 N/m^2 .

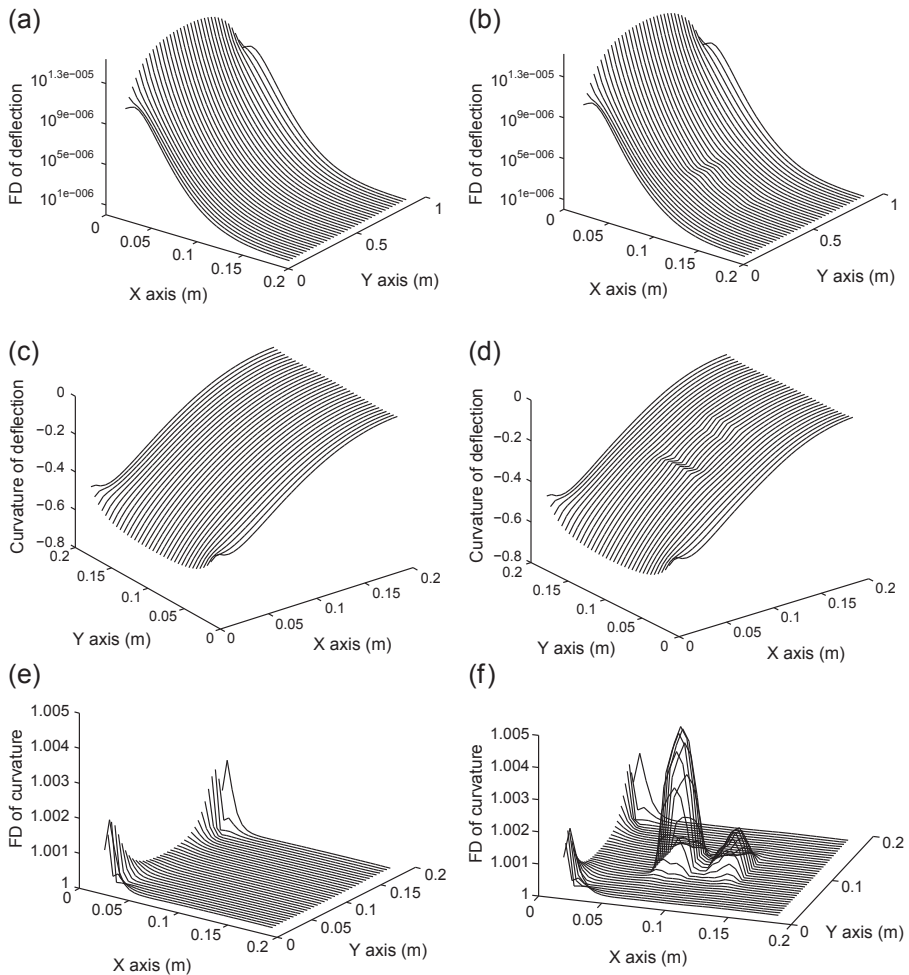


Figure 13.4 Fractal dimension of deflection, curvature of deflection, and fractal dimension of curvature for undamaged (a, c, e) and damaged (b, d, f) (damage in area A in Fig. 13.1) case.

represent the damaged case. There is a clear difference in the plots given in Fig. 13.4 due to damage at area A. FD of curvature shows a clearly visible change due to damage. Fig. 13.5 shows the center line values of the plots given in Fig. 13.4. Fig. 13.5(a) shows the FD of the deflection curve varies from 0.08 to 0.12 for the damaged case. This region represents the damage location for area A shown in Fig. 13.1. Similar trend can also be seen in Fig. 13.5(b) and (c) but FD of curvature shows significant change due to damage which is shown in Fig. 13.5(c). Some of the boundary effects near the edges of the plates may be due to the localized change in the curve at these points.

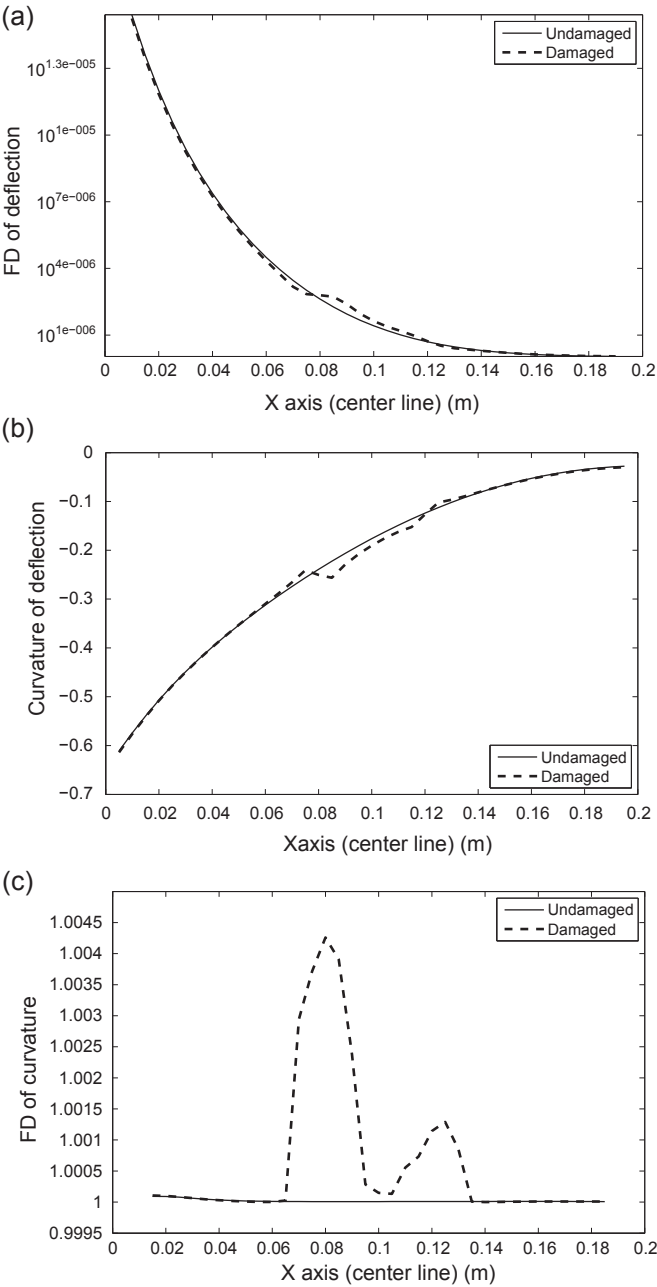


Figure 13.5 Center line values of Fig. 13.4. (a) Fractal dimension of deflection, (b) Curvature of Deflection, (c) Fractal dimension of curvature.

Next, damage is considered at different locations other than at the center of the plate (area A). Here three cases are considered: (1) damage at area B, (2) damage at area C, and (3) damage at both areas B and C, which are shown in Fig. 13.1. Fig. 13.6 shows the curvature and FD of curvature plots for three damage cases. It is clear from Fig. 13.6(e) and (f) that the proposed method is capable of detecting multiple damage locations from the static deflection information. Fig. 13.7 shows the curvature values at $y = 60$ mm of Fig. 13.6. It can be seen that the deviation of curve for damaged case indicates the position of the damage for the three cases.

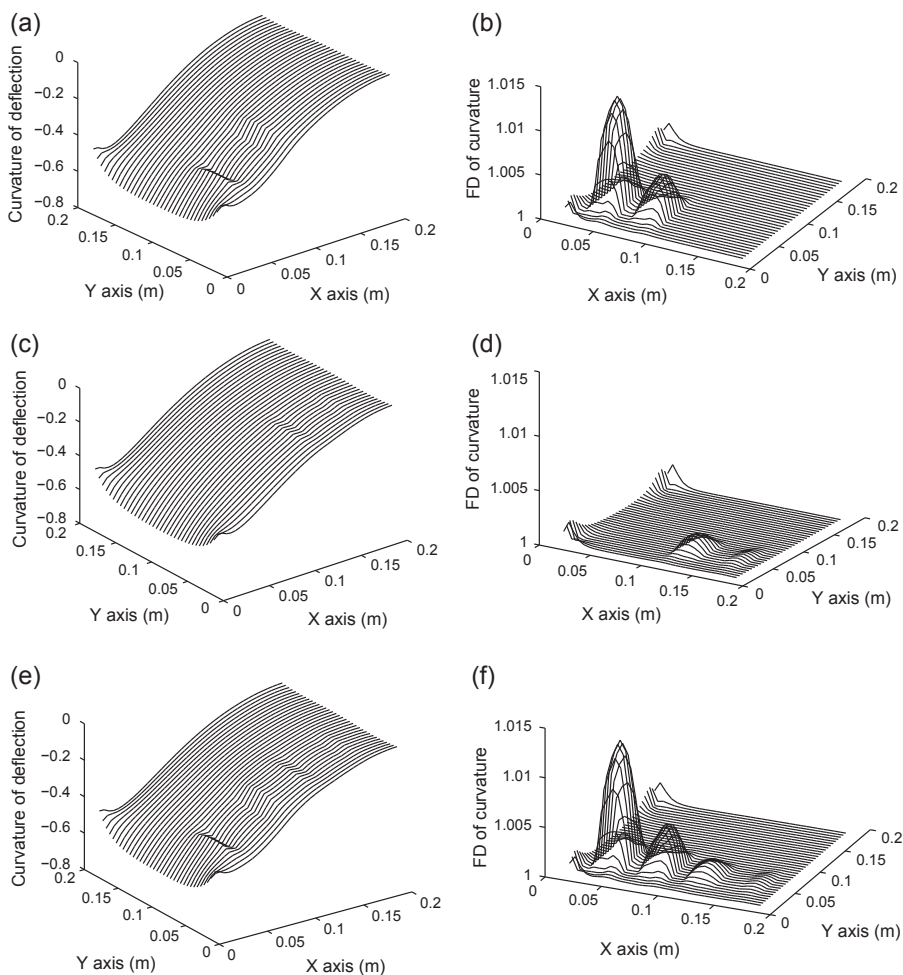


Figure 13.6 Curvature of deflection and FD of curvature for three different damage cases (area B (a, b), area C (c, d), and areas B and C (e, f)).

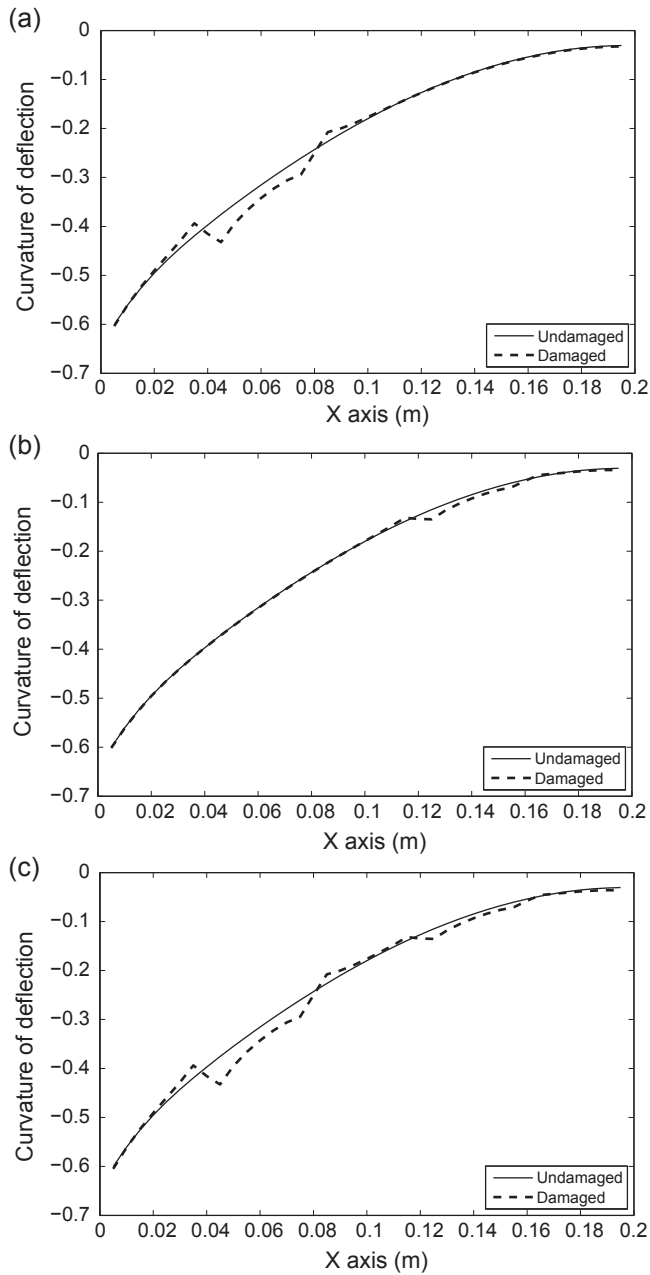


Figure 13.7 Curvature at $(x, y = 60 \text{ mm})$ shown in Fig. 13.6. (a) Curvature in 13.6(a), (b) Curvature in 13.6(c), (c) Curvature in 13.6(e).

Area *B* is located between 0.04 and 0.08 along *x* direction and area *C* between 0.12 and 0.16. Fig. 13.7(c) shows the curvature for the case 3 with multiple damages. The damaged curve (dashed line) clearly shows the multiple location of the damage. Fig. 13.8 shows the FD of the curvature shown in Fig. 13.7. The peaks show the location of the damage for the three cases. These results show the ability of FD-based damage detection method to amplify the effect of damage on curvature and thereby help to detect localized matrix cracks in a composite structure.

13.3.2 Spatial uncertainty

It is important to evaluate the performance of a new damage indicator in the presence of random uncertainty. Due to their multiscale nature, composite materials are subject to spatial uncertainty as microlevel uncertainties show up in the mesoscale stiffness variable field. To address the spatial uncertainty in composite material properties, the lamina property E_{11} is considered as a Gaussian homogeneous random field. E_{11} has a mean value of 150 GPa and coefficient of variation of 6.97% [50]. The continuous random field is discretized according to a finite element mesh consisting of 1600 elements. The covariance matrix is calculated using Eq. (13.41) considering the center of the element as the discretization point. Here the correlation length for the graphite/epoxy laminate is assumed as 10 mm [34,51]. The eigenvalues and eigenvectors of the covariance matrix of size 1600×1600 is calculated. Fig. 13.9 shows the variation of eigenvalues of the covariance matrix. Eigenvectors with smaller eigenvalues are neglected according to Eq. (13.44) while formulating the KL expansion. A total of 969 terms are used in the KL expansion to represent the random field with 10 mm correlation length. Latin hypercube sampling technique is used to generate 969 Gaussian (zero mean and unit standard deviation) independent random variables. Generated independent random variables are used to form a two-dimensional Gaussian random field (shown in Fig. 13.10) using Eq. (13.42). Random field information is fed into the finite element code to calculate static deflection with spatially varying material properties.

FD-based damage detection method is applied to the static deflection of composite plate with spatially varying material property. Fig. 13.11 shows that the proposed method is able to detect damage with spatial uncertainty. The location of the damage is clearly visible in Fig. 13.11(b) and (c). To compare the effect of material uncertainty on the effectiveness of the proposed method, a delta plot (damaged value—undamaged value) is shown in Fig. 13.12 for a situation with and without material uncertainty. From these center line plots, it is clear that the damage location is between 0.08 and 0.12 along the *x* axis. There are some false peaks due to spatial uncertainty because of correlation length of 10 mm which represents a sudden spatial change in material properties. Fig. 13.13 shows the delta plots for different correlation lengths. It can be seen from Fig. 13.13(c) that the FD-based damage detection method is robust against spatial uncertainty up to a correlation length of 20 mm. The main advantage of this method is that a baseline undamaged data are not required to identify the damage location.

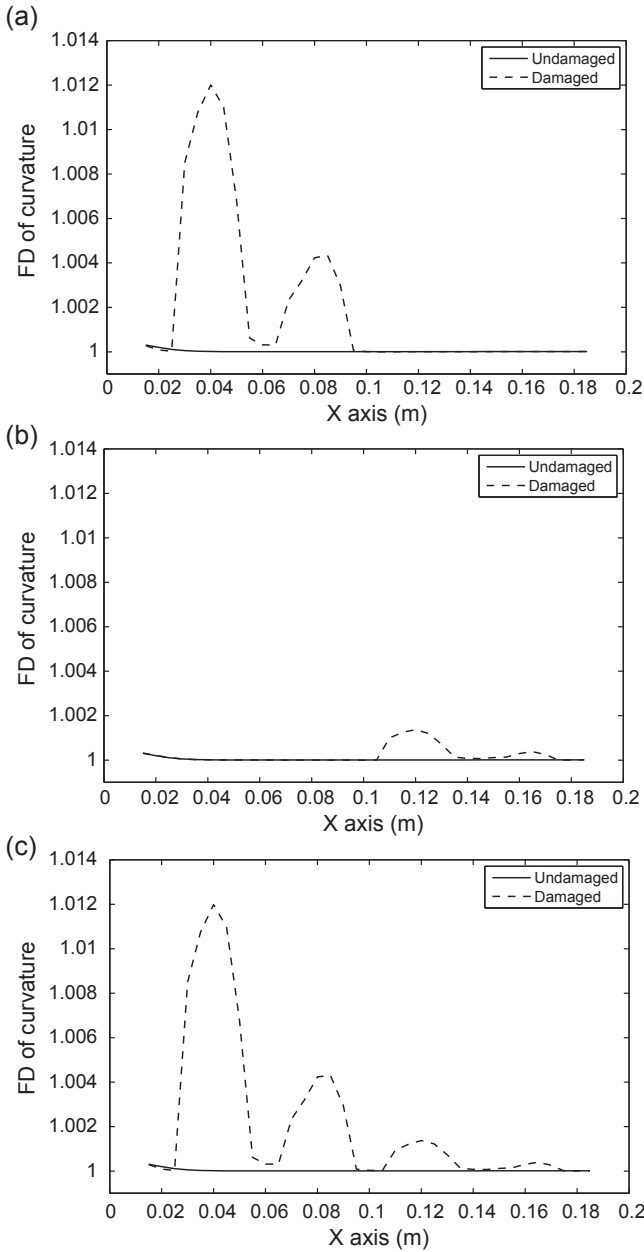


Figure 13.8 FD of curvature at $(x, y = 60 \text{ mm})$ shown in Fig. 13.6. (a) Fractal dimension of curvature in 13.6(b), (b) Fractal dimension of curvature in 13.6(d), (c) Fractal dimension of curvature in 13.6(f).

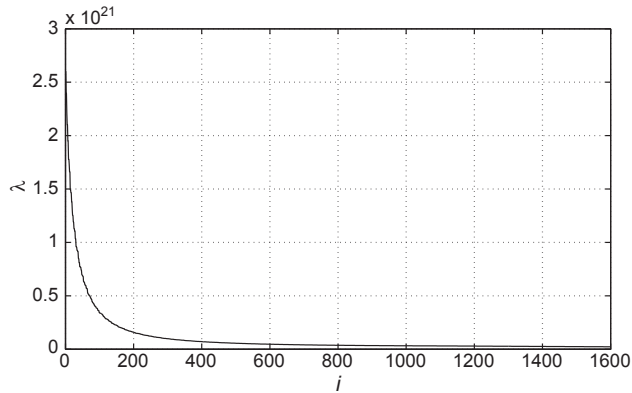


Figure 13.9 Eigenvalues of the covariance matrix for a correlation length of 10 mm.

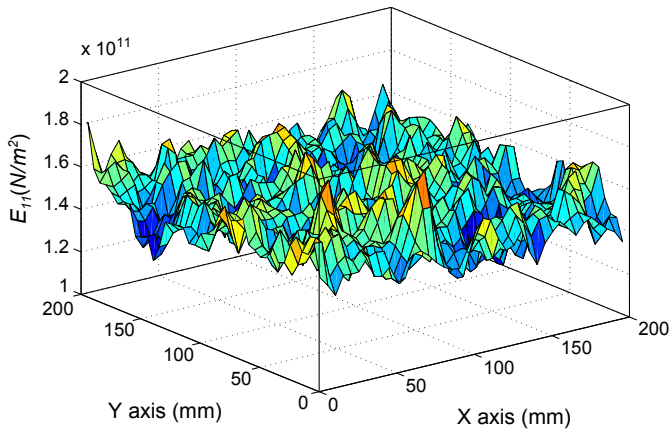


Figure 13.10 Gaussian random field for a correlation length of 10 mm.

13.4 Conclusions

The effectiveness of FD-based damage detection method is studied considering spatial uncertainty in composite material properties. Numerical simulation of a composite cantilevered plate is carried out using finite element model. Localized matrix cracks (4% of the total plate area) are considered as damage in a composite plate. Static analysis is carried out using a finite element model and static deflection is used as input data to the damage detection algorithms. Three different methods are used for damage detection: FD of deflection, curvature of deflection, and FD of

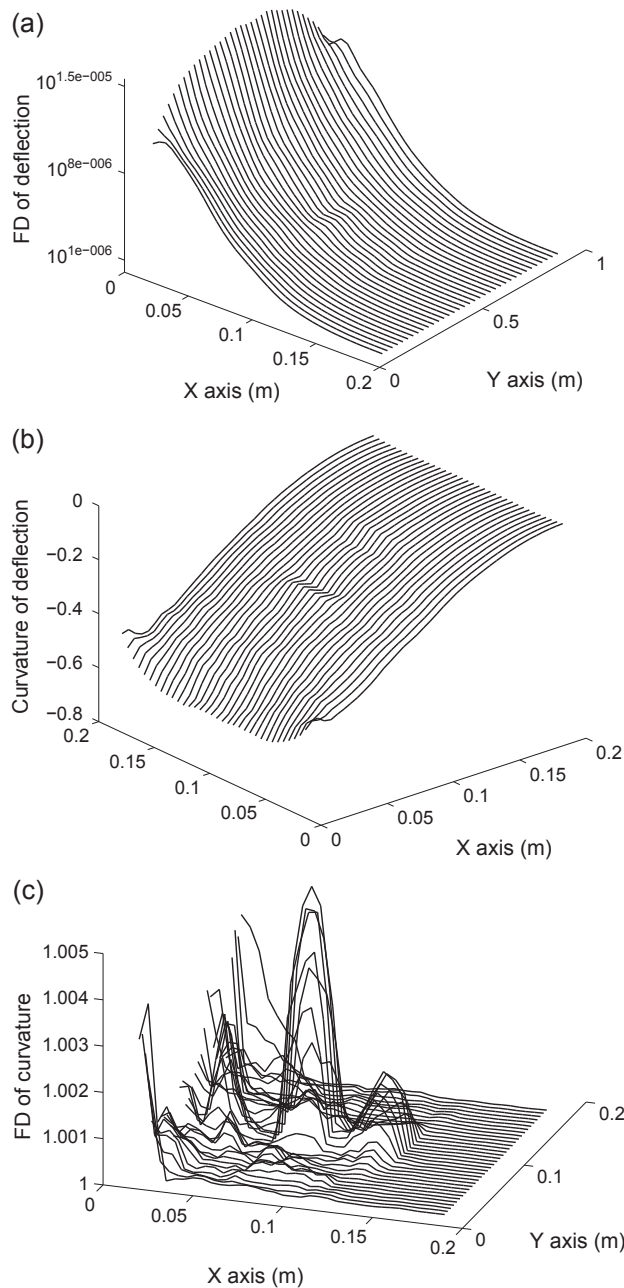


Figure 13.11 (a) Fractal dimension of deflection, (b) curvature of deflection, and (c) fractal dimension of curvature for damaged (area A) case with spatial uncertainty.

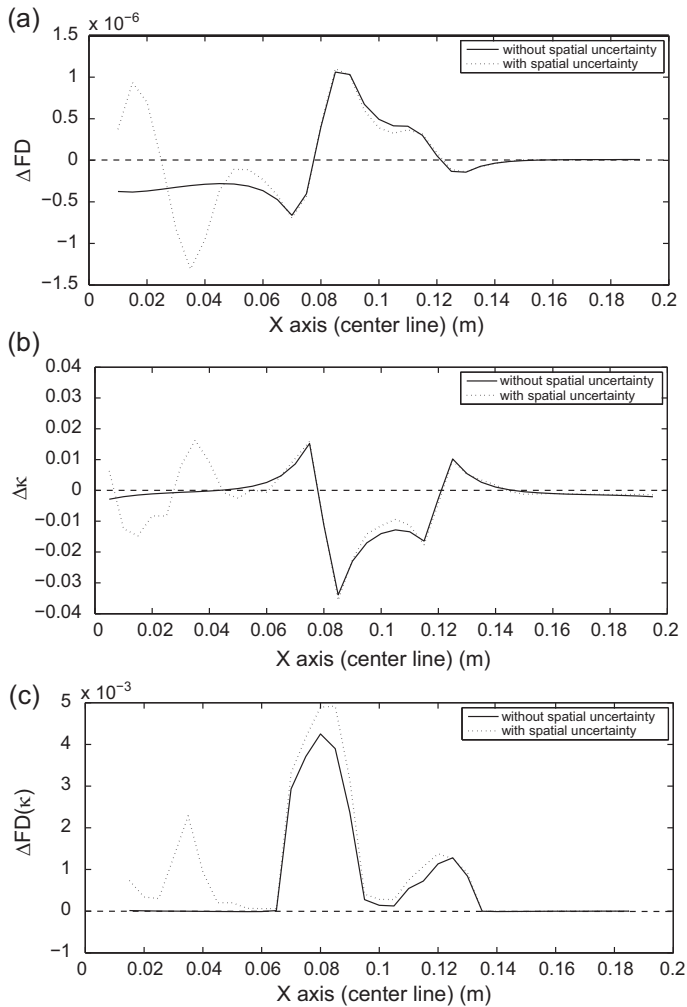


Figure 13.12 Delta plot of *center line* values of Fig. 13.11. (a) Change in fractal dimension of deflection, (b) Change in curvature of deflection, (c) Change in fractal dimension of curvature.

curvature. The results show that while these three methods are able to determine the damage location from the static deflection information of a damaged structure, the FD of curvature is the best approach. The effectiveness of these methods in the presence of spatial uncertainty is also studied. Here, composite material properties are considered as a two-dimensional Gaussian homogeneous random field. KL expansion method is used to create the random field for probabilistic analysis. Results show that the proposed methods are robust to the spatial uncertainty in composite material. Hence, these methods can be used to detect small damage such as matrix cracks in a composite structure. The main advantage of these methods is the baseline

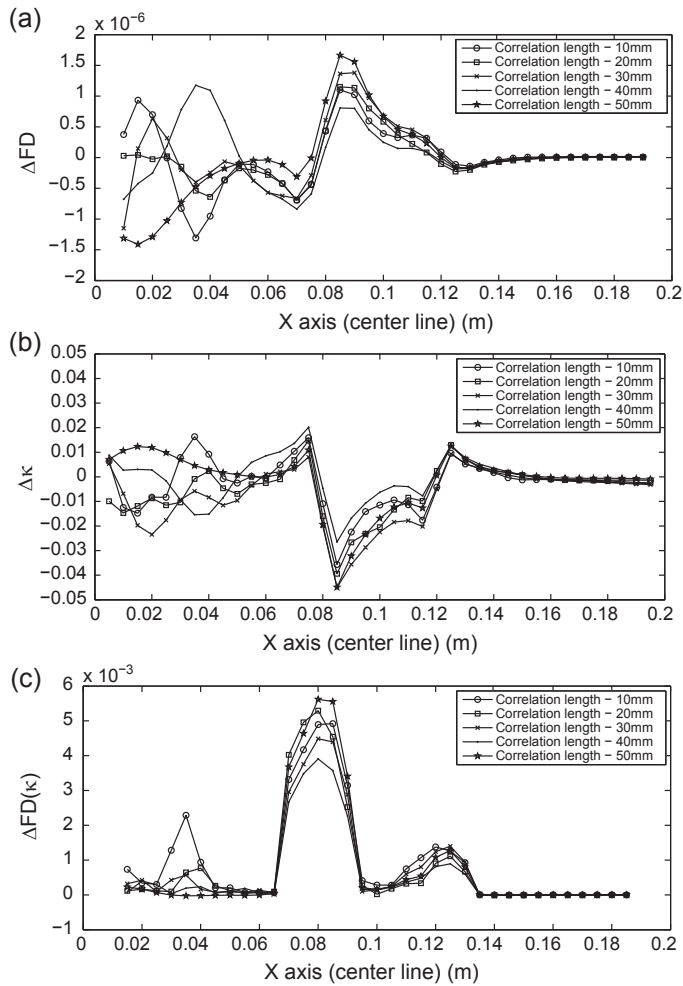


Figure 13.13 Delta plots for different correlation length. (a) Change in fractal dimension of deflection, (b) Change in curvature of deflection, (c) Change in fractal dimension of curvature.

undamaged information is not required for damage detection and these methods are able to detect damage from static deflection data which can be obtained easily relative to dynamic data such as natural frequencies and mode shapes.

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Hierarchical multiscale model calibration and validation for materials applications

14

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14.1 Introduction

Multiscale models of material behavior offer certain advantages compared to simpler single-scale modeling approaches. For example, multiscale models can predict discontinuities in macroscale response which arise as changes in a dominant physical mechanism. Nonlinear and path history—dependent evolution of defects in materials poses particular challenges. Handling the additional complexity of calibrating these models is an important concern. Two challenges are addressed in this chapter. First, the quantity of interest (QoI) predicted by a material model may not be directly measurable (e.g., too small to observe). In such cases, model calibration must rely on information obtained from other scales. Here, a calibration approach is formulated that allows for the use of available information across scales in the calibration of a multiscale model. Second, discrepancy exists between sources of information. Models can describe the same QoI from different perspectives or at different scales (e.g., first-principles vs. thermodynamics description of phase transitions). Uncertainty is also introduced when the linkage across scales is established or assumed based on either physical or statistical models. A method is formulated for investigating the assumed link between length scales which is fundamental to the use of the multiscale model, via consideration of the uncertainties of the link. A detailed introduction of each contribution follows.

Recent advances to calibration in multiscale models address existing limitations. In a hierarchical multiscale model (HMM), data are incorporated in either a bottom-up (BU) or a top-down (TD) manner [1]. Broadly, BU cases propagate information upward through models, while TD cases estimate parameters through inverse relations. Either method is limited in its own right. TD calibration often fails to identify unique values for inputs, especially within an HMM. Multiscale BU calibrations typically map idealized unit-process configurations to experimental observations which manifest

many-body interaction effects; BU calibrations may omit details needed to accurately model responses at higher length and time scales. To alleviate these limitations, a combined TD, BU (TDBU) approach has been formulated [2] which performs a reconciliation between TD and BU estimation. This methodology is summarized in this chapter to support new applications.

An interscale connection between models is a key component of an HMM. Individual models (e.g., an atomistic simulation of kink-pair nucleation, or a crystal plasticity (CP) model of bcc Fe) are included in an HMM after demonstrating a single-scale validity. An assumption is introduced by which the results of one model are used to inform another model; it may be supported by theoretical work. Importantly, this assumption must be considered as an addition to the validated individual single-scale contents of the HMM. This assumption, a formulated interscale connection, is critical to the HMM. A simple example of an interscale connection is a single parameter, whose value approximates the output of one model and calibrates the parameters of another model. A formal treatment of the interscale connection in terms of calibration and validation is the foundation of this work.

HMMs use connections between scales which may or may not be supported by data. In model selection and development, the best form of a model is identified by considering both theoretical and empirical support. Currently, interscale connections are not selected using a formal approach. Given that such connections are embedded in the assumption of a model (or models), it is appropriate to consider the selection of connections as they relate to the calibration of those models. This chapter presents the underlying formulation of the TDBU calibration connection test and explores the role of an interscale connection in HMM validation. A delineation is made between the details of the models pertinent to an example application, and the model-agnostic aspects of the TDBU calibration approach. In doing so, our intent is to promote pursuit of applications to HMMs of other types. The approach presented here considers the uncertainty which is associated with the interscale connection between models. This recently introduced concept of connection uncertainty [2] supports decision making in the construction of HMMs in data-scarce problems which are typical of models for nonequilibrium behavior of materials. It relates not only to parametric uncertainty but also to uncertainty of model form.

This chapter is organized in sections as follows: the TDBU calibration methodology is introduced in [Section 2](#). Its application to the CP model of bcc Fe is demonstrated in [Section 3](#). The test of interscale connections with the generalized formulation is outlined in [Section 4](#). The test is then applied in [Section 5](#) to show its usage.

14.2 Multiresponse, multiscale TDBU HMM calibration

The TDBU calibration method is generalized from previous work [2]. A surrogate-based method is used to map from TD data to likelihood in calibration parameter space. BU reference parameter estimates are incorporated in penalty functions in calibration parameter space. An integrated TDBU estimate is formulated which combines

the likelihoods and penalties in a maximum likelihood (ML)-based estimate of parameters. Background is provided regarding the techniques used, and the formulation of the approach is given in detail.

14.2.1 Background

The techniques used in the calibration of multiscale models naturally build upon the calibration of scientific models. Techniques for calibrating expensive and complex materials models have been documented [3–6], including those which incorporate uncertainty quantification [7–9].

Multiresponse calibration is an important method to improve identifiability in single-scale models [10–12]. By inspecting multiple measurable responses which depend on a common set of parameters, model parameters can be more uniquely identified. Multiscale models allow for the joint consideration of multiple responses measured at different length and time scales. The methods demonstrated in a multi-response calibration are relevant to a TDBU calibration. An additional complicating feature of multiscale calibration is the reliance on a connection between scales which is not itself directly measurable. The novelty of the approach generalized here lies in the test which is formulated for selecting connections of models between scales. This connection is framed in the context of the usual situation in modeling and simulation of nonlinear material response, for which calibration data are expensive and therefore sparse.

Surrogate models are used in the presented method. A surrogate model is a computationally inexpensive approximation of the full model response built from sampling [6]. Some examples include Gaussian process models and their derivative forms [4,6,13–18] and regression models [4] which can also be replaced by other surrogate methods as appropriate or desired.

More precisely, measurement error and model discrepancy are distinguished in surrogates [6,14,17], i.e.,

$$Y^E = Y^M - \delta - \varepsilon \quad (14.1)$$

where Y^E is the experimental measurement, Y^M is the model prediction, δ is the model discrepancy or model error, which is often defined as a function of model parameters, and ε is the measurement error. Defining the form of δ requires prior information which may be unavailable. The approach described here does not perform this separation and requires no such prior definition of δ . Thus, we assume the difference between the experimental measurement and model prediction can be represented by a zero mean Gaussian error model.

14.2.2 Formulation

An overview of the TDBU calibration method is presented in this section. The details of the calibration method are described, including how TD data are formulated in a

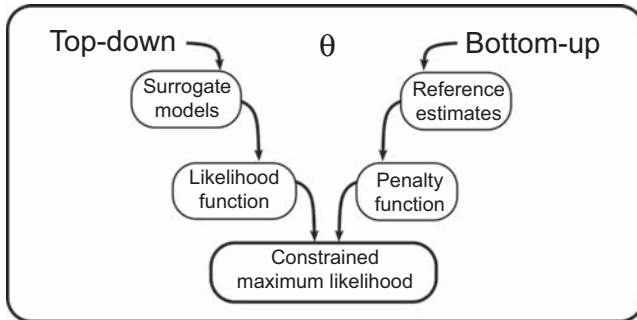


Figure 14.1 A flowchart of the method for combining TD and BU data in calibration of model parameters θ .

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likelihood function and how BU estimates are used in a penalty function. The flowchart in Fig. 14.1 outlines the process for reconciling the information from TD and BU for the purposes of informing the to-be-calibrated model parameters, θ , which are defined as common to both scales in the HMM. Assume the model to be calibrated was initially constructed based on the TD approach or perspective. It can also be a surrogate model based on TD experimental data. When additional information about the parameters along the BU path is available, the model parameters need to be calibrated based on the data of both information paths, and the discrepancy needs to be reconciled. The calibration process is formulated as maximizing the constrained likelihood which includes the likelihood function from one path and a penalty function from the other.

BU reference estimates and TD measurements originate in terms of inputs and outputs of a material model, respectively. The methods in this section are introduced to bring the information into the same calibration space. The use of likelihood methods in TD allows the TDBU combination to reflect nonlinear mappings from output to input space (which are likely to occur in a material model). Surrogate modeling is not essential to the method and may be replaced with a suitable approach to finding an inverse relation (e.g., Markov chain Monte Carlo).

Surrogate model-based likelihood functions are used to approximate the influence of TD data on the calibration of parameter values. The TD data are measured in material model response space (e.g., stress vs. strain). Here, second order regression (SOR) surrogate modeling [4] is used to approximate the model input to output relationship [19]. In practice, the SOR could be replaced by a Gaussian process or any surrogate which can be queried at any value of θ and which can incorporate quadratic effects (which is needed for ML estimation). The procedure for determining these surrogate-based functions is clarified as follows.

The TD calibration depends on a relation between model and data, i.e.,

$$Y^E(\mathbf{x}_i) = Y^M(\mathbf{x}_i, \boldsymbol{\theta}) + \varepsilon_i, \quad (14.2)$$

where $Y^E(\mathbf{x}_i)$ is the value of the experimental response at the i th value of $\mathbf{x}$, the model's physical parameter set. $Y^M(\mathbf{x}_i, \boldsymbol{\theta})$ is the model response at the i th physical parameter value and is a function of the calibration parameter set $\boldsymbol{\theta}$. In this work, a Gaussian error term is assigned to ε_i with mean of zero and variance of σ_e^2 , i.e., $\varepsilon \sim N(0, \sigma_e^2)$, with subscript e to distinguish it from other variances. Errors are assumed independent and identically distributed (i.i.d.), which is plausible for "good" estimates of $\boldsymbol{\theta}$. In practice, the appropriate error model may vary from this example case; however, some model of error is a requirement of the TDBU approach.

A likelihood function is derived from the data relation, expressed here as

$$\text{Likelihood}(\boldsymbol{\theta}) = \exp \left(-\frac{1}{2} \sum_{i=1}^{N_{\text{data}}} \frac{(Y^M(\mathbf{x}_i, \boldsymbol{\theta}) - Y^E(\mathbf{x}_i))^2}{\sigma_{\text{exp}, i}^2} \right), \quad (14.3)$$

where the number of data points is N_{data} , and $\sigma_{\text{exp}, i}^2$ is the expected variance of the i th datum. Expected data variance $\sigma_{\text{exp}, i}^2$ can vary to reflect the differences in the expected precision of different measurements in a dataset. The values of Y^E and $\sigma_{\text{exp}, i}^2$ are determined a priori. Here, the values for these $\sigma_{\text{exp}, i}^2$ are given by $\sigma_{\text{exp}, i}^2 = (Y^E(\mathbf{x}_i)\sigma_e)^2$. In practice, the determination of $\sigma_{\text{exp}, i}^2$ is highly dependent on the specifics regarding the TD data obtained. Users are encouraged to closely consider the origins of possible errors in their data.

An admissible parameter space is defined for the calibration parameters, thus constraining the material model to a finite parameter domain. The admissible parameter space establishes a uniform or noninformative prior probability density for $\boldsymbol{\theta}$, in a Bayesian sense, i.e., $\text{Prior}(\boldsymbol{\theta}) = \text{Uniform}(\boldsymbol{\theta}_{\min}, \boldsymbol{\theta}_{\max})$, where $\boldsymbol{\theta}_{\min}$ and $\boldsymbol{\theta}_{\max}$ are bounds on the values of $\boldsymbol{\theta}$ which reflect physical or numerical limitations. The material model response $Y^M(\mathbf{x}_i, \boldsymbol{\theta})$ is recorded for each of N_{data} samples, at multiple values across the admissible space $[\boldsymbol{\theta}_{\min}, \boldsymbol{\theta}_{\max}]$. In practice, setting the prior density as uniform simplifies the procedure; where possible, transformation of variables (e.g., changing θ to θ^2) is recommended as an alternative to assigning a form other than uniform to the prior. In cases where a transformation is not sufficient, a nonuniform prior can be used.

In the case to be demonstrated, the SOR surrogate models approximate $Y^M(\mathbf{x}_i, \boldsymbol{\theta})$ by fitting a reduced training set of simulation results. This training set is selected via a restrictedly randomized factorial design of experiments (DoE). Also used in response surface methods [20], the SOR surrogate model is well documented [4], including for this approach [2]. It is a regressive method for selecting a quadratic surrogate function, $f_i(\boldsymbol{\theta})$, applied in this case such that

$$Y^M(\mathbf{x}_i, \boldsymbol{\theta}) \approx f_i(\boldsymbol{\theta}) \sim [Y^M(\mathbf{x}_i, \boldsymbol{\theta}_j)] \text{ for } j = 1 \cdots 4^n \text{ in DoE} \quad (14.4)$$

The DoE consists of a randomized factorial sampling that uses 4^n subgroups or subdomains of the admissible $\boldsymbol{\theta}$ space. One random sample is taken from each subdomain. For brevity, the full description is omitted here. These surrogate models are informed on a per datum basis. The values of Y^M as functions of $\boldsymbol{\theta}$ are interpolated per the relationship

$$f_i(\boldsymbol{\theta}) = Y^M(\mathbf{x}_i, \boldsymbol{\theta}) + \varepsilon_{\text{sur},i} \quad (14.5)$$

where each surrogate $f_i(\boldsymbol{\theta})$ depends only on $\boldsymbol{\theta}$, and mismatch between the material model and the surrogate is explained with the surrogate error term $\varepsilon_{\text{sur},i}$. In practice, another option is to use one surrogate model to interpolate between both the physical parameters varied in the dataset and the calibration parameters. The error term $\varepsilon_{\text{sur},i}$ can be estimated using a test set of material model runs (the application in [Section 3](#) approximates $\varepsilon_{\text{sur},i} \cong 0$).

The TD surrogate-based likelihood functions are formulated as

$$\text{Likelihood}(\boldsymbol{\theta}) \cong \exp \left(-\frac{1}{2} \sum_{i=1}^{N_{\text{data}}} \frac{(f_i(\boldsymbol{\theta}) - Y^E(\mathbf{x}_i))^2}{\sigma_{\text{exp},i}^2} \right). \quad (14.6)$$

Finding the maximum of [Eq. \(14.6\)](#) will return an ML estimate of the calibration parameters on the TD data, $\hat{\boldsymbol{\theta}}_{\text{TD}}$. To find $\hat{\boldsymbol{\theta}}_{\text{TDBU}}$, the BU information must be included.

BU reference estimates of $\boldsymbol{\theta}$, $\hat{\boldsymbol{\theta}}_{\text{BU}}^{\text{ref}}$, alter [Eq. \(14.6\)](#) as penalty functions [\[21\]](#). The penalty functions used here impose constraints on $\boldsymbol{\theta}$, i.e.,

$$\boldsymbol{\theta} = \hat{\boldsymbol{\theta}}_{\text{BU}}^{\text{ref}} \quad (14.7)$$

The penalty is defined as a Gaussian error term, i.e.,

$$\text{Penalty}(\boldsymbol{\theta})_j = \exp \left(-\frac{1}{2} \frac{\left(\theta_j - \hat{\theta}_{\text{BU},j}^{\text{ref}} \right)^2}{\sigma_p^2} \right) \quad (14.8)$$

where $\hat{\theta}_{\text{BU},j}^{\text{ref}}$ is the j -th component of the BU reference estimates, and σ_p^2 is the variance of the penalty, which modulates the influence of the BU information on the constrained likelihood function (CLF). In practice, BU reference estimates may include uncertainty. This BU uncertainty may be used to formulate the penalty function. The Gaussian error assumed in this case is shown as a default. In any formulation of the penalty functions, it is important to include a term σ_p^2 as a tuning parameter.

A CLF is used to incorporate TD and BU information. With the assumption of independence, the penalty functions are imposed multiplicatively on the likelihood function to establish the CLF, as

$$\text{Constrained Likelihood}(\boldsymbol{\theta}) = \text{Likelihood}(\boldsymbol{\theta}) \prod_{j=1}^{n_v} \text{Penalty}(\boldsymbol{\theta})_j \quad (14.9)$$

$$\text{CLF}(\boldsymbol{\theta}) \cong \exp \left(-\frac{1}{2} \sum_{i=1}^{N_{\text{data}}} \frac{(f_i(\boldsymbol{\theta}) - Y^E(\mathbf{x}_i))^2}{\sigma_{\text{exp}, i}^2} \right) \prod_{j=1}^{n_v} \exp \left(-\frac{1}{2} \frac{\left(\theta_j - \hat{\theta}_{\text{BU},j}^{\text{ref}} \right)^2}{\sigma_p^2} \right) \quad (14.10)$$

or equivalently,

$$\text{CLF}(\boldsymbol{\theta}) \cong \exp \left(-\frac{1}{2} \left(\sum_{i=1}^{N_{\text{data}}} \frac{(f_i(\boldsymbol{\theta}) - Y^E(\mathbf{x}_i))^2}{\sigma_{\text{exp}, i}^2} + \sum_{j=1}^{n_v} \frac{\left(\theta_j - \hat{\theta}_{\text{BU},j}^{\text{ref}} \right)^2}{\sigma_p^2} \right) \right) \quad (14.11)$$

Finding the maximum of the CLF returns the combined TDBU ML estimate, $\hat{\boldsymbol{\theta}}_{\text{TDBU}}$. The tuning parameter σ_p^2 is a measure of information precision associated with the BU information path. Thus, the $\hat{\boldsymbol{\theta}}_{\text{TDBU}}$ estimate can be described as a function of σ_p^2 with known limiting values, i.e.,

$$\hat{\boldsymbol{\theta}}_{\text{TDBU}} \rightarrow \hat{\boldsymbol{\theta}}_{\text{BU}} \text{ as } \sigma_p^2 \rightarrow 0, \quad \hat{\boldsymbol{\theta}}_{\text{TDBU}} \rightarrow \hat{\boldsymbol{\theta}}_{\text{TD}} \text{ as } \sigma_p^2 \rightarrow \infty \quad (14.12)$$

It is noted that near these extremes (0 or ∞), the resulting estimate may not constitute a meaningful combination of the two information sources. It is also noted that the presence of multiple local maxima in the CLF may lead to discontinuities in the function $\hat{\boldsymbol{\theta}}_{\text{TDBU}}(\sigma_p^2)$.

14.3 Usage: TDBU calibration of CP of bcc Fe

Details of a specific use-case are employed here to clarify the usage of the TDBU calibration approach [2]. A CP slip system flow rule for bcc Fe [2,22] is identified as the material model. The theoretical basis of the interscale connection is identified. The QoI for the calibration is defined. The TD and BU information sources are detailed.

Parameters are selected and admissible ranges are defined for the calibration set. The combined TDBU informing of the CP model is also described in this section. TDBU ML estimates are presented.

14.3.1 Background

Prior work has been done to understand the multiscale relationships of non-Schmid stress effects, Peierls stress, and kink-pair activation enthalpy in bcc metals [23,24] to inform a mesoscopic slip system level flow rule. A physics-based model of bcc Fe [22] CP was selected [2] to be included as a TD formulation along with a BU formulation [25] based on atomistic simulations of a rate-limiting mechanism of screw dislocation motion to be included in a TDBU calibration [2]. The parameters included in the calibration method are associated with the CP model response QoI: the temperature- and crystallographic orientation-dependent yield strength of single crystal bcc Fe. The relevant information pathways are summarized with regard to calibration of parameters of this mesoscale model.

The TD pathway employs experimental data from the uniaxial tension tests of single crystal bcc Fe performed by Ref. [26,27]. Data are fit by a CP model [22] with a Kocks-type activation enthalpy-driven flow rule [28] governing the activity of slip systems. Five parameters in the flow rule are included in the calibration parameter set.

The BU pathway informs the calibration parameter set via atomistic simulations. First, the coordinated thermal activation of a kink-pair on a screw dislocation segment is taken as the rate-limiting step for dislocation motion [25,29]. Invoking transition state theory, the nudged elastic band method [30], and molecular dynamics simulations of kink-pair nucleation [25] are used to inform the CP model [22]. Estimates of the calibration parameter set are gathered through fitting the Kocks-type flow rule to the atomistic results.

A QoI may have differing estimates when measurements are made at different length and time scales. For example, atomistic simulations predict the Peierls stress to be around 1040 MPa for bcc Fe [31,32]. Determinations based on experiments cluster near 390 MPa [33–35], clearly different from atomistic estimates. The TDBU calibration process incorporates these contrasting estimates from different scales into a single reconciled estimate.

14.3.2 Crystal plasticity model

The CP model in the TDBU calibration is taken from the work of [22] on constitutive equations to incorporate non-Schmid effects on yield strength in single crystal bcc Fe. The model is formulated for use with the finite element software Abaqus [36]. In this work, it is executed via single material point simulations. This single material point simulation assumes that the material experiences homogeneous deformation at the single crystal level. This work is only concerned with initial onset of slip. Thus, this assumption is reasonable. A few details of the CP model are included here. The kinematics and the full description of the model are available elsewhere [2,22].

Constitutive equations are used to define the slip system shearing rates $\dot{\gamma}^\alpha$ as a function of the resolved shear stress τ^α , and the internal state variables on each slip system α . In bcc metals at low to moderate homologous temperatures, inelastic deformation is rate limited by thermally activated glide of $\frac{1}{2}\langle 111 \rangle$ screw dislocations, which occurs via kink-pair formation [37]. At the mesoscale, the crystallographic slip system shearing rates are defined using a phenomenological Kocks-type activation enthalpy-driven flow rule [28], i.e.,

$$\dot{\gamma}^\alpha = \begin{cases} \dot{\gamma}_0 \exp\left(-\frac{\Delta F_g}{kT} \left(1 - \left(\frac{\tau_f^\alpha - s_a^\alpha}{s_t^\alpha}\right)^p\right)^q\right); & \text{for } \tau_f^\alpha > s_a^\alpha \\ 0; & \text{for } \tau_f^\alpha \leq s_a^\alpha \end{cases} \quad (14.13)$$

for the 24 $\{110\}\langle 111 \rangle$ slip systems indexed with α . Here, $\dot{\gamma}_0$ is the preexponential factor, ΔF_g is the activation energy for dislocation glide in the absence of external stress, k is the Boltzmann constant, T is absolute temperature, τ_f^α is the driving stress for dislocation glide, s_a^α is the athermal slip resistance to dislocation glide, s_t^α is the thermal slip resistance, typically controlled by the characteristically high Peierls stress of bcc metals, and p and q are parameters that model the shape of the activation enthalpy function. Parameters of this flow rule are the primary subject of the TD and BU calibration in the present work.

14.3.3 Parameter estimates and data

CP parameters other than those involved in the TDBU calibration can be found elsewhere [2]. In practice, parameters not addressed by both TD and BU information pathways do not belong in the TDBU calibration set. Additionally, parameters which have little uncertainty or little influence on the response QoI (in this case, yield strength) are not good candidate parameters for TDBU calibration. In any given approach, these considerations may lead to a calibration parameter set which excludes most of the model parameters.

The TDBU calibration incorporates both TD and BU data to estimate parameters. Some modifications to the methods used in single-scale calibrations are necessary to ensure similarity in the treatment of information from either source. These modifications amount to including or excluding parameters to define a common calibration parameter set and performing a change of variable as needed to support uniform prior probability densities. The connections used in establishing prior information [22,25] are accordingly somewhat modified in the TDBU calibration.

The unmodified TD and BU estimates are used to provide guidance in the definition of admissible parameter ranges. Summaries of these information pathways are documented in previous work [2]. The documented parameter estimates are shown in Table 14.1. These estimates are referred to as reference estimates, due to their preexisting status. In practice, these TD and BU estimates may originate by expert elicitation, though the use of more rigorous methods is preferred.

Table 14.1 Reference estimates of the key flow rule parameters (Eq. 14.13) from both TD and BU information pathways.

Parameter	$\dot{\gamma}_0$	$\Delta F_g \text{ or } H_0$	p	q	s_t
TD reference estimates $\hat{\theta}_{\text{TD}}^{\text{ref}}$	$1.00 \times 10^7 \text{ s}^{-1}$	0.825 eV	0.47	1.0	390 MPa
BU reference estimates $\hat{\theta}_{\text{BU}}^{\text{ref}}$	$3.19 \times 10^7 \text{ s}^{-1}$	0.57 eV	0.67	1.18	1040 MPa

When BU and TD modeling efforts are performed independently, model form decisions may differ between the two. A common mesoscale (CP) model form with the same parameters is used here to perform the TDBU calibration. If the parameters between BU and TD models are different, a mapping between the unlike parameter spaces will need to be defined. In this usage case, the differences in the models do not pertain to the output QoI of the calibration. As a result, the implementation of changes to either TD or BU approach does not substantially affect the functional relationship between calibration inputs and output QoIs. Therefore, the reference estimates of parameters gathered from unmodified model calibrations are relevant to determining appropriate ranges for the modified-for-TDBU forms. If inappropriate parameter ranges are used, the results of the calibration may be biased and suboptimal.

14.3.4 Implementation of the method

The QoI of the TD model response is identified as the proportional limit yield strength of single crystal bcc Fe. Data from experiments [26,27,38] provide the means of estimating the calibration parameters through fitting. After identifying response QoIs, a common model form, and reference estimates for a common calibration parameter set, the TDBU calibration procedure may proceed. The steps involved include the definition of a prior probability density of the calibration parameters, the evaluation of the likelihood functions as defined in Section 2, and the evaluation of certain procedural tuning parameters. The practical concerns of the implementation process are highlighted in the usage example which follows.

Admissible parameter ranges are defined for the calibration parameters, $[\theta_{\min}, \theta_{\max}]$, where in this case $\theta = [\dot{\gamma}_0, \Delta F_g, p, q, s_t]$. Each parameter range is defined by simple bounds, chosen to reflect expert knowledge on the parameters, shown in Table 14.2. For the parameters $\Delta F_g, p, q$, and s_t , the estimates from TD and BU reflect the general range of estimates given by atomistic simulations and empirical measurements, including the reference estimates of Table 14.1. For these parameters, a uniform prior probability density is assumed within the bounding values.

A transformation is applied to the calibration parameter $\dot{\gamma}_0$. The admissible range for $\dot{\gamma}_0$ spans two orders of magnitude, which is much larger than the ranges of the other parameters. The output QoI is less sensitive with respect to $\dot{\gamma}_0$. The parameter is transformed to $\ln(\dot{\gamma}_0)$ to support a uniform definition of the prior probability density

Table 14.2 Admissible parameter bounds for the calibration parameters θ .

Parameter	$\dot{\gamma}_0$	ΔF_g or H_0	p	q	s_t
θ_{min}	$5.00 \times 10^5 \text{ s}^{-1}$	0.55 eV	0.4	1.0	300 MPa
θ_{max}	$5.00 \times 10^7 \text{ s}^{-1}$	0.95 eV	0.8	1.5	1100 MPa

function (PDF) for θ . The change of variable may be indicated by the functional form itself. Incidentally, the flow rule contains the exponent of θ . The flow rule is equivalently written in terms of the transformed variable

$$\dot{\gamma}_{TD}^\alpha = \begin{cases} \exp\left(\ln(\dot{\gamma}_0) - \frac{\Delta F_g}{kT} \left(1 - \left(\frac{\tau_f^\alpha - s_a^\alpha}{s_t^\alpha}\right)^p\right)^q\right); & \text{for } \tau_f^\alpha > s_a^\alpha \\ 0; & \text{for } \tau_f^\alpha \leq s_a^\alpha \end{cases} \quad (14.14)$$

Here, the transformed variable $\ln(\dot{\gamma}_0)$ is no longer the only parameter outside of the exponential function. Now all variables have similar levels of sensitivities. In cases where analysis of model form is used to conduct a change of variable, it is recommended to investigate the sensitivity of the QoI to the transformed variable for uniformity within the admissible parameter ranges.

The uniform prior PDF for θ is linearly mapped to intervals of [0,1] to remove the influence of units. This holds for transformed parameters as well (e.g., $\ln(\dot{\gamma}_0)$). Calculations are performed in these unitless terms, though results are shown in original units.

The surrogate model form that is most appropriate in practice may vary by application. It is noted that the example case includes a separate surrogate model for each data point i of N_{data} . Each surrogate f_i takes the calibration parameter values as inputs (normalized to their admissible ranges) and provides an estimate of the material model response (yield strength) at one physical parameter value $\mathbf{x}_i$, i.e., $f_i(\theta) = Y^M(\mathbf{x}_i, \theta) + \varepsilon_{\text{sur},i}$. Alternatively, a single surrogate could interpolate across both calibration parameters and physical parameters, i.e., $f(\theta, \mathbf{x})$. The trade-offs between the demand for running the computational material model and the magnitude of error between the surrogate and the material model must be evaluated to inform surrogate model selection. In this application, the surrogate models have coefficients of determination, the equally weighted mean of which is 0.98.

The proportional limits (definition of yield strength employed here) from the experimental TD data [26] and from the various calibrations of the CP model are shown for three temperatures and orientations in Fig. 14.2. The angle χ is the misorientation between the maximum resolved shear stress plane of the loading and the reference (110) slip plane. The BU calibrated model returned yield strengths that greatly exceeded those from experimental data at lower temperatures. At 250 K, the BU had much more agreement with experimental data. The TDBU-based calibration performed nearly as well as the purely TD-based calibration.

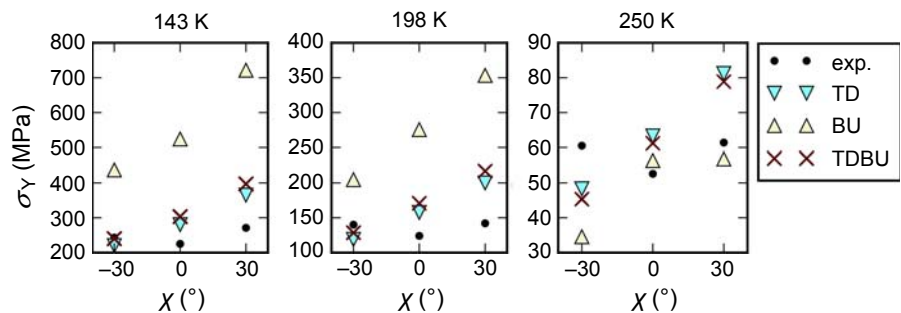


Figure 14.2 The proportional limit at three temperatures for loading along three crystallographic orientations. The BU used here is later referred to as simulated BU. Reproduced with permission A.E. Tallman, L.P. Swiler, Y. Wang, D.L. McDowell, Reconciled top-down and bottom-up hierarchical multiscale calibration of bcc Fe crystal plasticity. *Int. J. Multiscale Comput. Eng.* 15. 2017, <https://doi.org/10.1615/IntJMultCompEng.2017021859>.

Calibrated parameter values are presented in Table 14.3. Note that the values of $\hat{\theta}_{\text{TD}}$ and $\hat{\theta}_{\text{TD}}^{\text{ref}}$ (from Table 14.1) do not match. The two estimates are produced by distinct calibration procedures carried out using different data.

The function $\hat{\theta}_{\text{TDBU}}(\sigma_p^2)$ is explored to demonstrate the need for tuning of σ_p^2 , shown in Table 14.3. The TDBU calibration is susceptible to finding solutions which are dominated by the influence of one of the datasets. It is the responsibility of those who execute the TDBU procedure to consider the relative levels of influence desired from each pathway. If such an influence breakdown can be defined, the parameter σ_p^2 can in turn be well defined.

14.4 Between the models: connection testing

As previously mentioned, the uncertainty associated with connections between multiple models in an HMM chain has rarely been considered. A previously developed test

Table 14.3 Maximum likelihood estimated values for the calibration parameters. TD corresponds to the unconstrained likelihood function, and TDBU corresponds to the likelihood function constrained by penalty terms. Values of $\sigma_{\text{exp},i}^2 = (0.1 Y^E(\mathbf{x}_i))^2 \forall i$ were used.

Parameter	$\dot{\gamma}_0 \text{ (s}^{-1}\text{)}$	$\Delta F_g \text{ or } H_0$	p	q	$s_t \text{ (MPa)}$
$\hat{\theta}_{\text{TD}}$	5.00×10^7	0.79 eV	0.4	1.5	860
$\hat{\theta}_{\text{TDBU}} \mid \sigma_p = 0.5$	5.00×10^7	0.78 eV	0.4	1.38	796
$\hat{\theta}_{\text{TDBU}} \mid \sigma_p = 0.2$	3.93×10^7	0.75 eV	0.43	1.29	686
$\hat{\theta}_{\text{TDBU}} \mid \sigma_p = 0.1$	3.07×10^7	0.68 eV	0.52	1.28	652
$\hat{\theta}_{\text{TDBU}} \mid \sigma_p = 0.05$	3.12×10^7	0.60 eV	0.58	1.25	800
$\hat{\theta}_{\text{TDBU}} \mid \sigma_p = 0.02$	3.56×10^7	0.55 eV	0.63	1.21	972
$\hat{\theta}_{\text{BU}}$	3.19×10^7	0.57 eV	0.67	1.18	1040

of uncertain model–model connections in an HMM [2] is presented for use as a general methodology here. A likelihood-based estimate of parametric uncertainty is used to track changes introduced by the inclusion of an interscale connection in an HMM. Evaluation of such a change captures a trade-off between the benefit of additional data and the cost of imposed uncertainty associated with dissimilarities in the data sources. A previously introduced approximation of connection uncertainty [2] is highlighted. A diagram of these steps is shown in Fig. 14.3. Generally, this test addresses HMMs which augment a single-scale method with the addition of a BU link, here specified as $\theta_{TD} = \theta_{BU}$.

14.4.1 Background

The multiscale connection test is a departure from information theory-based model selection criteria. For example, Akaike information criterion [39] and Bayesian information criterion [40] apply Occam's razor by incorporating the sum of squared errors and the number of model parameters in criteria for selecting the best, simplest model. In the HMM problem considered here with the connection test, the number of parameters is not changed in the BU augmentation of TD data, and as such these traditional selection procedures are not applicable to the decision at hand.

The connection test previously derived [2] can be introduced in terms of information theory and data collection. As observations are added to the training set of a simple regression model, the uncertainty of the estimated values of the parameters decreases. This decrease in uncertainty does not depend on the values of the individual observations or on any statistical measure of their values. It is assumed in the formulation of the regression model that only valid observations are included in the training set, and while this assumption holds, the decrease in uncertainty is consistent with expectations. However, if erroneous, irrelevant, or otherwise disqualified values are included in the training set, the assumption breaks down and

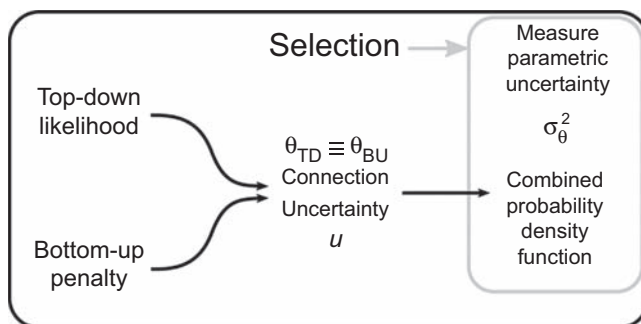


Figure 14.3 Flowchart of the method for the selection of uncertain connections between pathways of informing calibration of model parameters.

Reproduced with permission A.E. Tallman, L.P. Swiler, Y. Wang, D.L. McDowell, Reconciled top-down and bottom-up hierarchical multiscale calibration of bcc Fe crystal plasticity. *Int. J. Multiscale Comput. Eng.* 15. 2017, <https://doi.org/10.1615/IntJMultCompEng.2017021859>.

the uncertainty reduction due to each marginal datum becomes suspect. This suspicion is included in the formulation of the connection test as an exponent u , as

$$CLF(\boldsymbol{\theta}|\text{Uncertainty}) = CLF(\boldsymbol{\theta})^u, u \in (0, 1] \quad (14.15)$$

and allows the uncertainty of parameter estimates to depend on the number of observations multiplied by u , the connection cost parameter. It is more intuitive to consider the reciprocal of u to be the “connection cost,” as $\frac{1}{u}$ is zero when no cost is imposed by the connection and approaches infinity as the connection becomes infinitely costly.

14.4.2 Formulation

The intent of u is to capture the degree to which the inclusion of a connection interferes with the assumption of a qualified dataset. This can be explored. If observations from BU and TD are taken from one-dimensional continuous distributions, the value of u could be estimated by the probability that the two samples (TD and BU) are from the same distribution, as opposed to two different distributions. The K–S two-sample test offers a concise solution to this problem [41]. In higher dimensional parametric spaces, however, no test of this nature is as readily available to provide this probability.

In lieu of a probability from a K–S test in a multivariate setting, the performance of the CLF ML estimated parameters is used as a substitute. The sum of squared errors and penalties at $\hat{\boldsymbol{\theta}}_{\text{TDBU}}$ is taken to inform u , per

$$\begin{aligned} u|_{\text{TDBU}} &= \frac{1}{\max \left\{ \text{SSE} + \text{Penalty} \left(\hat{\boldsymbol{\theta}}_{\text{TDBU}} \right), 1 \right\}} \\ &= \frac{1}{\max \left\{ -2 \ln \left(CLF \left(\boldsymbol{\theta} \middle| \boldsymbol{\theta} = \hat{\boldsymbol{\theta}}_{\text{TDBU}} \right) \right), 1 \right\}} \end{aligned} \quad (14.16)$$

for the TDBU case. The sum-square error (SSE) is calculated as

$$\text{SSE} = \sum_{i=1}^{N_{\text{data}}} \left(\frac{Y^M(\mathbf{x}_i, \hat{\boldsymbol{\theta}}) - Y^E(\mathbf{x}_i)}{\sigma_{\text{exp}, i}} \right)^2 \quad (14.17)$$

The BU penalty contribution was calculated for each estimate, $\hat{\boldsymbol{\theta}}$, i.e.,

$$\text{Penalty} = \sum_{j=1}^{n_v} \left(\frac{\hat{\theta}_j - \hat{\theta}_{j, \text{BU}}^{\text{ref}}}{\sigma_p} \right)^2 \quad (14.18)$$

When SSE is large (indicating a poor fit), the value of u is small (indicating high connection cost), leading to a broadening of the CLF. An equivalent approximation for the prior, TD-only model includes $\hat{\boldsymbol{\theta}}_{\text{TD}}$ and the TD-only likelihood function. Here, u is informed per

$$u|_{\text{TD}} = \frac{1}{\max \left\{ -2 \ln \left(\text{Likelihood} \left(\boldsymbol{\theta} \middle| \boldsymbol{\theta} = \hat{\boldsymbol{\theta}}_{\text{TD}} \right) \right), 1 \right\}} \quad (14.19)$$

In cases which use a BU-only model as the prior form, it is necessary to have a more detailed representation of the likelihood across the calibration space than can be furnished using a single reference estimate, in order to give a value of u compatible with the approximations given.

Posterior PDFs are obtained using Bayes' rule, i.e.,

$$\text{PosteriorPDF}(\boldsymbol{\theta}) = \frac{\text{CLF}(\boldsymbol{\theta})^u \text{PriorPDF}(\boldsymbol{\theta})}{\text{Normalizing Const.}} \quad (14.20)$$

Here, the normalizing constant is found using the law of total probability, the changes of variable used, and the admissible parameter space. Because this problem involves a uniform prior with constant density and a Gaussian likelihood function, the posterior is also Gaussian. This allows us to calculate the posterior distribution using analytical expressions derived from the surrogate models. We obtained the posterior Gaussian distribution by performing a quadrature-based numerical integration of the CLF across the admissible parameter space. The numerical error of the integration is limited to 0.01% of the calculated solution, through iterative subdivision. The integrated value provides the normalizing constant and the Gaussian posterior PDF. The posterior PDF is calculated for both TDBU and TD-only models.

The connection test is formulated using a measure of the posterior PDF of both the TDBU and the TD-only model. The measure, $\sigma_{\boldsymbol{\theta}}^2$, is called the calibration variance and is intended to describe the parametric uncertainty which remains in the calibrated model after connection cost is considered. The test for support of including the connection is shown as

$$\text{if: } \sigma_{\boldsymbol{\theta}, \text{TDBU}}^2 < \sigma_{\boldsymbol{\theta}, \text{TD}}^2, \quad \text{then include BU} \quad (14.21)$$

In other words, if the calibration variance decreases when the additional dataset is included, the addition is supported by the test. The calibration variance is measured with a numerical integration, i.e.,

$$\sigma_{\theta}^2 = \int_{\theta\text{-space}} \text{PosteriorPDF}(\theta) \sum_{j=1}^{n_v} (\theta_j - E[\theta_j])^2 d\theta \quad (14.22)$$

where $E[\theta_j]$ is the expected value of parameter j . This formulation penalizes for nonuniqueness in parameter estimates.

The comparison of σ_{θ}^2 is affected by the value assigned to σ_p^2 . A sensitivity study of σ_p^2 may be necessary to identify appropriate σ_p^2 values which allow both TD and BU data to influence the CLF. The relative influence of BU and TD can be estimated by comparing the variance of the TD-only likelihood function and the variance of the product of the BU penalty functions, where the smaller the variance, the larger the influence on the TDBU combination.

14.5 Usage: test of TDBU connection in CP of bcc Fe

The empirical connection test is demonstrated in terms of providing decision support, to reject or accept connections. Two hypothetical estimates are included to illustrate a gamut of connection scenarios. Additionally, the result of the test applied to the TDBU calibration of the HMM of bcc Fe is interpreted.

14.5.1 Background

Decisions in HMM design are often complicated and yet are often the least well-articulated aspect of an HMM exercise. The TDBU method here is an example of one type of HMM decision, specifically the augmentation of TD data with BU through an uncertain connection. In other cases, the BU information may be the default calibration set or the pending decision may involve the selection of experimental datasets to include in a larger analysis. In each case, the test which is demonstrated here may be altered as necessary to inspect the configurations in consideration.

The connection test is itself tested: if positive and negative results can be generated for different BU estimates to reflect the feasibility of a connection, the test works as intended. Two alternate BU reference estimates are introduced as the basis of this assessment. They represent two potential scenarios: the “cooperative” estimate mimics the TD likelihood function, whereas the “spurious” estimate strongly disagrees with the TD and leads to a poorly performing CP model when used directly. These estimates are presented in [Table 14.4](#) with the BU estimate from atomistic simulations. It is noted that these estimates are not combined, rather they are used as distinct alternative candidates. The TD data are used to connect with each case in turn, forming the common basis for comparison.

Table 14.4 Contrived BU reference estimates shown alongside the simulated estimates from the referenced atomistic modeling [25].

$\hat{\theta}_{BU}^{ref}$	$\dot{\gamma}_0$	$\Delta F_g \text{ or } H_0$	p	q	s_t
Simulated	$3.19 \times 10^7 \text{ s}^{-1}$	0.57 eV	0.67	1.18	1040 MPa
“Cooperative”	$1.58 \times 10^7 \text{ s}^{-1}$	0.75 eV	0.48	1.3	540 MPa
“Spurious”	$5.00 \times 10^5 \text{ s}^{-1}$	0.95 eV	0.8	1.5	1100 MPa

14.5.2 Implementation

Using the CP example case and the formulae of Section 4.2, the values of $\sigma_{\theta,TD}^2$ and each case of $\sigma_{\theta,TDBU}^2$ (simulated, cooperative, and spurious) are calculated. For reference, model performance indicators (SSE and Penalty) are shown alongside the calibration variances in Table 14.5. These performance measures are shown alongside the parametric uncertainty estimate σ_{θ}^2 for each calibration in Table 14.5. Across all shown BU reference estimates, the SSE is best for the TD-only calibrations. The SSE + Penalty is always minimized by the TDBU calibration. If the trend demonstrated by the examples holds for all BU reference estimates (and connections), the SSE and SSE + Penalty measures are insufficient as measures of empirical support for the TDBU connection. The parametric uncertainty estimate can increase or decrease with the addition of BU data, depending on the relationship between the TD likelihood function and the BU penalty function. This is shown in the change in the variance of the calibrated parameter values, σ_{θ}^2 , also in Table 14.5.

The results shown in Table 14.5 indicate that a connection with the “cooperative” estimate is supported and connection with the other estimates is not supported. The connection test is therefore assessed to be working as intended.

Table 14.5 The relative performance of TD and TDBU calibrations of the CP model for $\sigma_p = .1$, based on different BU reference estimates of θ . For each BU reference estimate, the better performing calibration is underlined.

BU estimate $\hat{\theta}_{BU}^{ref}$	Calibration	SSE	SSE + penalty	u	σ_{θ}^2
Simulated	TD	37.7	161.7	5.98×10^{-2}	0.296
	TDBU	83.1	102.3	1.17×10^{-2}	0.317
“Cooperative”	TD	37.7	81.0	5.98×10^{-2}	0.296
	TDBU	56.1	57.5	4.34×10^{-2}	0.249
“Spurious”	TD	37.7	262.6	5.98×10^{-2}	0.296
	TDBU	78.0	224.4	5.69×10^{-3}	0.340

14.5.3 Sensitivity study of σ_p^2

The parameter σ_p^2 determines the magnitude of the penalty functions. In theory, it maps uncertainty of the BU estimate to θ -space. In practice, it tunes the relative influence of the BU estimate on the TDBU calibration result. If σ_p^2 is too small, TD data have no impact on the TDBU calibration. Similarly, if σ_p^2 is too large, the BU data have no effect.

The value of σ_p^2 is varied in a sensitivity study, and the results of the TDBU calibration are shown in Table 14.6. The values of $\hat{\theta}_{\text{TDBU}}$ are shown in Table 14.3 for all the values of σ_p^2 explored in this parametric study. The value of σ_0^2 returned for BU-only calibrations is a function of the value chosen for σ_p^2 as is shown in the lower portion of Table 14.6. Here, the BU-only calibrations cannot be easily compared with TD or TDBU in terms of σ_0^2 , because σ_p^2 is not informed by uncertainty of the BU model in this case.

The pitfall of poor values for σ_p^2 can be seen in Table 14.6. The value of σ_0^2 is lowest for the TDBU with σ_p^2 equal to 0.02, where TD information is effectively ignored. If the maximum of σ_0^2 as a function of σ_p^2 is not found at the limit corresponding to a TD-only informing of θ , the TDBU connection is not supported.

In this example, the HMM of bcc Fe plasticity does not improve upon the single-scale TD-only informed model in predicting the onset of yielding. This result does not indicate which, if any, component of the approach is at fault. The result indicates that improvements to the model will likely be found in improving the connection between scales, as opposed to increasing the complexity of predictions. For a detailed description of the interpretation of the results repeated here, refer to the original implementation of the approach [2]. In practice, the benefit of performing the test as seen here is maximized when coordinated with a scientific goal. In this application, finding the connection between the unit-process and the many-body effects manifested through experiments was a goal of the TDBU approach. The useful conclusion is that more details are needed to make such a connection, and that unit-process results from atomistics are not useful if taken alone to calibrate parameters of the mesoscale flow rule. This is important as “wishful thinking” of atomistic modelers might suggest otherwise.

14.6 Discussion and extensions to validation

A TDBU calibration method and corresponding interscale connection test for HMMs are described and demonstrated. These methods reflect one possible approach to the use of multiscale information in the calibration of HMM parameters. Alternative approaches are discussed here as comparison and are described using the terms calibration and validation to provide common context. Here, calibration and validation are distinguished in that calibration leads to the selection of values for parameters, whereas validation test values that have been previously selected.

Distinctions between the calibration domain and validation domain have critical influence on multiscale inference (domain here refers to the viable set of observable cases for use in each procedure). Commonly for rigorous models, validation and

Table 14.6 Parametric study of σ_p^2 . The simulated $\hat{\theta}_{\text{BU}}^{\text{ref}}$ is used for all cases. Penalty is 0 for BU-only calibration. The values of σ_0^2 for BU-only calibrations are shown for the different values of σ_p^2 .

	Calibration	SSE	SSE + penalty for $\sigma_p^2 = \{0.5^2, 0.2^2, 0.1^2, 0.05^2, 0.02^2\}$					u	σ_0^2
σ_p			0.5^2	0.2^2	0.1^2	0.05^2	0.02^2		
–	TD	37.7	42.6	68.4	160.5	529.2	3110	5.98×10^{-2}	0.296
0.5	TDBU	39.2	43.3	64.8	141.6	448.7	2598	4.70×10^{-2}	0.301
0.2	TDBU	52.7	55.9	72.5	131.9	369.5	2033	2.48×10^{-2}	0.311
0.1	TDBU	83.1	85.0	95.2	131.6	276.8	1294	1.17×10^{-2}	0.317
0.05	TDBU	130.6	131.3	134.9	147.9	199.6	561.7	5.79×10^{-3}	0.312
0.02	TDBU	213.2	213.3	213.8	215.7	223.1	274.9	3.53×10^{-3}	0.222
		SSE	$\sigma_0^2 \text{ for } \sigma_p^2 = \{0.5^2, 0.2^2, 0.1^2, 0.05^2, 0.02^2\}$						
–	BU	671.9	0.647	0.161	0.042	0.011	0.006	–	–

calibration domains are similar, i.e., data used to validate a model resemble closely the data used to calibrate. Under scarcity of data, consistency between the domains of calibration and validation becomes difficult to achieve without using the same data for both purposes, itself a problematic practice.

Consider the use of models in prediction. Often, predictive models are validated such that the mismatch between the calibration data and validation data resembles the mismatch expected between the calibration data and the prediction domain. For example, this inference testing is often necessary in the case of statistical models, for which it is often unclear a priori whether a training (calibration) dataset and a chosen model structure are sufficient to meet the predictive burden demanded by an application. In such cases, a validation of the calibrated model is a basis of estimation of predictive uncertainty. This basis is useful *when it resembles an application* of the model. The consideration of this *resemblance* is of key interest in multiscale modeling.

In HMMs, the relation of validation domain and calibration domain determines the role taken up by the connection between scales/models. In the TDBU approach given, the connection provides a means of extending the calibration domain to include datasets of different length scales. The connection test shown indicates one means of justifying the inclusion of a connection used in that manner. Validation of the connection is not performed here; however, an ideal validation dataset would include TD and BU pathways and would closely resemble the calibration dataset. For models with scarce data support, this ideal case is challenging.

A BU-only calibration of a connection is often validated using TD data. This type of formulation is unlike the approach used in this chapter. By introducing the TD data in validation, the connection is used as a means of predicting TD data from BU calibration. When such predictions are successful, this approach is satisfactory for identifying multiscale connections. However, an unsuccessful prediction of this type provides no incremental evidence for use in evaluating (and subsequently improving) the connection. A mismatch between TD and BU (regardless of origin, e.g., unlike errors, missing physics, etc.) may suggest that the connection does not exist (because the connection is judged in a binary fashion as either predictive or incorrect). This limitation is a result of the profound difference between calibration and validation domains, as the same limitation applies in a TD-only calibration with BU-only validation. This approach may still be an appropriate strategy in certain cases, especially when the model form uncertainty is low.

In designing a multiscale model calibration procedure, the role of the connection must be considered. In the application briefly included, some mismatch between BU and TD pathways was expected. In reconciling the TD/BU mismatch during calibration, the connection definition method (the CLF of Eq. 14.11) was formulated to seek compromise in the presence of this mismatch. The goal of the work was to augment a TD dataset with BU data (if beneficial), as opposed to replacing a TD dataset with a BU dataset. Therefore, a predictive connection between scales was superfluous to requirements in this case. In general, consideration along these lines can guide decisions in calibration of HMMs.

We close by noting that concurrent multiscale models differ from HMMs by achieving concurrency of execution of models at various length and time scales. As

such, means of connecting information between scales to inform parameters are typically established directly in the model form, i.e., the very structure of the multiscale model framework, or more specifically the boundary conditions which enforce consistency between adjacent models. The uncertainty of the model form in this case is distinct from the HMM connection pursued in this chapter but is of equal importance. Very little work has been devoted to degree of uncertainty conveyed in such concurrent schemes.

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Efficient uncertainty propagation across continuum length scales for reliability estimates

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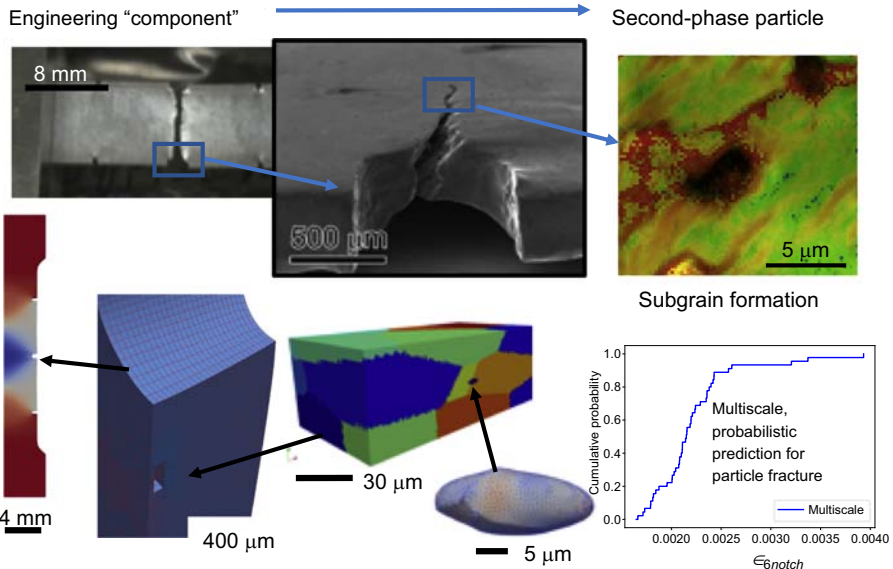
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15.1 Introduction

The primary goal of this research is to develop tools and capabilities for efficient multi-scale uncertainty propagation (UP) using the finite element (FE) method for tractable multiscale structural reliability calculations and uncertainty quantification (UQ). The outcomes impact high-consequence engineering designs that require high reliability, e.g., failure probability $< 1 \times 10^{-6}$, such as aircraft, biomedical applications, nuclear weapons safety and security, and space flight vehicles. We propose a hierarchical concept that attempts to rationally prioritize where computational resources are expended. This is, in many regards, a sequel to an earlier manuscript that developed the hierarchy for fatigue life prediction of aerospace structures [1]. Here, we refresh the methodology with a focus on ductile failure, a modern theory for UP, and a deeper physical representation.

There are many sources of aleatoric and epistemic uncertainty that impact performance and reliability, e.g., environment, boundary conditions, materials' processing, personnel handling, constitutive model error, discretization errors, etc. A most useful summary of sources of uncertainty arising due to materials' structure can be found in Chernatynskiy et al. [2]. The authors present a state-of-the-art report on sources of aleatoric and epistemic uncertainties, and methods for quantifying them, including probability theory, interval analysis, Bayesian methods, and sensitivity analysis. They further demonstrate how uncertainty in atomistic simulations can be propagated at larger scales. Our work, in contrast, focuses on material-scale variability and methods to propagate mesostructural uncertainties across continuum length scales. We consider materials' variability and its fundamental importance to failure governed by localization processes such as fracture, a very complex and stochastic phenomenon as illustrated by the image in Fig. 15.1. In one of our numerical examples, we consider uncertainty in boundary conditions, to illustrate the path forward for other categories of uncertainty.



**SEM & HREBSD images courtesy of Kacher Lab, GA Tech

Figure 15.1 Physical illustration and accompanying computational models, demonstrating the continuum length scales of concern.

SEM and high-resolution EBSD images courtesy of Prof. Josh Kacher, Georgia Institute of Technology.

Philosophically, we believe that concurrent multiscale coupling is required for a high-fidelity representation of the relevant physical processes and mechanisms present during a localization event, particularly when ultrahigh reliability requirements exist. So-called hierarchical multiscale methods [3] exist, and we hope to avoid confusing them with our proposed hierarchical reliability approach. In these multiscale methods, information about differing length scales is passed via micromechanically motivated internal state variables and homogenization [4] is employed to represent average material behavior. Certainly, homogenization techniques can be developed to account for fine-scale damage mechanisms and many capable researchers have successfully employed them [5–7]. In Greene et al., random constitutive laws for materials based on statistical volume elements and probabilistic microstructure models are constructed [8]. Copula and polynomial chaos representations are employed to capture the dependence between the uncertain parameters of these constitutive laws and examples are used to illustrate the proposed method and illustrate its performance. Their proposed constitutive laws capture a significant part of the uncertainty in material microstructure, and they rely on homogenization, making it difficult to capture localization. Other nice work employs polynomial chaos and homogenization algorithms to capture a hierarchy of materials' length scales, but again avoids focus on characterization of extreme material responses [9]. In fact, we rely on internal state variable damage models for the first-level calculations in our approach. However, for the purposes of developing accurate

estimates of the probability of failure, homogenization techniques are insufficient because as fracture or localization initiates, it shifts the relevant length scale down to that of the fine-scale materials' structures and necessary separation-of-scale is lost [10,11]. That is, as a body deforms and localization is triggered, e.g., due to $5\text{ }\mu\text{m}$ second-phase particle fracture or debond, the higher-order gradient effects neglected by homogenization become of paramount importance [12–14].

Therefore, we advocate carefully constructed microstructural models that explicitly represent the physical mechanisms at the relevant length scales and concurrently coupled with the coarse scale. We do not endeavor to develop a new multiscale numerical method (MNM). There are many robust methods available in the literature and under investigation [15,16]. Rather, the focus of this work is on what we consider to be the larger aspect of multiscale UQ: how to efficiently make use of an MNM for reliability predictions. Our hierarchical approach is not limited to our choice of MNM; use your favorite. The only assumption we make is that the MNM will be computationally demanding and that practical applications cannot include fine-scale details throughout the problem domain due to exorbitant computational demand. Hence, to account for microstructural uncertainties in reliability estimates for high consequence applications, a concurrent MNM is necessary but not sufficient.

Consider this scenario: *A multiscale FE analysis including a polycrystalline subdomain at one hotspot in a component can easily require the solution to tens of millions of equations or more for one realization of the microstructure—a very computationally expensive endeavor. However, this calculation represents only one data point for the conditional probability of failure, conditioned on the assumption that failure occurs at that hotspot. For engineering structures, there are presumably many hotspots. To complete the reliability assessment, Monte Carlo simulation (MCS) is necessary at each hotspot, requiring many thousands of such analyses—this is intractable (Fig. 15.2).*

Brute-force direct numerical calculation cannot generate sufficient Monte Carlo samples for prediction of ultrahigh reliability, i.e., probability of failure less than 1×10^{-6} , when the analyses are as cumbersome as described by this scenario. To avoid this conundrum, we introduce a novel approach for multiscale reliability that employs stochastic reduced-order models (SROMs) at a hierarchy of length scales. The hierarchy of length scales provides a rational basis to select subdomains for concurrent multiscale simulation, while the SROMs provide a reduced-order representation of the uncertain inputs that enable construction of a response surface for rapid Monte Carlo sampling [17]. Although not a limitation of the approach, the present treatment involves just two length scales. In the hierarchy, we use an FE model at the engineering length scale to develop a low-fidelity estimate for structural response and reliability. Subsequently, we build a higher-fidelity FE model of the fine scale to refine the predicted response. The framework for this hierarchy is discussed below in [Section 15.2](#), followed by a review of some necessary background mathematics supporting the stochastic reduced models and summarized with several numerical application examples illustrating the method.

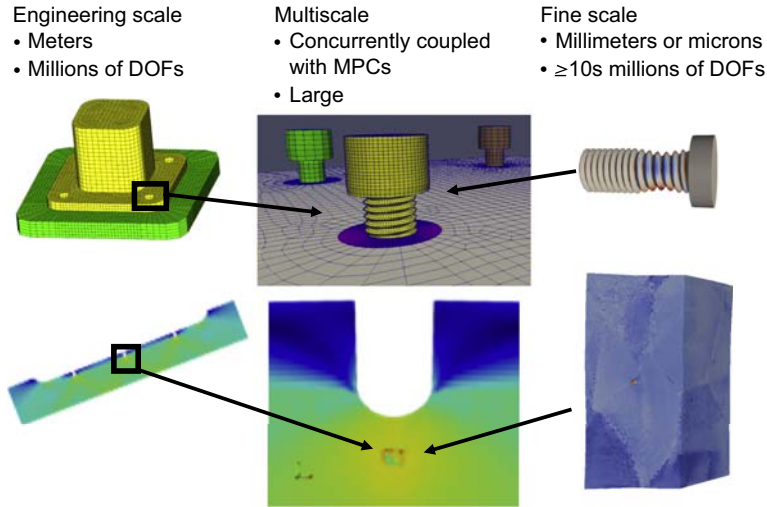


Figure 15.2 Two examples of multiscale calculations that concurrently couple the engineering scale with the fine scale and result in very large calculations.

Our hierarchical approach requires low-fidelity models, which are developed at the engineering length scale. Referred to in other multiscale literature as the coarse scale, this is the length scale that is most practically employed for design calculations. The low-fidelity modeling follows closely the developments in Refs. [18,19], where uncertainties observed in materials' characterization are lumped into the material parameters. Further, the hierarchy requires high-fidelity models, which are fine-scale models developed to emphasize improved geometric representation and increased phenomenological physics representation in the constitutive model. To connect the length scales—reiterating that we are not focused on the development of a new MNM—we employ a rather simplistic approach whereupon we decompose the engineering-scale domain in the vicinity of hotspots identified by the engineering-scale model and couple the fine-scale model with multipoint constraints (MPC) to achieve continuum-to-continuum coupling of the engineering-scale domain with the fine-scale domain [20].

We present a series of three example applications. In the first, the entire hierarchy is illustrated for a multiscale problem whose high-fidelity model improves the geometric representation of a series of threaded fasteners. While this illustration does not blend high-fidelity materials' modeling, it does concisely illustrate the hierarchical method in a straightforward and easy-to-follow manner. The second illustration emphasizes the use of SROMs to expedite reliability predictions for polycrystalline microstructures whose crystallographic texture is described by a vector-valued random field. This illustration does not computationally bridge length scales, but it illustrates UP for the fine scale. In our final demonstration, we concurrently couple the polycrystalline length scale of a rolled aluminum alloy 6061-T6 (AA 6061-T6) plate with an engineering length scale to make probabilistic statements about the fracture load in the material's second phase.

15.2 Hierarchical reliability approach

We propose a hierarchical methodology for multiscale UQ, shown with the notional flowchart in Fig. 15.3. Each level in the hierarchy takes a set of random inputs (left) and results in a probabilistic prediction of system performance (right). The random inputs can include all known sources of uncertainties, but we focus on materials' properties and boundary conditions. Other uncertainties, e.g., geometric tolerances *etc.*, can easily be included in the method. Each successive level in the hierarchy has two additional inputs: the prediction from the preceding model and model-specific parameters. The prediction from the preceding level is used to focus the higher-fidelity model on specific “hotspots,” and outcomes of the performance predictions from each level can be synthesized by some multifidelity modeling technique, *c.f.*, [21–23]. Model-specific inputs at each level may include probabilistic descriptions that are likely related to the improved physics model and can be stochastic. The hierarchy can continue to burrow down in length scale as long as there is sufficient value in adding more layers and methods exist to couple the scales. The intent is to start with relatively low-cost computational tools and gradually increase the fidelity by improving the physical models, presumably at greater cost. Thus, Level I sacrifices accuracy, emphasizing speed and volume, while the finest length scale considered, Level XX, is computationally heavy yet physically realistic and accurate.

To illustrate the application of the hierarchy for solid mechanics problems, consider Fig. 15.4, which illustrates an arbitrary solid defined on spatial domain $\mathcal{D} \subset \mathbb{R}^3$ subjected to some applied load $q(t)$. It is of interest to determine, for example, the load q_f or time t_f at which the solid fails. In reality, the material makeup of the solid has random defects, spatial inhomogeneities, and other variabilities that lead to general

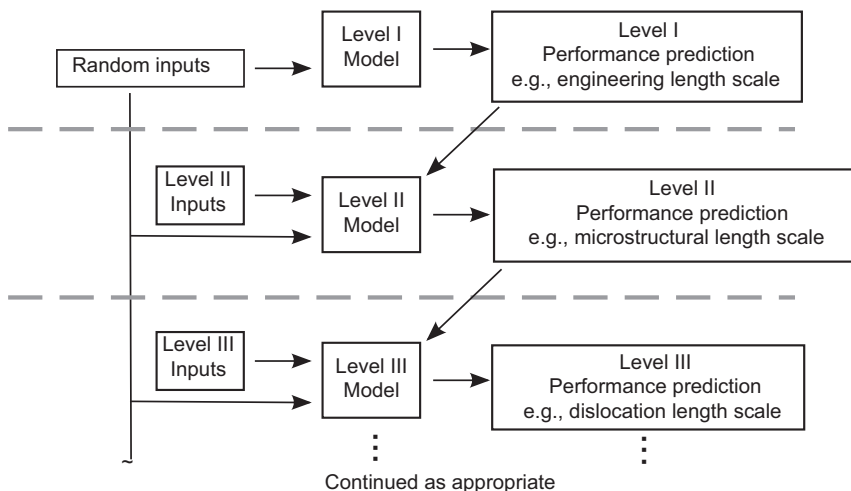


Figure 15.3 Flowchart of the hierarchical reliability approach.

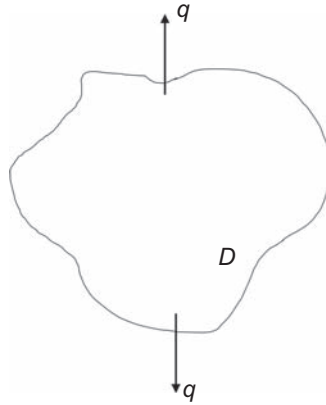


Figure 15.4 Arbitrary solid subjected to applied load.

uncertainty in the material behavior. Because of this, the load at which failure occurs is uncertain and treated as a random variable, denoted by Q . Our objective is to determine the probability law of Q . There are many choices of models to account for the materials' defects, but in this work we consider models at two distinct length scales: the engineering length scale, S , which assumes spatial homogeneity, and the fine-scale M , which includes refined geometry and details of the materials' microstructure.

Ideally, we would use the fine-scale M model everywhere in $\mathcal{D}$, and perform direct MCS by drawing many random samples of M and computing the corresponding samples of Q , the load at failure. This approach is not feasible for two reasons. First, the computational cost associated with using the fine-scale material model is so great that its use must be limited to a small spatial subset of the domain $\mathcal{D}_M \subset \mathcal{D}$ containing the fine-scale model M . Second, performing this type of calculation thousands of times as needed for traditional Monte Carlo is also not feasible. The first reason can be addressed by multiscale calculations while utilizing the fine-scale material model at a *carefully chosen and finite* number of spatial subdomains, perhaps one location at a time. The use of SROMs has been shown previously to be one possible solution for the second reason. The algorithm looks like this:

- 1 Assemble a low-fidelity representation for the engineering-scale model S . Construct an SROM for the random parameters governing the uncertainty in S and compute a low-fidelity estimate of the probability law of failure $\Pr_L(Q \leq a)$. Also, observe and record the spatial location of failure to be used for an idea of where the hotspots are located and how likely failure is to occur at each location. We will prioritize these hotspots based on this estimate of their marginal probabilities.
- 2 Partition the domain $\mathcal{D}$ into n non-overlapping regions $\mathcal{D}_1, \dots, \mathcal{D}_n$ as illustrated by Fig. 15.5.
- 3 Assemble a high-fidelity model by inserting the fine-scale model M into region $\mathcal{D}_k$ concurrently coupled with the engineering-scale material model S everywhere else, that is, in $\mathcal{D}, \mathcal{D}_k$. We represent this modeling scenario with notation $(\mathcal{D}, \mathcal{D}_k = S, \mathcal{D}_k = M)$.
- 4 Construct an SROM for the random parameters associated with $(\mathcal{D}, \mathcal{D}_k = S, \mathcal{D}_k = M)$ and compute the corresponding probability law of Q , the load at failure. Let F_k denote the event

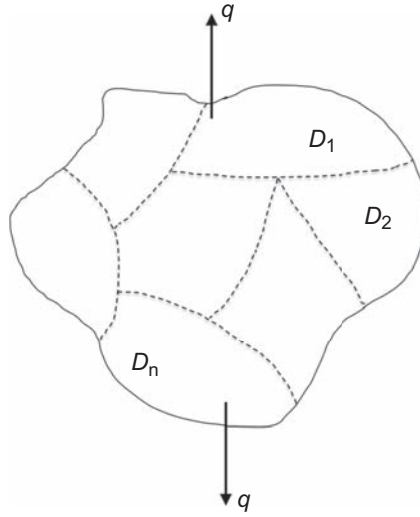


Figure 15.5 Spatial partition of solid into n regions.

that failure occurs in region $\mathcal{D}_k$, then in this step we have computed $\Pr_H(Q \leq a|F_k)$, the probability of failure conditioned on the event occurring in region $\mathcal{D}_k$.

- 5 Repeat steps 3 and 4 for a selection of the n regions illustrated by Fig. 15.5 and chosen based on the low-fidelity estimates of marginal probability and the computational budget.

With F_k denoting the event that failure occurs in region $\mathcal{D}_k$, the high-fidelity probability law of Q can then be quantified by the theorem of total probability, i.e.,

$$\Pr_H(Q \leq a) = \sum_{k=1}^n \Pr_H(Q \leq a|F_k) \Pr(F_k) \quad (15.1)$$

where the marginal probabilities $\Pr(F_k)$, $k = 1, \dots, n$, are estimated in step 1 above. Note further that low-fidelity estimates of the conditional probability $\Pr_L(Q \leq a|F_k)$ can be obtained from step 2. Our method relies on two underlying assumptions. First, that it is intractable to compute $\Pr_H(Q \leq a|F_k)$ for all n -subregions. Hence, in practice a threshold $\Pr(F_k)$ is set, based on the required confidence in the solution or criticality to the component. In the case that the marginal probability is below the threshold for a subregion, the low-fidelity estimate for conditional probability could be used in Eq. (15.1), thus saving the considerable computational effort of coupling the microstructure in that region. Second, the low-fidelity model is sufficiently robust to capture the predominant failure mechanisms that occur, even if they are highly localized events. Certainly, our methodology will not account for the lack of essential physics in the low-fidelity model, and caution to build an appropriate relationship between low- and high-fidelity modeling scheme should be applied. Ideally, validation of the second assumption by direct numerical simulation with fine-scale

calculations throughout the domain would always be conducted. However, our first assumption precludes this inevitability and will for the foreseeable future.

Here, for crack nucleation in polycrystalline, rolled AA 6061-T6, we use an anisotropic Hill plasticity constitutive model [24] with damage [25] to relate stress with strain for the material's behavior at the engineering-scale S . Our model for the fine-scale M explicitly includes a grain and second-phase geometry, with a crystal plasticity constitutive formulation [26] governing the deformation. Both S and M are assumed to contain material uncertainties that are propagated with SROMs. The higher-fidelity model concurrently couples S with M through a domain decomposition method that uses MPC to connect the length scales. For the threaded-fastener demonstration problem, our engineering- and fine-scale constitutive models have identical J2 isotropic yield surfaces with hardening minus recovery evolution. The engineering-scale model S uses a reduced-order representation for the fasteners, considering them to be cylindrical plugs of material, embedded with tied contact, and calibrated to experimental tension tests [27]. The fine-scale model M systematically improves the geometric representation by replacing the plug with a geometrically accurate model, including helical threads [28,29].

15.3 Stochastic reduced–order models

SROMs were introduced by Grigoriu [30] and have been subsequently used to solve a range of stochastic problems including random vibrations [31,32], conductivity [33], corrosion [34], nonlinear deformation [19], and constructing Bayesian credible intervals [35], and their efficiency has been studied in comparison to stochastic collocation and stochastic Galerkin [36] methods. For completeness, we here attempt to outline the salient features requisite for our use, and we refer to any of the aforementioned for the underlying mathematical theory and proofs.

15.3.1 Construction of a stochastic reduced–order model

Let Θ be a random variable describing some parameter in our multiscale modeling hierarchy with known probability, or available data to construct an estimate of its probability law. Let $\tilde{\Theta}$ be a discrete random variable with samples $\{\tilde{\theta}_1, \dots, \tilde{\theta}_m\}$, whose samples we will carefully choose based on the probability law of Θ . We will see that m is a user-prescribed variable that controls the accuracy of the SROM and is chosen with regard for the computational budget. The random variable $\tilde{\Theta}$ corresponds to the same physical quantity in our model as Θ . Denote by Γ the range of Θ , so that the samples $\{\tilde{\theta}_k\}$ of $\tilde{\Theta}$ are in Γ . Let $\{\Gamma_k\}$, $k = 1, \dots, m$, be a Voronoi partition of Γ with centers at the samples $\{\tilde{\theta}_k\}$ of $\tilde{\Theta}$. These partitions are situated so that a point $\theta \in \Gamma$ belongs to Γ_k if its distance to $\tilde{\theta}_k$ is shorter than to any other samples $\tilde{\theta}_l$ of $\tilde{\Theta}$, that is, $\theta - \tilde{\theta}_k < \|\theta - \tilde{\theta}_l\|$, $l \neq k$. The probability of the samples $\{\tilde{\theta}_k\}$ are $p_k = \Pr(\Theta \in \Gamma_k) \geq 0$, $k = 1, \dots, m$, and $\sum_{k=1}^m p_k = 1$. The samples $\{\tilde{\theta}_k\}$

and the corresponding partition $\{\Gamma_k\}$ of Γ define completely the probability law of $\tilde{\Theta}$. For example, the moments of any order $b \in \mathbb{Z} \geq 1$ and the distribution of $\tilde{\Theta}$ are

$$\tilde{\mu}(b) = \mathbb{E}[\tilde{\Theta}^b] = \sum_{k=1}^m p_k (\tilde{\theta}_k)^b, \text{ and} \quad (15.2a)$$

$$\tilde{F}(x) = \Pr(\tilde{\Theta} \leq x) = \sum_{k=1}^m p_k 1(\tilde{\theta}_k \leq x) \quad (15.2b)$$

where $1(\diamond)$ denotes the indicator function that is equal to 1 if the argument is true and 0 otherwise.

The SROM is defined by the collection $\{\tilde{\theta}_k, p_k\}$, $k = 1, \dots, m$, that minimizes the discrepancy between properties of $\tilde{\Theta}$ and Θ . Hence, the choices for the $\tilde{\theta}_k$ are selected to minimize an objective function of the form

$$\min_{\tilde{\theta}_k} e = \sum_{i=1}^2 w_i e_i, \quad (15.3a)$$

$$e_1 = \max_{1 \leq b \leq \bar{b}} |\tilde{\mu}(b) - \mu(b)|, \quad (15.3b)$$

$$e_2 = \max_x |\tilde{F}(x) - F(x)|, \quad (15.3c)$$

where appropriate constraints are applied for p_k , $\mu(b) = \mathbb{E}[\Theta^b]$ and $F(x) = \Pr(\Theta \leq x)$ denote the moments and distribution of Θ , $\bar{b} \geq 1$ is an integer representing the user-specified largest moment of interest, and $w_i > 0$ are weighting factors. Weight factors are chosen to emphasize statistics of interest, e.g., the coefficient w_2 can be set to zero if only moments are of interest. The random vector $\tilde{\Theta}$ that minimizes e defined by Eq. (15.3a,b,c) is said to be an SROM for Θ . When the probability law for Θ is not known, estimates $\hat{\mu}(b)$ for $\mu(b)$ and $\hat{F}(x)$ for $F(x)$ are used and computed from n available data as

$$\hat{\mu}(b) = \sum_{k=1}^{n_s} (1/n_s) (\theta_k)^b, \quad (15.4a)$$

$$\hat{F}(x) = \sum_{k=1}^{n_s} (1/n_s) 1(\theta_k \leq x), \quad (15.4b)$$

where $\{\theta_k\}$ denote the available samples of Θ , $k = 1, \dots, n_s$.

Example 3.1. Suppose we have data to construct a probability model for Θ , the yield stress of NAS 1352 A286 #02 threaded fasteners. The data suggest a Beta distribution with shape parameters equal to 0.48 and 1.32, location parameter equal to 747 MPa, and a scale parameter equal to 84.8. Fig. 15.6 shows the cumulative distribution of Θ and two SROMs $\tilde{\Theta}$ with $m = 10$ and $m = 40$. For these SROMs, the objective function of Eq. (15.3a,b,c) evaluated to 0.3738 when $m = 10$, and 0.1199 when $m = 40$ for $w_1 = 1$, $w_2 = 3$, and $\bar{b} = 6$. The weights are chosen by experience and to appropriately emphasize the cdf. ♦

When the problem of interest is described with multiple random inputs, the inputs can be collected into a random vector whose coordinates describe the inputs and whose correlation matrix describes their relationship. For random vectors, the developments follow the same line of reasoning, with an additional term in the objective function to account for marginal moments, marginal distributions, and correlation between coordinates of the vector. Let Θ be a d -dimensional random vector with known probability. Let $\tilde{\Theta}$ be another d -dimensional random vector with samples $\{\tilde{\theta}_1, \dots, \tilde{\theta}_m\}$. Now, it is the components $\tilde{\theta}_s$ of $\tilde{\Theta}$ that correspond to the same physical quantities as the components Θ_s of Θ . Partitioning of the range Γ of Θ is analogous, with application of an appropriate measure of length. The marginal moments of any order $b \geq 1$, the marginal distributions, and the correlations of $\tilde{\Theta}$ are

$$\tilde{\mu}_s(b) = E[\tilde{\Theta}_s^b] = \sum_{k=1}^m p_k (\tilde{\theta}_{k,s})^b, \quad (15.5a)$$

$$\tilde{F}_s(x) = \Pr(\tilde{\Theta}_s \leq x) = \sum_{k=1}^m p_k 1(\tilde{\theta}_{k,s} \leq x), \text{ and} \quad (15.5b)$$

$$\tilde{c}_{st} = E[\tilde{\Theta}_s \tilde{\Theta}_t] = \sum_{k=1}^m p_k \tilde{\theta}_{k,s} \tilde{\theta}_{k,t}, \quad (15.5c)$$

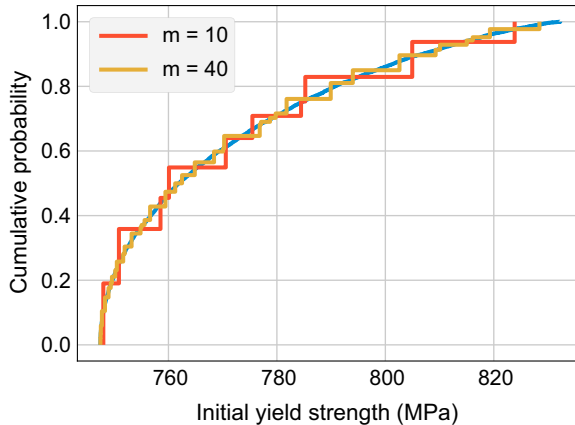


Figure 15.6 Cumulative probability of Θ and $\tilde{\Theta}$ with $m = 10$ and $m = 40$.

where $\tilde{\Theta}_s$ and $\tilde{\theta}_{k,s}$ denote coordinates of $\tilde{\Theta}$ and $\tilde{\theta}_k$, $1(\cdot)$ is as previously defined, and $s, t \in \{1, \dots, d\}$. To accommodate the additional coordinates, the objective function is modified to be

$$\min_{\tilde{\theta}_k} e = \sum_{i=1}^3 w_i e_i, \quad (15.6a)$$

$$e_1 = \max_{1 \leq b \leq \bar{b}} \max_{1 \leq s \leq d} |\tilde{\mu}_s(b) - \mu_s(b)|, \quad (15.6b)$$

$$e_2 = \max_x \max_{1 \leq s \leq d} |\tilde{F}_s(x) - F_s(x)|, \quad (15.6c)$$

$$e_3 = \max_{s,t} |\tilde{c}_{st} - c_{st}|, \quad (15.6d)$$

where $\mu_s(b) = E[\Theta_s^b]$, $F_s(x) = \Pr(\Theta_s \leq x)$, $c_{st} = E[\Theta_s \Theta_t]$, Θ_s denotes the s -component of Θ , $\bar{b} \geq 1$ is an integer representing the largest marginal moment of interest, and w_i are weighting factors. Weight factors are chosen to emphasize statistics of interest, e.g., the coefficients w_2 and w_3 can be set to zero if only moments are of interest. The random vector $\tilde{\Theta}$ that minimizes e defined by Eq. (15.6a,b,c,d) is said to be an SROM for Θ . Again, estimators for the marginal moments, marginal distributions, and correlations can be used in lieu of known marginal probability laws.

Example 3.2. Suppose we have data to construct a probability model for a two-dimensional random vector Θ , where Θ_1 corresponds to the initial yield stress and Θ_2 corresponds to the hardening modulus of NAS 1352 A286 #02 threaded fasteners. The data suggest Θ_1 is a Beta distribution with shape parameters equal to 0.48 and 1.32, location parameter equal to 747 MPa, and a scale parameter equal to 84.8. Θ_2 is uniformly distributed between 4460 and 9690 MPa, and their Pearson correlation coefficient is -0.2 . Fig. 15.7 shows the Voronoi partition of the random vector Θ generated by SROM $\tilde{\Theta}$ with $m = 20$ with the coordinates scaled and shifted to have zero mean and unit variance. The objective function of Eq. (15.6a,b,c,d) evaluated to 0.7866 with $w_1 = w_3 = 1$, $w_2 = 3$, and $\bar{b} = 6$. The “x” marks represent the Voronoi cell seeds $\tilde{\theta}_k$, the black dots represent the Voronoi cell’s center of mass, and the fine dots represent 10,000 samples of Θ colored by the Voronoi cell to which they belong. Note that there are several instances where the cell seeds are far from the cell’s center of mass, which has implications for the surrogate model we will develop what follows. ♦

When the problem of interest can be described with a random variable or a random vector that varies spatially (or temporally), our developments require treatment for a random field. Hence, next we consider a vector-valued random field, e.g., crystallographic orientation represented by three Euler angles. Let $\Theta(\mathbf{x})$ be a d' -dimensional, vector-valued random field with $\Theta(\mathbf{x}) \in \mathbb{R}^{d'}$ and $\mathbf{x} \in \mathbb{R}^D$ is the spatial position vector (or

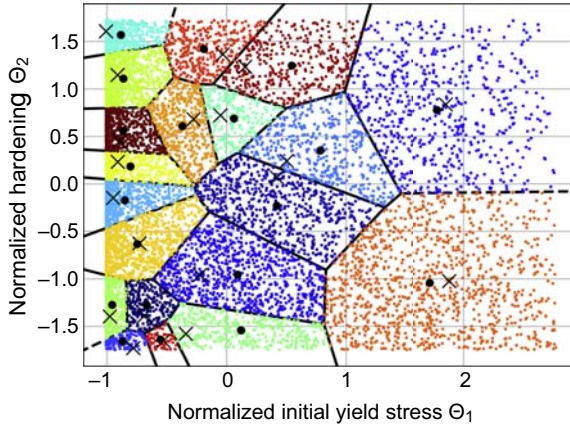


Figure 15.7 Voronoi partition of Θ generated by $\tilde{\Theta}$ with $m = 20$.

if $D = 1$ can be considered time). Under some assumptions, we can use a translation model [[37] Section 5.3.3] to represent $\Theta(\mathbf{x})$

$$\Theta(\mathbf{x}) = \mu + \mathbf{a}\mathbf{Y}(\mathbf{x}) \quad (15.7)$$

where $\mathbf{Y}(\mathbf{x})$ is a vector-valued translation random field with zero mean, unit variance, and coordinates,

$$Y_k(\mathbf{x}) = F_k^{-1} \circ \Phi(G_k(\mathbf{x})), \quad k = 1, \dots, d'. \quad (15.8)$$

Each of F_k is a cumulative distribution function (cdf), and $\Phi(\cdot)$ denotes the cdf of the standard Gaussian random variable $N(0, 1)$. The $G_k(\mathbf{x})$ are homogeneous Gaussian fields that we will approximate following [[37] Section 5.3.1.2]

$$G_k^{(r)} = \sum_{j=1}^r \left(A_j \sin(\mathbf{v}_j^T \cdot \mathbf{x}) + B_j \cos(\mathbf{v}_j^T \cdot \mathbf{x}) \right), \quad (15.9)$$

where $\mathbf{v}_j \in \mathbb{R}^D$ are constants discretizing the range of the field's spectral density, which is related to its second-moment properties, A_j and B_j are correlated Gaussian random variables with zero mean and unit variance, and $r \in \mathbb{Z}$ sets the order of the approximation.

There are two ways to proceed with construction of an SROM $\tilde{\Theta}(\mathbf{x})$ for $\Theta(\mathbf{x})$:

1. Let $\{\mathbf{x}_1, \dots, \mathbf{x}_{n_s}\}$ discretize the spatial domain $\mathcal{S}$ or $\mathcal{S}_k$, generate n_t samples of $\Theta(\mathbf{x})$, and choose an SROM with $m < n_t$ samples using Eq. (15.6a,b,c,d). In this case, we are forming a $d = n_s \cdot d'$ -dimensional random vector and using the previously demonstrated procedure for an SROM.
2. Alternatively, we could generate n_a samples of a $2r$ -dimensional random vector $\{A_1, B_1, A_2, B_2, \dots, A_r, B_r\}^T$ and construct the SROM for it.

For the work in this chapter, the first procedure is attractive because we use this model to represent the crystallographic orientation of a polycrystal, which presents an obvious discretization for $\mathcal{D}_k$. For this case, the stochastic dimension of $\Theta(\mathbf{x})$ is $d' = 3$ and the spatial domain is discretized by the number of grains in the polycrystal, $n_x = \text{number of grains}$. The performance demands of the latter procedure are dictated by the order r of the approximation of G_k , which could be quite large.

15.3.2 *SROM-based surrogate model and Monte Carlo simulation*

In this section, we outline the construction of an SROM-based surrogate model that provides a piecewise constant or piecewise linear response surface to map samples of Θ to a quantity of interest [17,19]. The surrogate method can be viewed as smart MCS. In contrast to traditional Monte Carlo, which propagates uncertainty by a large number of function evaluations with equally likely input samples, the proposed method utilizes a small number of carefully selected samples to construct a surrogate model. Evaluating the surrogate is many times less expensive than the original function, e.g., complex FE calculations, and is subsequently evaluated with a large number of equally likely input samples. Further, the method can be wrapped around any existing analysis code with no intrusive developments required for implementation.

Engineering models frequently result in systems of differential equations that can include random inputs Θ , making them stochastic equations. These stochastic equations define mappings from Θ to solutions $\mathbf{U}$ and quantities of interest Q , i.e., $\Theta \rightarrow \mathbf{U}(\Theta) \rightarrow Q$, so that $Q = \Pi(\Theta)$ and Π is evaluated by the analysis code. The surrogate is based on the SROM $\tilde{\Theta}$ for Θ and is constructed on either $\mathbf{U}$ or Q , so we use the notation $\tilde{\mathbf{U}}$ or $\tilde{Q}$. Our objective is to compute the distribution and/or statistics of Q . Given $\tilde{\Theta}$, two surrogate models are developed for the quantity of interest Q . They approximate the response surface of $\Pi(\Theta)$ with support equal to the range Γ of Θ by piecewise constant and piecewise linear functions over the cells $\{\Gamma_k\}$ of the Voronoi tessellation in Γ . The models are denoted by $\tilde{\Pi}(\Theta)$ and $\tilde{\Pi}_L(\Theta)$, respectively, and have the expressions

$$\tilde{\Pi}(\Theta) = \sum_{k=1}^m 1(\Theta \in \Gamma_k) \tilde{\pi}_k \quad \text{and} \quad (15.10a)$$

$$\tilde{\Pi}_L(\Theta) = \sum_{k=1}^m 1(\Theta \in \Gamma_k) [\tilde{\pi}_k + \nabla \tilde{\pi}_k \cdot (\Theta - \tilde{\theta}_k)], \quad (15.10b)$$

where $\tilde{\pi}_k = \Pi(\tilde{\theta}_k)$ and $\nabla \tilde{\pi}_k = (\partial \Pi(\Theta)/\partial \Theta_1, \dots, \partial \Pi(\Theta)/\partial \Theta_d)^T|_{(\Theta=\tilde{\theta}_k)}$ are the gradients of $\Pi(\Theta)$ at $\Theta = \tilde{\theta}_k$, $k = 1, \dots, m$. Alternatively, one can build the expansion about the Voronoi cell center of mass [19]. Usually, the gradients are approximated by a finite difference. Hence, once an SROM has been constructed, the

calculation of the surrogate requires $m(d+1)$ deterministic runs of the analysis code. Subsequently, statistics of $\tilde{\Pi}(\Theta)$ are known by the partitioning $\{\Gamma_k\}$ and the statistics of $\tilde{\Pi}_L(\Theta)$ can be obtained efficiently through MCS by rapid evaluation of Eq. (15.10b).

Example 3.3. Let Θ be a d -dimensional random vector collecting the random entries of a stochastic equation, which may include forcing functions, initial and/or boundary conditions, and coefficients. The equation defines an input–output mapping $\Pi: \Theta \rightarrow U$. Generally, this mapping is a complex, unknown function Θ which may also depend on spatial and temporal arguments. At arbitrary but fixed values of these arguments, the solution is a response surface over the range of Θ . The SROM surrogates in Eq. (15.10a,b) are piecewise constant and piecewise linear approximations of this response surface.

For illustration, suppose the quantity of interest Q coincides with the solution $U(\Theta)$ of a stochastic equation, a real-valued function of Θ and that

$$U(\Theta) = \alpha_0 + \sum_{i=1}^d \alpha_i \Theta_i + \sum_{i,j=1}^d \alpha_{ij} \Theta_i \Theta_j, \quad (15.11)$$

where $\{\alpha_i\}$, $i = 0, 1, \dots, d$, and $\{\alpha_{ij}\}$, $i, j = 1, \dots, d$, are real-valued coefficients. Denote by $\tilde{\Theta}$ an SROM of Θ with samples $\{\theta_k\}$, $k = 1, \dots, m$, and associated Voronoi cells $\{\Gamma_k\}$, $k = 1, \dots, m$. The implementation of the surrogates in Eq. (15.10a,b) requires to calculate the solution $U(\Theta)$ and its gradients at the sample of $\tilde{\Theta}$. For $d = 2$, we have

$$\tilde{u}_k = \alpha_0 + \sum_{i=1}^2 \alpha_i \tilde{\theta}_{k,i} + (1/2) \sum_{i,j=1}^2 \alpha_{ij} \tilde{\theta}_{k,i} \tilde{\theta}_{k,j} \quad (15.12a)$$

$$\nabla \tilde{u}_k = (\alpha_1 + 2\alpha_{11} \tilde{\theta}_{k,1} + (\alpha_{12} + \alpha_{21}) \tilde{\theta}_{k,2}, \alpha_2 + (\alpha_{12} + \alpha_{21}) \tilde{\theta}_{k,1} + 2\alpha_{22} \tilde{\theta}_{k,2}) \quad (15.12b)$$

where $\tilde{\theta}_{k,i}$ denotes the component $i = 1, 2$ of sample $\tilde{\theta}_k$ of the SROM $\tilde{\Theta}$ of Θ . We reiterate that the solutions $\{\tilde{u}_k\}$ and the gradients $\{\nabla \tilde{u}_k\}$ have to be obtained numerically in realistic applications.

The following plots are for $\alpha_0 = 0$, $\alpha_1 = 2$, $\alpha_2 = 3$, $\alpha_{11} = -1$, $\alpha_{12} = 0.5$, $\alpha_{21} = -0.5$, and $\alpha_{22} = -3$ and an $m = 9$ SROM with samples located at the nodes of a mesh defined by $\theta_1; \theta_2 = 0.2, 0.5$, and 0.8 . The response surface $U(\theta_1, \theta_2)$ is shown in Fig. 15.8. The left and right panels of Fig. 15.9 show histograms of U and $\tilde{U}_L$ based on 10,000 independent samples of Θ assumed to have independent $U(0, 1)$ components. The scatter plot of the samples of U and $\tilde{U}_L$ are in Fig. 15.10. The estimated means of U and $\tilde{U}_L$ are 1.1707 and 1.2096. The estimates of standard deviations of these solutions are 0.3718 and 0.3626. ♦

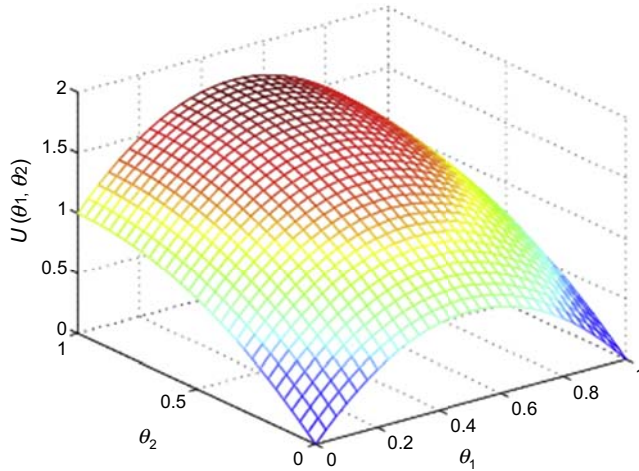


Figure 15.8 The solution $U(\theta_1, \theta_2)$ of a stochastic equation.

15.4 Concurrent coupling

Here we outline the method we used to concurrently couple our engineering-scale model with the fine-scale models. The objective of concurrently coupling the models that represent physical phenomena occurring on differing length scales is to add physical fidelity where necessary, but not everywhere. This is a necessity given the complexity and computational expense of the fine-scale models. Moreover, for the complex, highly nonlinear behavior associated with ductile failure, it is insufficient to merely track deformation on the engineering scale and push boundary conditions downward with no feedback reminding the engineering scale of the particulars of deformation on the fine scale.

We do not develop a new MNM. To connect the length scales, we employ a rather unsophisticated domain decomposition method with MPCs to achieve continuum-to-continuum coupling of our engineering-scale domain with, e.g., a polycrystalline, mesoscale domain. There are more eloquent methods in development for this scale coupling, e.g., the Schwarz alternating method [15] and the domain coupling method [38]. Eloquence aside, their value for the present application remains to be proven. One area in which they promise to improve efficiency is in model development and meshing. Although they also require decomposition, the interface between the engineering scale and the fine scale is not required to be exact, and in fact, these methods require a domain overlap. This means that with appropriate engineering-scale mesh density, the coupling could be readily achieved by simply deleting patches of engineering-scale elements in region of the hotspots.

For our use of MPCs, we require a bit more finesse wherein, upon identifying the hotspot, we carefully alter the geometry model of the engineering-scale model to make

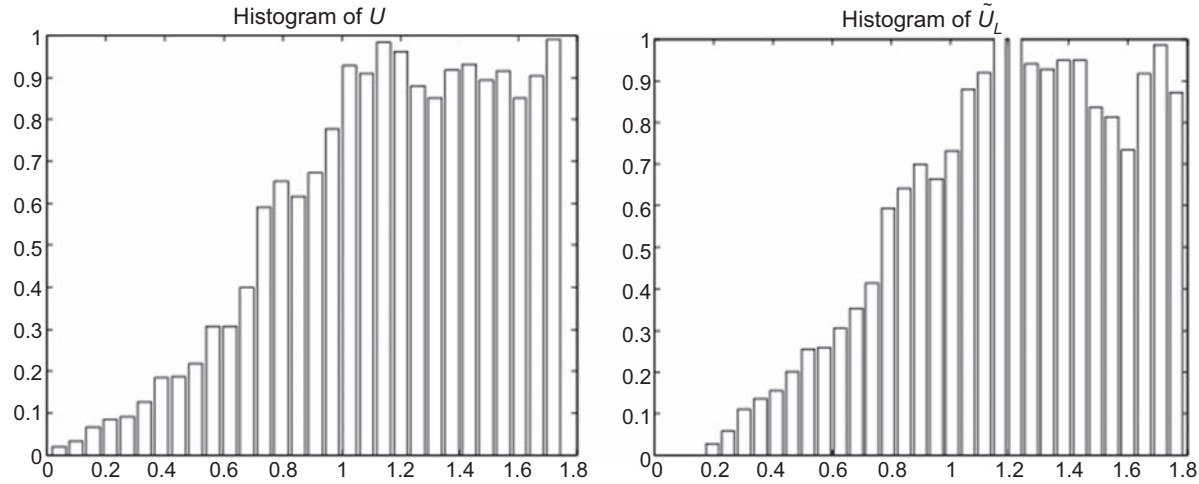


Figure 15.9 Histograms of U and $\tilde{U}_L$ (left and right panels).

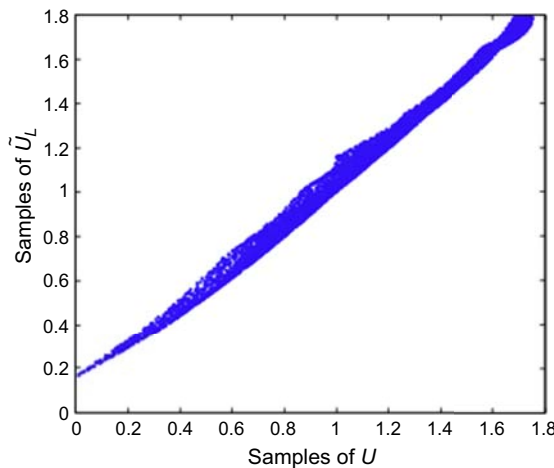


Figure 15.10 Scatter plot of $(U, \tilde{U}_L)$.

room for a small representative volume of fine-scale material.¹ Referring to notation from [Section 15.2](#), the procedure follows.

- 1 Identify the location to embed the fine-scale model, region $\mathcal{D}_k$, using the engineering-scale calculation.
- 2 Decompose the engineering-scale geometry and remesh so that its domain is $\mathcal{D}$, $\mathcal{D}_k = S$. Exercise care while meshing the engineering-scale model to consider the fine-scale mesh size so that fields are smoothly transferred.
- 3 Prepare the microstructural FE model to fit the domain in region $\mathcal{D}_k$.
- 4 Prepare node and surface sets, which are used to construct the MPC relations, on both FE models.
- 5 Make appropriate modifications to the analysis input file to add constraints coupling the displacements on the mating surfaces, and merge the engineering-scale and fine-scale mesh models if required by the analysis code.
- 6 Solve the full problem to compute displacements and other fields of interest in both domains concurrently.

[Fig. 15.11](#) illustrates this procedure. In the illustration, the engineering-scale model was constructed so that a set of elements exactly align with the mesoscale model. This facilitated meshing because elements can be easily removed from the engineering-scale model to embed the fine-scale model with no overlap (and no gap). The engineering-scale meshing is evident in the figure and the fine-scale mesh has considerably smaller edge length.

¹ The term representative volume element has a careful and rigorous definition, which we do not intend to imply in this case. Here, we mean simply a small volume of material that is constructed to emulate the fine scale of the physical specimen in some way, and the implications of the choice of size for this subvolume have not yet been fully investigated.

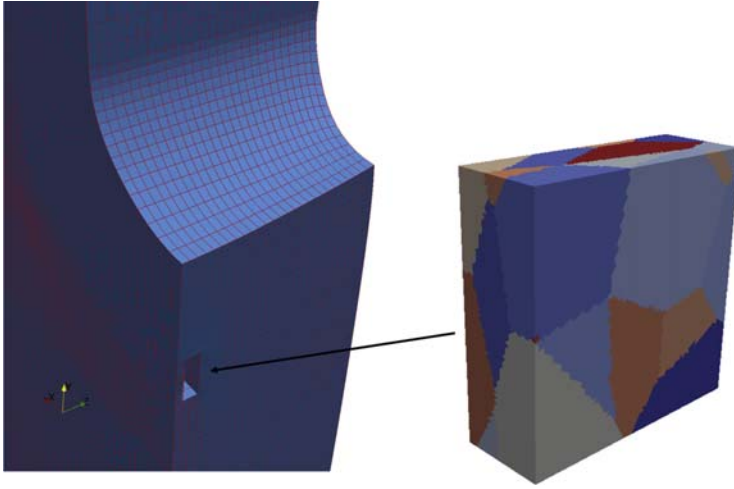


Figure 15.11 Engineering-scale model is decomposed to contain region $\mathcal{S}$, $\mathcal{S}_k = S$ (left) so that the microstructural model (right) has a tight (numerical precision) fit.

15.5 Applications examples

We present three application examples to demonstrate the proposed hierarchical method and reduced-order modeling techniques presented. The first example illustrates the entirety of the hierarchical method and we compute the probability of failure of a jointed housing assembly. In this case, both the engineering- and fine-scale constitutive models share identical J2 isotropic yield surfaces with hardening minus recovery evolution, which makes the hierarchy simpler and allows comparison to truth calculations. The primary difference between the engineering-scale model and the fine-scale model is in their geometric representation of the fasteners.

The second example illustrates the development and use of an SROM for a vector-valued random field. In this example, we consider electron backscatter diffraction (EBSD) measurements of crystal orientation for AA 6061-T6 to calibrate the translation model in Eq. (15.7). Following, we build an SROM for the random field and use it for forward propagation of the uncertainty introduced by the crystallography on the apparent elastic modulus of a small plate. While contrived, the example provides a straightforward demonstration of the efficiency and accuracy of the SROM approach for polycrystal simulation and has applications in miniature devices, electronics packaging, and microelectromechanical systems design.

The final example considers an engineering component constructed from rolled AA 6061-T6 and seeks to make probabilistic statements about crack nucleation. As such, we concurrently couple the engineering scale with a polycrystal model using MPCs. For this alloy, it is well known that void nucleation occurs due to particle fracture or pull-out after some considerable local plastic deformation [39,40]. Hence, the

fine-scale model in this example includes the crystallography, as from the previous example, and adds a brittle second-phase particle and crystal plasticity to examine the statistics of the load in the particle as a function of the global boundary conditions and local microstructure.

15.5.1 Failure of a housing assembly

15.5.1.1 Objective

This model stems from a recent and ongoing effort to understand and improve modeling of threaded fasteners and connections [27,28,41,42]. The objective here is to compute the cumulative probability of time to failure for a housing assembly using models of threaded fasteners under development from that effort, i.e., we do not herein address validation of the models but focus on UP with them. The low-fidelity model S simplifies the geometry of the threaded fasteners by idealizing them as cylindrical plugs of material. The plugs interact with the base material via a tied contact interaction, identical to the interaction used for coupling length scales, c.f., Section 15.4. After the low-fidelity model is used to propagate the assumed variability, the geometric representation of the threaded fasteners is systematically refined for a subset of “important” fasteners. In this case, importance is determined based on the low-fidelity estimates of marginal probability, following step 3 in Section 15.2. The high-fidelity model M contains threaded fasteners at 2 of the 4 screw locations.

15.5.1.2 Model definition

The left side of Fig. 15.12 shows the geometry and mesh of a component. The figure shows the model of a housing, in yellow, screwed to a base plate, in green, with four NAS 1352 #02 A286 threaded fasteners (nominal diameter 2.2 mm). On the top right side, the low-fidelity representation of the fastener geometry and mesh is shown. On the bottom right side, the high-fidelity representation of the fastener geometry and mesh is shown. In each case, there is a small cylindrical section of base plate material included in their geometry and mesh models. The mesh was constructed to conveniently connect either version of the fastener model at any threaded hole, so the base plate on the left has an enlarged cylindrical section removed. At model assembly prior to FE analysis, the component and fastener are connected via tied contact.

The component mesh was comprised of 16,000 linear, reduced-integration hexahedral elements with minimum element-edge length of 0.91 mm. Kinematic boundary conditions were used to constrain all three degrees of freedom of the outer surface of the base plate. The distal y-face of the housing was extended 5 mm in the positive y-direction. Additionally, it was randomly laterally deformed in the positive z-direction, with a small, positive or negative component in the x-direction (further details provide below), the resultant of which was 2.7 mm. The low-fidelity fastener model contained 1920 linear hexahedral elements with minimum element-edge

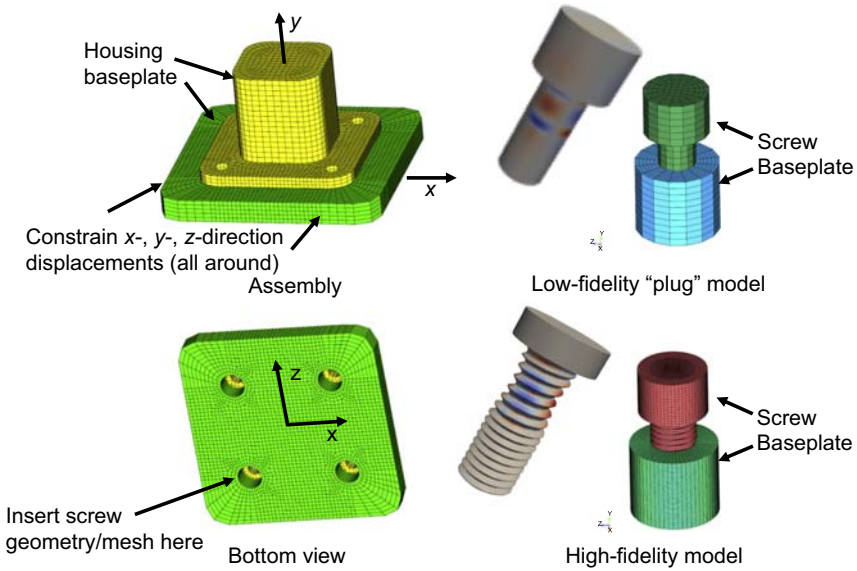


Figure 15.12 The FE model of the housing assembly (left) and the low- and high-fidelity models (right).

length of 0.56 mm. The high-fidelity fastener model contained 180,000 linear hexahedral elements with a minimum element-edge length of 0.069 mm. The threads of the high-fidelity model interacted with the base plate with a standard Coulomb friction model with coefficient equal to 0.4, based on previous investigations [28]. The effects of friction can be important, but are beyond the scope of this example.

Both models used identical J2 isotropic yield surfaces with hardening minus recovery evolution, $\sigma_e = \sigma_y + h/r(1 - \exp(-r\varepsilon_p))$, where σ_e is the evolving von Mises effective stress, σ_y is the initial yield stress, h and r are hardening and recovery parameters, and ε_p is the equivalent plastic strain. The hardening behavior was calibrated to experimental tension tests [27,41,42] and mean values of initial yield, hardening, and recovery were $\sigma_y = 770$ MPa, $h = 6196$ MPa, and $r = 11.27$, respectively. There was no pretension. The base plate and housing were assumed elastic, forcing failure to occur in the fasteners, and assigned elastic modulus 50 GPa and Poisson's ratio 0.3. The calculations for this example were completed with explicit time integration and the FE code SIERRA/SM [43]. The minimum time step required was approximately $1e-07$ s for the low-fidelity model and approximately $1e-08$ s for the high-fidelity model.

Failure of a fastener is defined by the event when any element in the fastener element block reported equivalent plastic strain = 0.45 or greater, which was chosen based on the available experimental data, and we assume the component failure follows immediately. This metric for failure introduces mesh and geometry dependence, and improvements for fastener failure modeling are a current topic of research.

15.5.1.3 Uncertainty

The left side of Fig. 15.13 shows a schematic of the component and labels the screws 1–4 for reference. There were insufficient data to construct probability models for the yield and hardening modulus directly from the available experiments, so appeals to other data were made to estimate reasonable probability distributions. This, of course, introduces an additional source of uncertainty which we herein neglect. The data suggested the initial yield strength followed a Beta distribution with shape parameters equal to 0.48 and 1.32, location parameter equal to 747 MPa, and a scale parameter equal to 84.8, and the hardening modulus was uniformly distributed between 4460 and 9690 MPa, and their Pearson correlation coefficient was -0.2 . Further, we assume there was Pearson correlation of $+0.5$ between screws 1 and 4, and 2 and 3. This is purely to illustrate how such a circumstance could be addressed with our modeling methodology, and there is no experimental evidence to support this. However, the capability could be used to calibrate this type of uncertainty with a Bayesian approach if sufficient experimental evidence existed [35]. Finally, adding a geometric parameter to the uncertainty, the applied lateral deformation was parameterized by an angle γ , shown in Fig. 15.13, that varied uniformly between $-\pi/16$ and $\pi/16$. Although there was no pretension in this example, it could be introduced and it could be among the uncertainties considered.

Hence, the uncertain parameters in this model can be collected in a nine-dimensional random vector Θ with coordinates $\{\gamma, \sigma_{y1}, h_1, \sigma_{y2}, h_2, \sigma_{y3}, h_3, \sigma_{y4}, h_4\}^T$, where σ_{yi} is the initial yield stress and h_i is the hardening modulus for screw B_i , $i = 1, 2, 3, 4$. The right side of Fig. 15.13 shows the correlation matrix $E[\Theta_i \Theta_j]$ for $i, j = 1, \dots, 9$. We use Eq. (15.6a,b,c,d) to construct an SROM with $m = 20$, and we use a translation model to obtain samples of Θ and Eq. (15.10b) for rapid MCS.

15.5.1.4 Results

Experimental evidence for validation was not available for this component, so we constructed a model with the high-fidelity representation of fastener geometry in all four

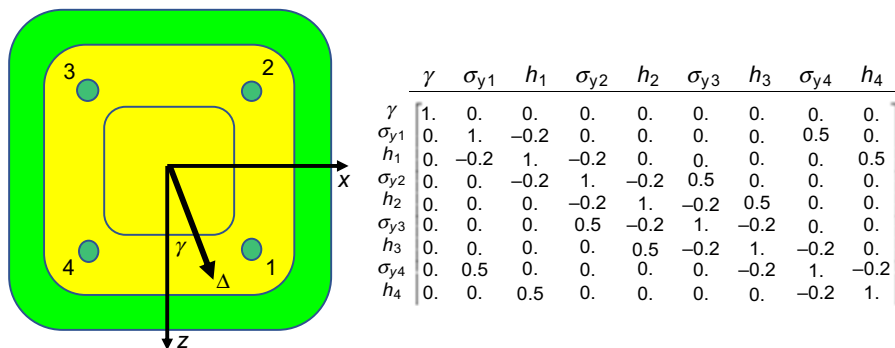


Figure 15.13 Schematic of the screw arrangement (left) and the assumed correlation matrix (right).

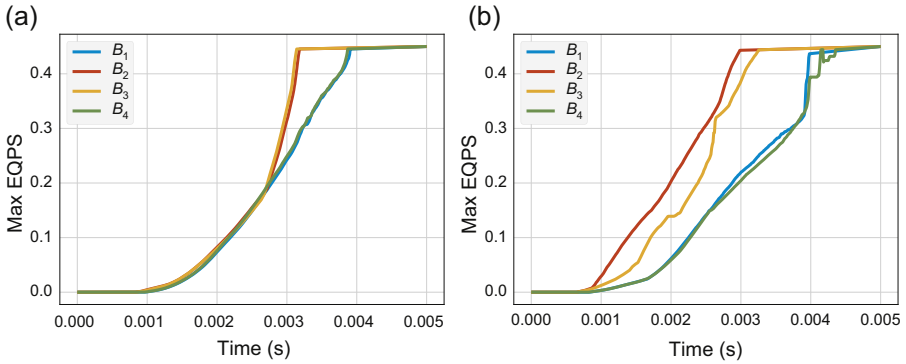


Figure 15.14 Equivalent plastic strain versus time for the average properties and $\gamma = 0$ for the low-fidelity model (a) and the truth model (b).

screw locations and refer to the model and results as “truth.” We performed deterministic calculations with mean material parameters and $\gamma = 0$ for the low-fidelity model and the truth model. Fig. 15.14 plots the maximum equivalent plastic strain versus time for each screw for the low-fidelity model (left panel) and truth (right panel). Interestingly, in the truth model, screw B_2 reaches the failure threshold of equivalent plastic strain equal to 0.45 first, which is contrary to intuition but is related to the way the threads align relative to the loading direction.² The low-fidelity model, however, predicts nearly identical failure time for screws B_2 and B_3 , with a barely discernible preference for screw B_3 .

Fig. 15.15 shows deformed geometry (left) and equivalent plastic strain versus time (right) for the first four low-fidelity Monte Carlo samples. The low-fidelity mean calculation from Fig. 15.14(a) is included in the strain plots for reference. The inset on the deformed shape tabulates the components of the lateral applied displacement and the screw governing failure is indicated with a blue circle on the left and in text in the strain plots. It seems that the stochasticity in the boundary condition dominates failure location, with positive x-component of applied displacement increasing the tensile load on screw B_3 and causing failure there, and negative x-component having the opposite effect causing failure in screw B_2 . Failure times are collected from curves like these generated with the SROM-based surrogate.

The translation model was used to generate 10,000 samples of Θ and propagated through the low-fidelity model with the surrogate. Construction of the surrogate required $m(d+1)$ or 200 low-fidelity FE calculations. Fig. 15.16 plots the conditional probabilities of failure for each of the screws, as well as the total probability of the component (heavy black line). The marginal probabilities $\Pr(B_i)$ were easily computed

² As an aside, as the research to understand and improve fastener failure modeling progresses, if this effect remains prominent, it would be possible to include screw rotation among the random variates in the model. Moreover, this effect may immediately disappear in the presence of pretension, which is not included here.

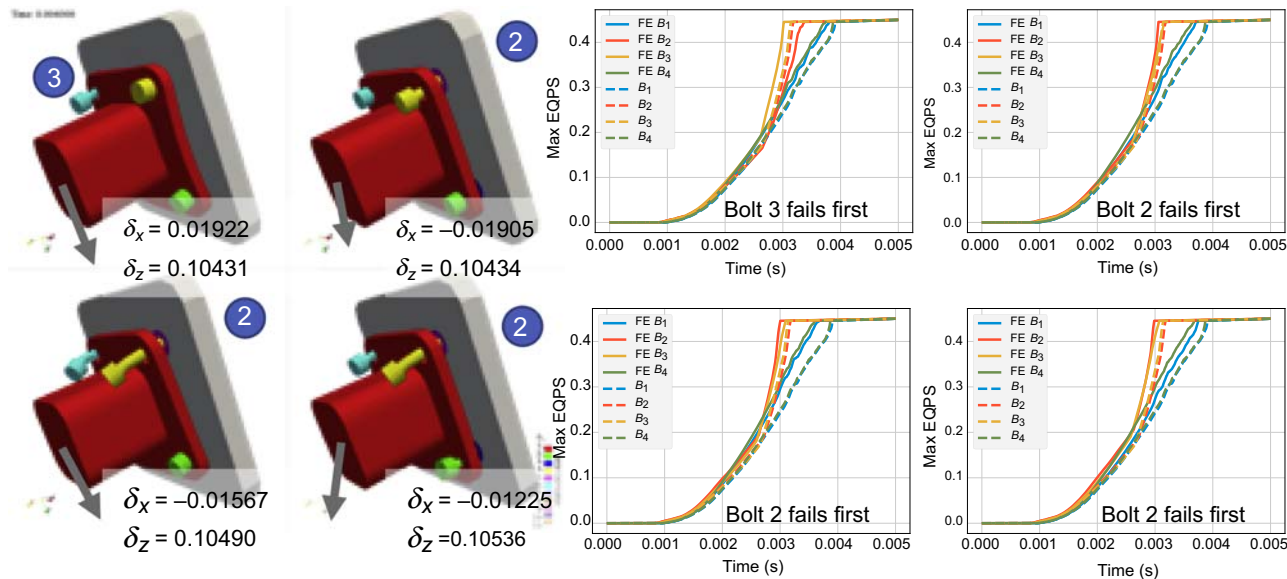


Figure 15.15 Results for the first four low-fidelity random samples. The left panel shows the deformed shape of the FE models at failure, the x- and z-component of applied displacement, the location of screw failure for each of the first four samples (clockwise starting from top left). The right panel shows time versus equivalent plastic strain plots for all four screws and each of the first four samples (clockwise starting from top left). The *dashed lines* in the plots correspond with a calculation of screw response with average properties and $\gamma = 0$.

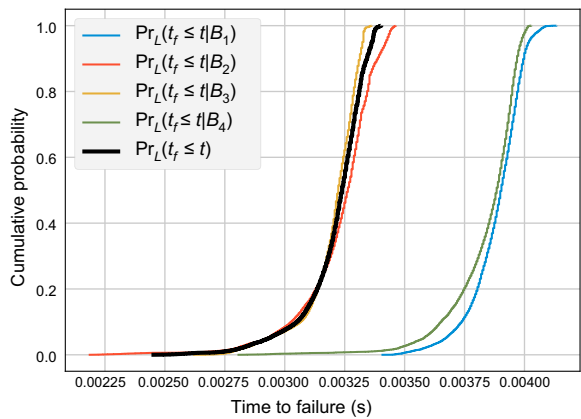


Figure 15.16 Low-fidelity predictions of conditional and total probabilities of time to failure.

as the fraction of occurrences when failure of screw B_i governed failure. The marginal probabilities are tabulated in Table 15.1 where it is apparent that screws B_1 and B_4 never failed first, screw B_2 governed failure 40% of the cases, and screw B_3 governed 60% of the time. The computational expense for this estimate was 197 CPU hours. From this evidence, and given the nearly identical time to failure for screws B_2 and B_3 from the average predictions in Fig. 15.14(a), the high-fidelity model was chosen to so that high-fidelity geometric representation of the threaded fasteners is used in locations 2 and 3 simultaneously, while the “plug” representation remains at locations 1 and 4.

Fig. 15.17 plots the conditional probabilities for screws B_2 (orange) and B_3 (yellow) and the total probability of failure (black) computed by the low-fidelity model Pr_L (dashed), the high-fidelity model Pr_H (bold), and with 200 Monte Carlo samples of the truth model Pr_T (solid). It is clear that the high-fidelity estimates are significantly improved from the low-fidelity estimates. There is some interesting behavior in the conditional truth estimates, and the lower tails of the truth do not extend as far, but it is important to emphasize that only 200 samples were used to generate the truth estimates. Table 15.2 lists the marginal probabilities associated with failure at each

Table 15.1 Low-fidelity estimate of the marginal probabilities of failure.

Screw	$\text{Pr}_L(B_i)$
1	0.
2	0.3973
3	0.6027
4	0.
CPU hours	196.7

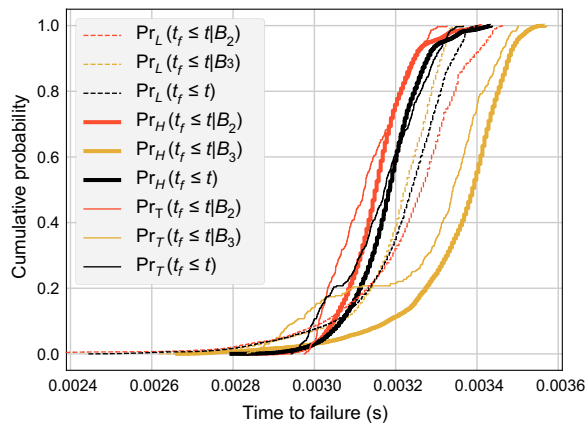


Figure 15.17 Estimates of conditional and total probabilities of time to failure.

Table 15.2 High-fidelity and truth estimates of the marginal probabilities of failure.

Screw	$\text{Pr}_H(B_i)$	$\text{Pr}_T(B_i)$
1	0.	0.
2	0.86	0.77
3	0.14	0.23
4	0.0	0.0
CPU hours	82,300.	196,036.

screw location as estimated by the high-fidelity and truth models. It also tabulates the relative compute budget, and the hierarchical approach, summing low and high-fidelity CPU time, is more than a factor of two faster than 200 truth simulations—and they provide estimates based on 10,000 samples of Θ . ♦

15.5.2 Apparent modulus of a cubic-elastic, micron-size plate in plane strain

15.5.2.1 Objective

This problem considers cubic elasticity in a small, plane strain polycrystalline plate. Constitutive data are taken from the literature for cubic aluminum. Multiscale coupling is avoided because the microstructure can tractably be modeled over the entire domain. The tractability of the problem enables us to again generate our own “truth” data by performing a large number of direct numerical calculations of the microstructural model, thereby allowing us to evaluate the accuracy and efficiency of the random-field reduced-order model (RFROM, a special case of an SROM) following the discussion in [Section 15.3.1](#).

The plate has stringent design requirements for extension displacement when loaded longitudinally, so the objective of this application example is to develop the probability law for apparent modulus of elasticity E_{app} , which can be used to quantify failure. However, the objective of presenting this application example is to establish a path forward for propagating uncertainty due to microstructural variability, namely crystallographic orientation. We leverage this presentation in our culminating example to follow.

15.5.2.2 Model definition

We considered a plate in plane strain with dimensions $240 \times 120 \times 0.5 \mu\text{m}$. The plate was comprised of a cubic-elastic pure aluminum with elastic constants taken from Ref. [44]. EBSD was performed on samples of AA 6061-T6 to establish the grain size, grain aspect ratio, and texture. The average grain size was approximately $40 \mu\text{m}$, so that there were approximately 18 grains in the specimen. Fig. 15.18 shows the assumed boundary conditions, simply supported with applied traction nominally extending the plate in the x-direction. Fig. 15.19 is a contour plot of the xx-component of stress, showing the random distribution of load in the plate from one sample of texture. The FE mesh used selectively reduced integration hexahedral elements on a uniformly spaced grid with grid spacing equal to the plate thickness. This resulted in approximately 80 brick elements per grain edge, sufficiently resolving the fields [12].

15.5.2.3 Uncertainty

For this application example, uncertainty was introduced by the randomly oriented crystals. Inverse pole figures constructed from the EBSD data are shown in the top row of Fig. 15.20. The translation model [[37] Section 5.3.3] was calibrated to the

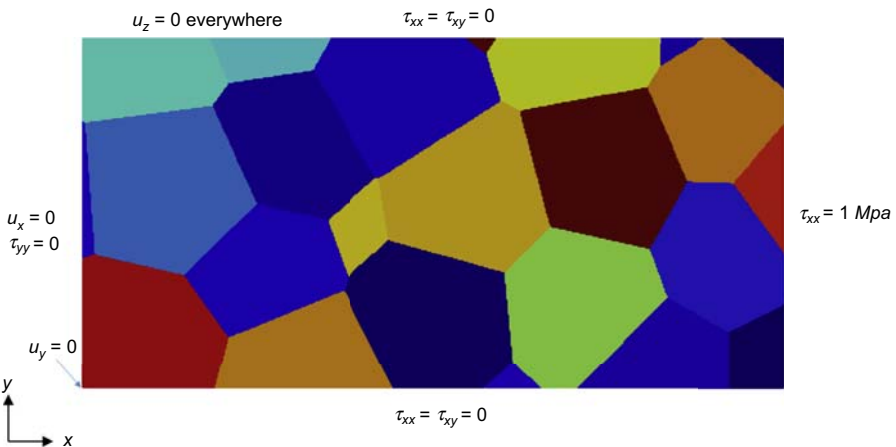


Figure 15.18 Boundary conditions for Example 3.2.

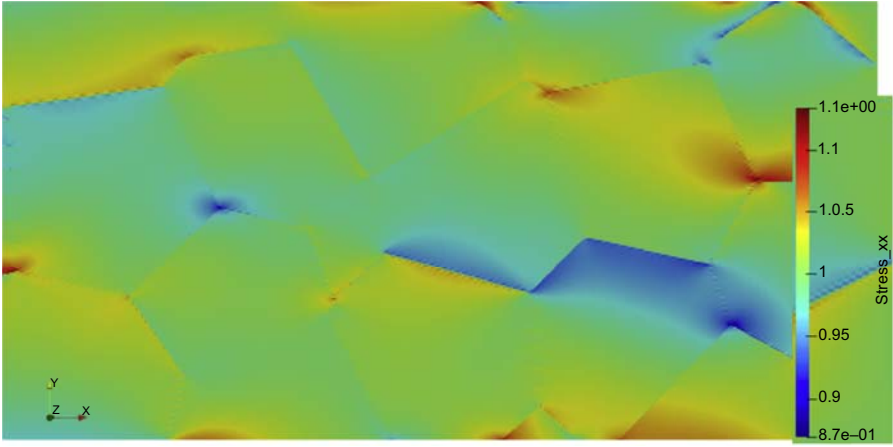


Figure 15.19 A σ_{xx} distribution for a microtextured sample in [Example 3.2](#).

EBSD data and inverse pole figures generated from sampling it are shown in the bottom row of the figure. From these figures, there is an apparent mild texture in the $\langle 100 \rangle$ direction, which is captured with the translation model.

For our numerical models, crystallographic orientation was quantified with three rotations, known as Euler angles, which can be calculated from the EBSD measurements. The Euler angles describe the orientation of the crystal lattice with respect to the lab reference frame as described by rotations from the reference in a specified pattern. There are many choices for convention, but here we followed the z-x-z convention. The first angle rotates the crystal away from the reference frame about the z-axis of the reference frame. The second angle rotates the lattice about the current x-axis. The final angle rotates the lattice about the current z-axis again.

Following [\[45\]](#) one can compute the rotation matrix for crystal A from the Euler angles using

$$g_A = \begin{bmatrix} c1c3 - s1c2s3 & s1c3 + c1c2s3 & s2s3 \\ -c1s3 - s1c2c3 & -s1s3 + c1c2c3 & s2c3 \\ s1s2 & -c1s2 & c2 \end{bmatrix} \quad (15.13)$$

where $c1$ is the cosine of the first Euler angle, $c2$ is the cosine of the second Euler angle, $c3$ is the cosine of the third Euler angle, $s1$ is the sine of the first Euler angle, $s2$ is the sine of the second Euler angle, and $s3$ is the sine of the third Euler angle. To describe the orientation of one grain with respect to another grain, one can write the rotation of grain B with respect to the rotation of grain A as

$$g_B = \Delta g_{AB} g_A \quad (15.14)$$

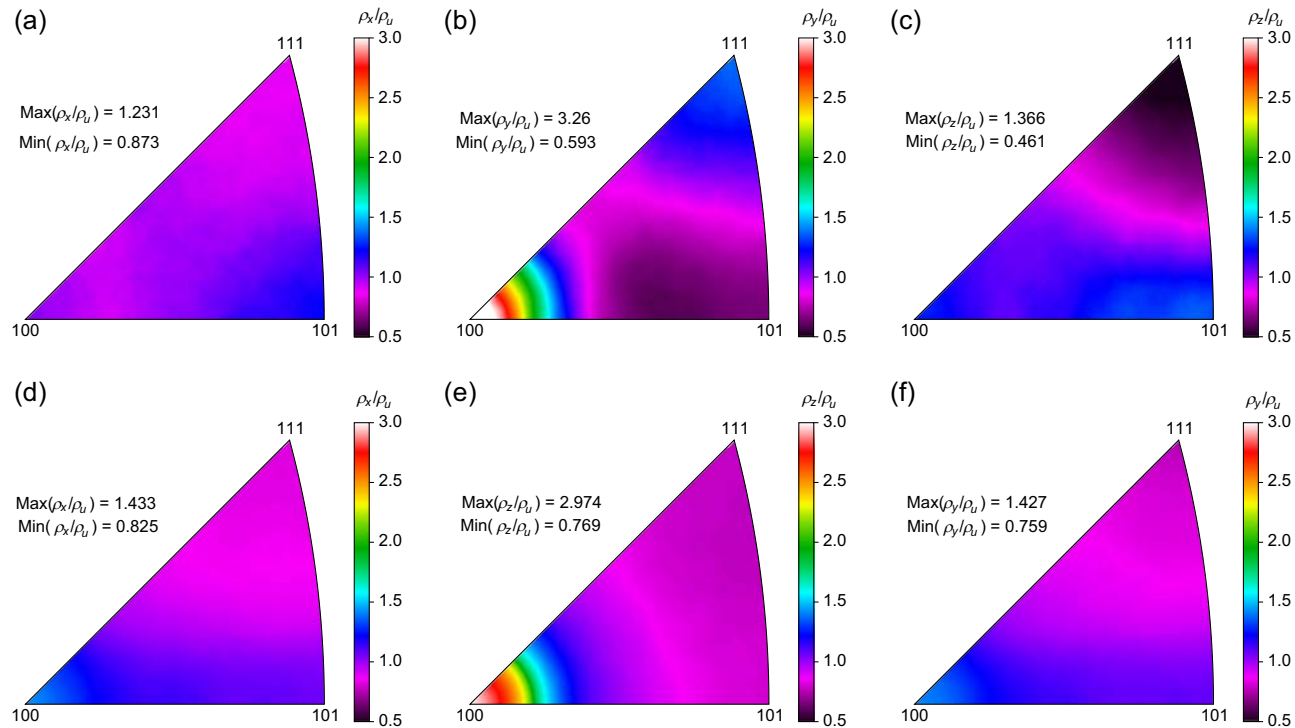


Figure 15.20 Inverse pole figures of the AA 6061-T6 microstructure generated from EBSD data (top row) and the translation model calibrated to the data (bottom row). (a) EBSD data Transverse. (b) EBSD data rolling. (c) EBSD data normal. (d) Model T. (e) Model R. (f) Model N.

so that

$$\Delta g_{AB} = g_B g_A^{-1} \quad (15.15)$$

describes the rotation from grain A to grain B. Converting this to the axis-angle convention for describing crystallographic orientation yields a measure of the grains' misorientation given as

$$\zeta = \min |\arccos((\text{tr}(\Delta g_{AB}) - 1) / 2)| \quad (15.16)$$

where $\text{tr}(\bullet)$ represents the sum of the diagonal of the matrix. Fig. 15.21 plots histograms of the misorientation angles computed from the EBSD data (top) and samples of the translation model (bottom). Apparently, the translation model also replicates the observed misorientation distribution because it accounts for spatial correlation.

15.5.2.4 Results

We generated “truth” data by FE simulation, varying crystallographic orientation using 10,000 samples from the translation model. Further, we constructed two RFROMs, one with $m = 20$ and the second with $m = 50$ and computed E_{app} with Eq. (15.10a). In this case, we do not use Eq. (15.10b) because the stochastic dimension is dictated by the number of grains in the polycrystal. Although feasible for this application, our aim is to illustrate the tool set for use with more complicated FE models, *c.f.*, following application example, where computing the gradient would quickly become intractable. Hence, we endeavor to extract as much as possible from the piecewise-constant form of the surrogate. Our procedure begs the question, how does this compare to a standard MCS with equivalent computational cost? For

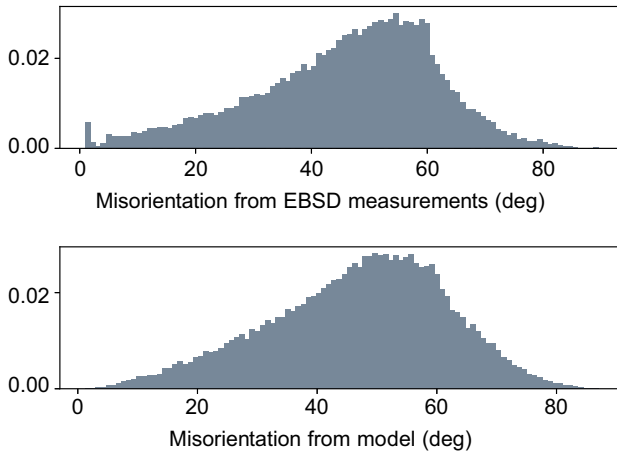


Figure 15.21 Normalized histograms of the misorientation angles computed from the EBSD data (top) and the translation data (bottom).

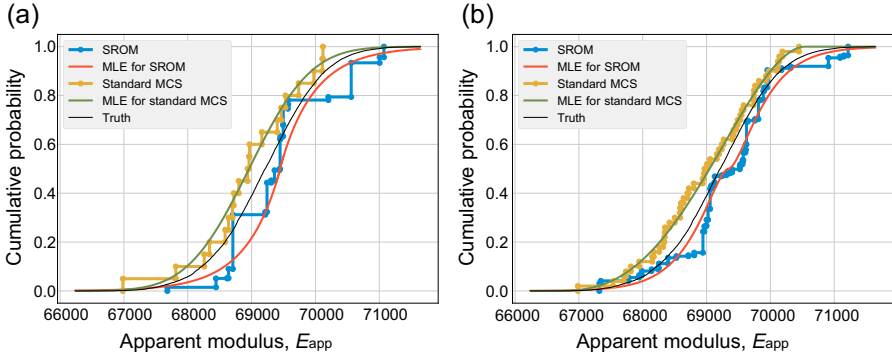


Figure 15.22 The estimated cdf of E_{app} computed by SROM, SROM-based MLE, standard MCS, and MLE, and with 10,000 MCS as “truth.” (a) $n_{\text{mcs}} = m = 20$. (b) $n_{\text{mcs}} = m = 50$.

comparison, we can randomly select $n_{\text{mcs}} = m$ samples from the truth data and construct estimates of the cdf. Fig. 15.22 shows the estimates of the probability of E_{app} computed five ways for an SROM with $m = 20$ (left) and $m = 50$ (right). First, the solid black line is the truth estimate based on 10,000 FE calculations. The dotted-blue line is the estimate computed by the surrogate. These estimates can provide statistics, but important information at the tails of the distribution is lost. The method of maximum likelihood estimation (MLE) [46] can be used to estimate parameters of probability distributions given data. Ordinarily, MLE uses a likelihood function that assumes identical and independent samples, which the SROM samples are not. However, we can use MLE with a modified likelihood function that accounts for the probabilities p_i of the SROM

$$\mathcal{L}_m = \prod_{i=1}^m \tilde{f}(E_{\text{app}} | \tilde{\theta}_i)^{p_i} \quad (15.17)$$

where $\mathcal{L}_m$ is the likelihood function for an SROM with m samples, $\tilde{f}$ is the SROM-based estimate for the probability density, and $\{(\tilde{\theta}_i, p_i)\}$ is the i th SROM sample. The estimated cdf of E_{app} computed by MLE is shown with the bold red curve in Fig. 15.22. Additionally, the dotted-yellow curve and the bold green curve are generated with $n_{\text{mcs}} = m$ randomly and independently chosen samples from the truth, representing the standard MCS approach where each sample is assumed to have equal probability, $1/n_{\text{mcs}}$. It appears the best match to the truth curve is provided from the MLE generated by the $m = 50$ SROM.

We seek to quantify the accuracy of the SROM estimates compared to the truth estimate. A common measure for comparing probability distributions to a reference is the Kolmogorov–Smirnov (K–S) two-sample test [[46] Section 10.8]. However, this approach requires the samples of both random variables to be independent and identically distributed (iid), and the SROM samples violate this requirement. Let $F(x)$ denote the empirical cdf obtained from the “truth” sample data. Let $F_{\text{MLE}}(x)$

denote the empirical cdf obtained from fitting the SROM data via MLE. Let $\tilde{F}(x)$ denote the cdf of the SROMs. The maximum difference norm is $\max |\tilde{F}(x) - F(x)|$ and the L^2 -norm of the difference between two cdfs is computed as

$$\begin{aligned} m_{MLE} &= \int_{\mathbf{R}} (F_{MLE}(x) - F(x))^2 dx \\ \tilde{m} &= \int_{\mathbf{R}} (\tilde{F}(x) - F(x))^2 dx. \end{aligned} \quad (15.18a)$$

These errors are listed in [Table 15.3](#) for the two SROMs $m = 20$ and $m = 50$, and their corresponding MLE, and ensemble averages of 1000 iterations of $n_{mcs} = 20$ and $n_{mcs} = 50$ samples of standard MCS. For the latter, we randomly selected n_{mcs} samples from the available truth data 1000 times. Included in the table in parenthesis is the maximum error observed during the 1000 iterations.³ In practice, if the computational budget allows for n_{mcs} simulations, there is no guarantee that the standard Monte Carlo approach provides the average error or, if unlucky, the maximum error. The SROM approach does not necessarily outperform a (lucky but) good choice of n_{mcs} , but appears to guard against a (unlucky but) bad choice.

The optimization problems in [Eqs. \(15.3a,b,c\)](#) and [\(15.6a,b,c,d\)](#) include an objective term for higher moments. In the construction of SROMs in this manuscript we set the user-specified parameter $\bar{b} = 6$. To further investigate the error of the SROM and standard MCS approach, we compute a difference metric comparing the moments of order up to $\bar{b} = 6$ such that the percent relative error is computed

$$P_{err} = 100 * \left| \frac{\mathbb{E}[\tilde{E}_{app}^b] - \mathbb{E}[E_{app}^b]}{\mathbb{E}[E_{app}^b]} \right|, \quad b = 1, \dots, \bar{b} \quad (15.19)$$

Table 15.3 Error in the cdfs relative to the “truth” data.

	$m = 20$	MLE ₂₀	$m = 50$	MLE ₅₀	$\overline{\text{MCS}}_{20}$ (max)	$\overline{\text{MCS}}_{50}$ (max)
L^∞	0.410	0.184	0.216	0.092	0.193 (0.43)	0.124 (0.32)
L^2	68.2	26.4	16.7	6.89	21.5 (139.4)	8.87 (83.2)

³ We choose to report the error computed directly from n_{mcs} samples rather than the MLE fit to that data. For the MLE fit, the mean was closer to the truth data, but the maximum errors were even further from truth than the values reported in the table.

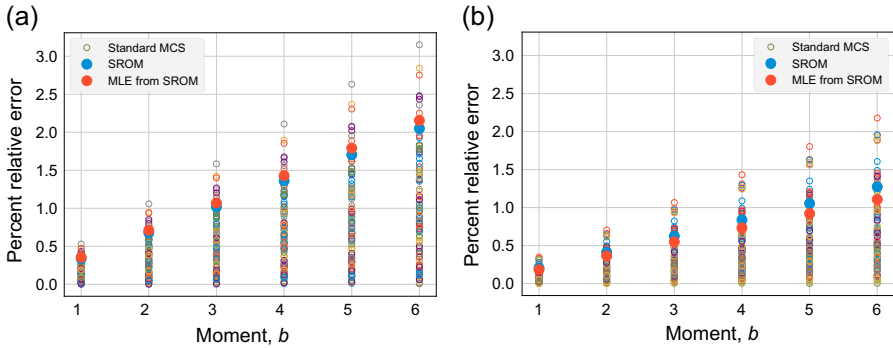


Figure 15.23 Percent error computed relative to the truth data for moments up to order 6. (a) $n_{mcs} = m = 20$. (b) $n_{mcs} = m = 50$.

where E_{app} is estimated with the truth data and $\tilde{E}_{app}$ is the SROM estimate (or n_{mcs} Monte Carlo estimate). Fig. 15.23 plots P_{err} for the $m = 20$ (left) and $m = 50$ (right) SROM, SROM-base MLE, and 100 iterations of $n_{mcs} = m$ standard MCS. Here again, the standard Monte Carlo can, and often does, outperform the SROM approaches; however, the largest errors are also represented by the standard Monte Carlo approach. ♦

15.5.3 Multiscale uncertainty propagation

15.5.3.1 Objective

In the final application example, we concurrently couple the length scales of a polycrystalline aluminum component with its microstructure, including a second-phase particle. The accurate modeling of ductile crack nucleation is a topic of ongoing research, and as with the fastener failure example, we do not focus here on the physics model at the fine scale. Nonetheless, this application example attempts to connect the fine-scale nucleating agents, a second-phase particle, embedded in a randomly oriented matrix with the boundary conditions applied on the engineering structure. For the purpose of predicting crack nucleation, we compute the load on the embedded particle as the engineering structure is subjected to monotonic and quasistatic applied deformation. We assume the particle fractures at a critical stress, and extract the applied deformation on the component corresponding with particle fracture and estimate its cdf.

15.5.3.2 Model definition

We considered an engineering component constructed of AA 6061-T6 rolled plate with several stress-concentrating features. The solution proceeded to build an FE model of the engineering structure and used the prediction to define a subdomain to embed the microstructure model. Subsequently, in a multiscale calculation, a polycrystal containing a second-phase particle was concurrently coupled to the engineering-scale FE model following Section 15.4. Fig. 15.24 shows stress contour

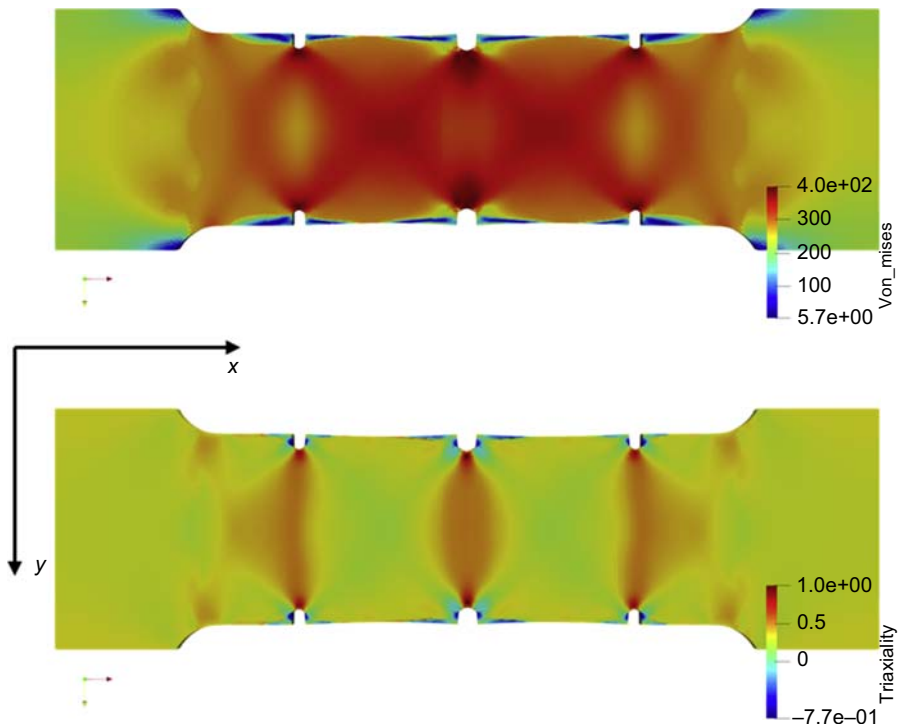


Figure 15.24 Von Mises effective stress contour plot (top) and triaxiality contour plot (bottom).

plots of von Mises stress (top) and triaxiality (bottom, defined as the ratio between the hydrostatic stress and the effective stress) on the modeled 6-notched component. The 6-notch specimens were designed to investigate stochastic failure with multiple possible crack initiation locations. The mesh included 129,428 linear, reduced-integration hexahedral. One-quarter of the plate was modeled with symmetry boundary conditions, restrained from x-direction deformation on the left edge, and applied x-displacement on the right edge.

The constitutive parameters were calibrated to a selection of smooth, gradually notched, and sharply notched tensile specimens stress–strain data. MatCal [25], a code that uses optimization algorithms to solve the inverse problem, was used to calibrate the constitutive parameters of the Hill plasticity model [47]. Fig. 15.25(a) plots the available stress–strain data characterizing the plasticity and fracture of the AA 6061-T6 plate when loaded in both rolling and transverse directions. Apparently the plate is anisotropic and, while the plastic response is fairly repeatable, there is considerable variation in the strain to failure. The yield surface is generally orthotropic, and hardening follows a hardening minus recovery form as in Section 15.5.1. The calibration routine resulted in the Hill plasticity parameters tabulated in Table 15.4. Fig. 15.25(b) plots the normalized load versus nominal engineering strain from six test samples of the component as well as the average model prediction.

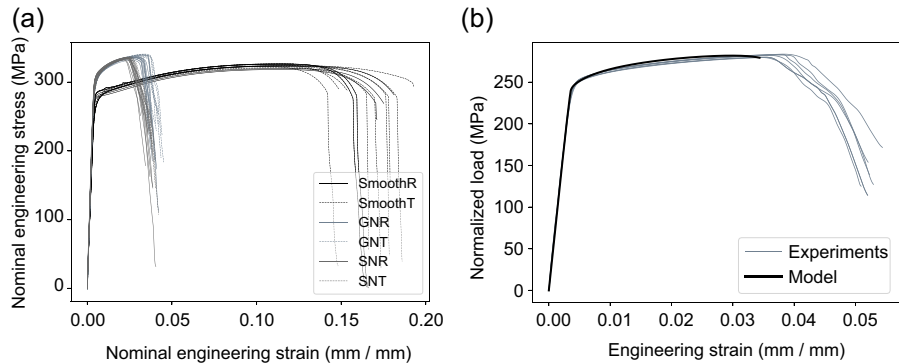


Figure 15.25 Test data for engineering stress—strain curves for smooth, gradual-notched (GN), and sharp-notched (SN) tensile specimens loaded in both rolling (R) and transverse (T) directions used for characterization (left) and the 6-notch specimen (right). (b) includes a curve generated from the FE model. (a) Characterization data. (b) 6-notch specimen.

Table 15.4 Hill plasticity parameters calibrated to the available smooth, gradual-notched and sharp-notched tension data.

E (GPa)	68.9
ν	0.33
R11	1.00e-00
R22	0.954
R33	1.5
R12 = R23 = R31	0.85
σ_y (MPa)	280
h (MPa)	1359
R	12.15

The microstructure considered here was constructed by first building the geometry of the particle, assumed to be an ellipsoid with dimensions and aspect ratio informed by metallurgical measurements of the sample plate characterized by Fig. 15.25(a). Subsequently, an unstructured tetrahedral mesh was used to fill the remaining volume and crystallographic orientation was overlain on the elements. The crystal domains were generated using a Voronoi tessellation, with linear mapping applied to achieve an appropriate grain aspect ratio, following closely [10,12]. Certainly more robust algorithms and codes exist to generate microstructures [48–50], but our studies indicated that for present purposes, the stress in the particle was relatively insensitive to the treatment of the grain boundaries in the matrix [51], and our overlay procedure has the advantages that it is robust, fast, and simple. Two examples of this type of

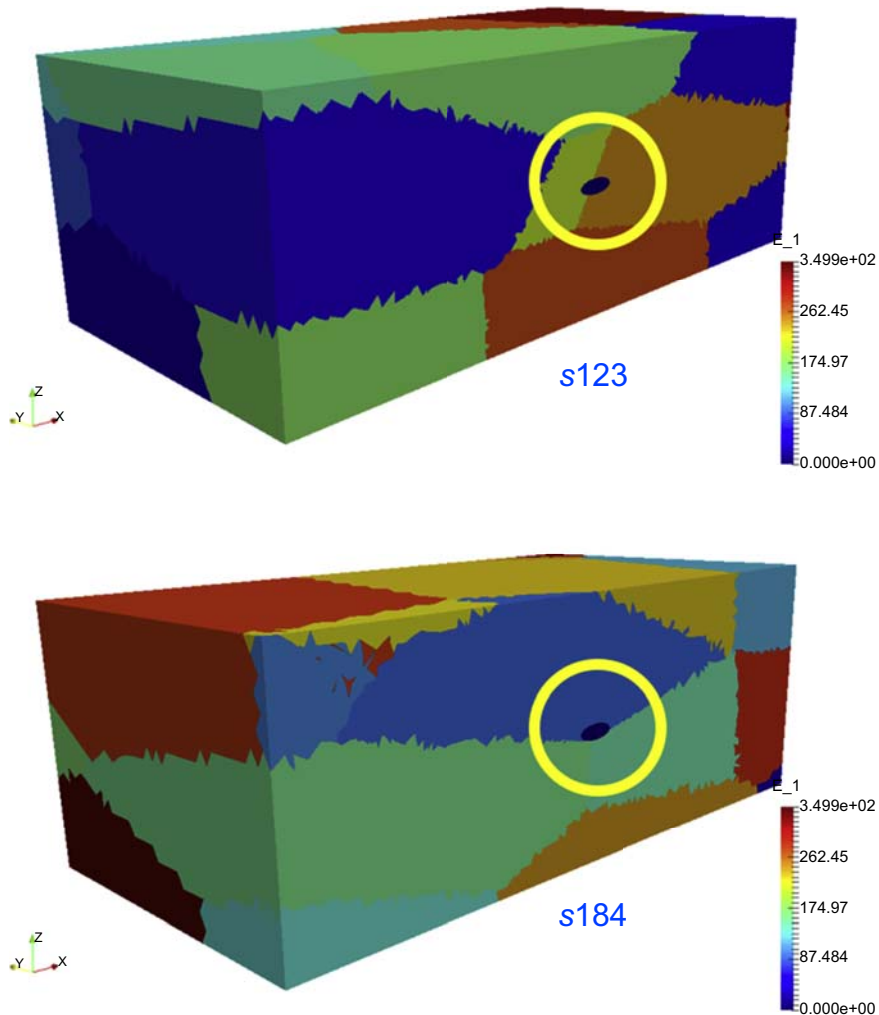


Figure 15.26 Particle/microstructure geometry for two instances of grain morphology. The images are taken at a cross section intersecting the particle for display. The coloring indicates the value of each grain's first Euler angle to aid in identifying individual grains.

microstructure are shown in Fig. 15.26 where the roughened edges of the grain boundaries produced by overlaying crystal orientation are obvious. This microstructure was considerably smaller than recommended in application, which is a shortcoming of this work, and future work entails building larger polycrystals, with significantly larger particle populations, and propagating cracks between the particles. In the end, there were only 32 grains and 548,351 composite tetrahedral elements [52].

We used a crystal plasticity model developed by Ref. [26], and it was calibrated to the average of the smooth tensile data for AA 6061-T6. The fit and material parameters appear in Fig. 15.27 and Table 15.5.

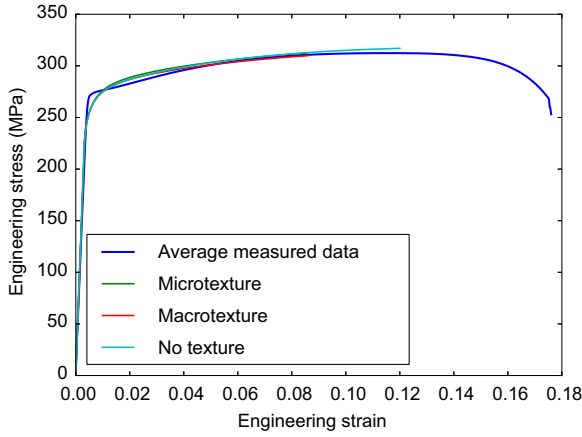


Figure 15.27 Crystal plasticity calibration to average smooth tensile data.

Table 15.5 Crystal plasticity material parameters.

g_0 (MPa)	114.0
g_{s0} (MPa)	172.8
G_0 (MPa)	116.6
M	0.01

The particle was assumed to be pure iron, with modulus of elasticity of 211 (GPa) (note: three times that of the aluminum) and Poisson's ratio of 0.29. We defined the probability of failure as the probability that the applied engineering strain on the microstructure causes particle fracture. That is, the probability that the engineering strain belongs to some limit set S_f ,

$$\Pr(\bar{\epsilon}_{RVE} \in S_f) \quad (15.20)$$

where $\bar{\epsilon}_{RVE}$ is the average applied engineering strain and S_f is defined as $S_f = \{\bar{\epsilon}_{RVE} \in \mathbb{R} : g(\bar{\epsilon}_{RVE}) \leq 0\}$ and g is the limit state function defined as $g(\bar{\epsilon}_{RVE}) = \bar{\sigma}_{p,cr} - \bar{\sigma}_p(\bar{\epsilon}_{RVE})$, and $\bar{\sigma}_p$ is some measure of stress in the particle. Here we used the average of the first principal stress over the entire particle volume with $\bar{\sigma}_{p,cr} = 540$ MPa. Assuming the particle is both perfectly brittle and coherently bonded to the matrix is conservative, as it neglects dissipative mechanisms that exist. On perhaps the opposite spectrum, we assumed the particle was elastoplastic and we used a power-law hardening plasticity model. The form of the hardening equation was

$$\sigma_e(\epsilon_p) = \sigma_y + h\epsilon_p^\lambda \quad (15.21)$$

where σ_e is the von Mises effective stress, ϵ_p , σ_y , and h are as previously defined, and λ is the hardening exponent. For the particle plasticity properties, we used 350 MPa for yield stress, 333 MPa for the hardening modulus, and 0.15 for hardening exponent. In some cases, the strain on the particle never reached the limit state within the simulated applied strain range. In such cases, we used the final few points in the history to extrapolate to a failure strain. If the slope of the final points was positive, we extrapolate. If the slope was negative, we assign an arbitrarily large value $\bar{\sigma}_{p,cr} = 0.1$, or 10% strain. Note, a negative slope does not imply loss of ellipticity—these are not material point stress—strain relations.

15.5.3.3 Uncertainty

Ductile fracture is attributed to the mechanisms of void nucleation, growth, and coalescence and has been studied extensively. In particular, recently there are a nice series of papers on AA 6061-T6 [39,40,53,54]. In general, void nucleating sites in an alloy can be attributed to a vast number of properties ranging from lattice vacancies to grain boundary imperfections to other-phase particles and inclusions. For the aluminum alloy focused on here, our measurements above, which are confirmed in the literature, show there were nominally two populations of second phase for concern. There were finer, micron-size iron (Fe) precipitates, and there were larger, 10 nm magnesium—silicon (Mg₂Si) and iron particles. The particle size and spatial distribution are random, but here we only consider a single and fixed sized particle. We used an average particle size, determined from measurements, to be 5 μm in the rolling direction with waste of 2 μm .⁴

Here the uncertainty at the engineering scale was lumped into the initial yield, hardening and recovery constants. An RFROM was used to predict the component response (average response is depicted in Fig. 15.25(b)), and a point near the middle set of notches was determined to be the most critical location to first embed the microstructure model. Henceforth, uncertainty was introduced by the crystallographic orientation for which we constructed an RFROM following the methods in Section 15.5.2. Noting here, the polycrystal was a modestly sized 32 grains. The required calculations for Eq. (15.10b) are $m * (d + 1)$. The stochastic dimension of a 32-grain polycrystal would be 96, for three Euler angles, so that a piecewise-linear surrogate with $m = 10$ RFROM would cost 970 FE simulations. Hence, like in Section 15.5.2, we used Eq. (15.10a). Fig. 15.28 shows a medium magnification image of the six notches in one of the test specimens. The dominant cracks were witnessed in the middle set of notches (equal probability between the north and south notch), as depicted in the figure where a large crack is seen in the middle—south notch.

⁴ The bimodality of the precipitate size suggests coupling damage models, representing the finer precipitates, with crystal plasticity models that explicitly include the larger particles in the mesh. The size and spacing of the larger particles would set a length scale, so local damage models may provide convergent estimates on global quantities [55].

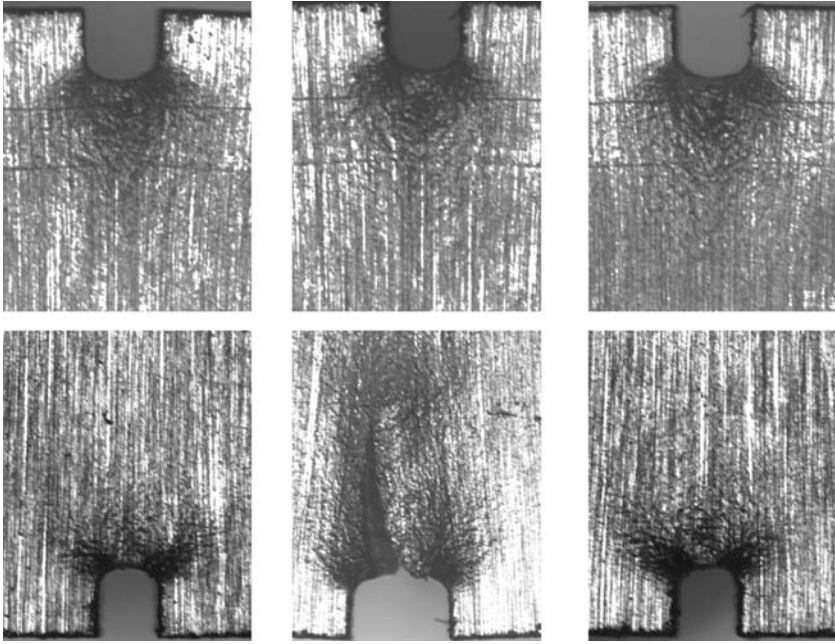


Figure 15.28 Medium magnification images at the root of the six notches demonstrating fracture initiation in the middle set of notches.

15.5.3.4 Results

Fig. 15.24 shows the von Mises effective stress (top) and triaxiality (bottom) contour plots. Clearly the middle set of notches was the most active for this engineering-scale scenario. We used the microtextured microstructure with elastic and brittle particle and coupled with the MPC approach. Fig. 15.29 shows contour plots of von Mises effective stress for one sample of the fully coupled calculation, from the engineering scale in (a) to the engineering-microstructure length scale interface near the notch in (b), ending with the embedded polycrystal and particle in (c). In part (c) of the figure, the heterogeneity of the fields due to the crystallography is apparent and the 3x stiffer particle has very high stress.

Fig. 15.30(a) quantifies the results of the load in the particle for $m = 20$ RFROM. Here we used the nominal applied strain on the 6-notch specimen, so that the strains coincide with Fig. 15.25(b). Fig. 15.30(b) plots the SROM-based cdf of strain-to-fracture of the particle. These results were achieved with a $m = 20$ SROM on Sandia's Eclipse cluster computer in 47,814 CPU hours. The experimentally observed apparent strain-to-failure of the plate ranged from 0.035 to 0.039, while the range for the SROM-predicted particle fracture was 0.0019–0.045 with a mean computed by Eq. (15.3a) of 0.0057. These results indicate that a particle in the high-triaxiality region in front of the notch is likely to fracture very early in loading. This is somewhat inconsistent with other research that suggest particles do not fracture until after peak load on

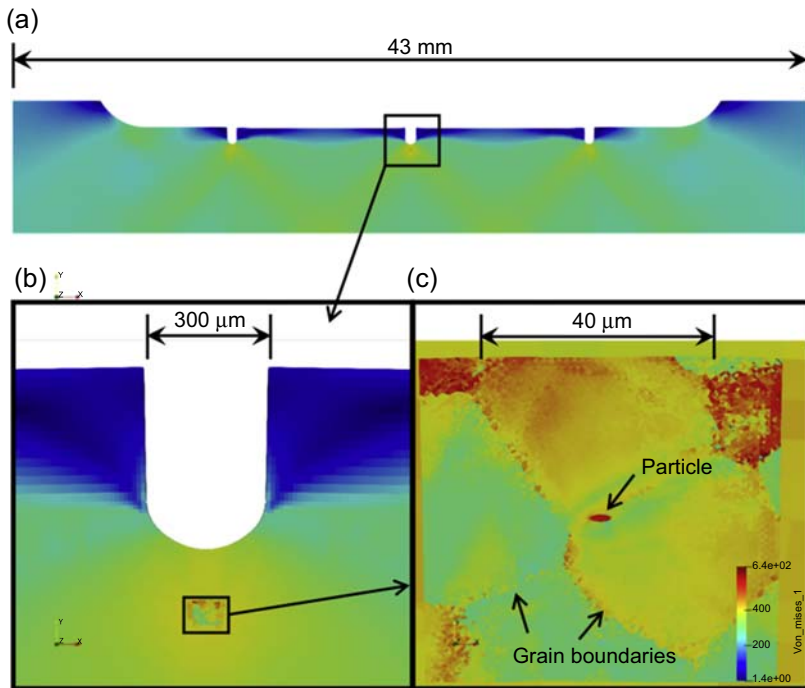


Figure 15.29 One sample of the concurrently coupled FE model from the engineering scale in (a) to the engineering-microstructure length-scale interface near the notch in (b), ending with the embedded polycrystal and particle in (c).

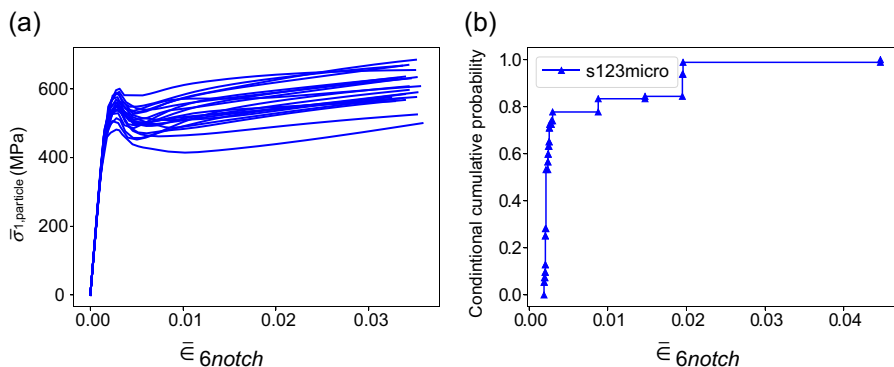


Figure 15.30 The average first principal stress in the particle versus the nominal applied engineering strain on the component (left) and the SROM estimated cdf of particle fracture. (a) Stress–strain multiscale. (b) cdf multiscale.

a notched specimen [39]. However, there are other findings in the literature that suggest in some high-cycle fatigue applications, surface particles near stress concentrations fracture during the first loading cycle [56]. Nonetheless, it is reasonable to suspect our results are missing some key physics. ♦

15.5.4 Summary and discussion

The first example illustrated the entirety of our hierarchical framework as we computed the probability of failure of a jointed housing assembly. In this case, both the engineering- and fine-scale constitutive models shared identical J2 isotropic yield surfaces with hardening minus recovery evolution, which made the hierarchy simpler and allowed comparison to truth calculations. The initial yield stress and the hardening modulus for each fastener were assumed random with known distributions and known correlation. There was an assumed correlation between the initial yield stresses at fastener locations 1 and 4, and 2 and 3, and the same correlation structure was assumed for the hardening modulus. Additionally, there was assumed-known randomness in the boundary conditions. The primary difference between the engineering-scale model and the fine-scale model was in the fidelity of the geometric representation of the fasteners.

In lieu of sufficient test data to validate the estimates, we constructed a “truth” model that included the threaded geometry at all four fastener locations, and computed statistics with 200 Monte Carlos samples (not using an SROM). This, in essence, provided validation through direct numerical simulation with a “full-fidelity” model. The estimated probabilities from the hierarchical approach were plotted in comparison to truth estimates in Fig. 15.17 and appeared to be reasonable approximates; however, the hierarchical approach required less than half of the computing time on equivalent processors. Mesh dependence abounds in the choice of failure model, but the hierarchical approach was consistent with truth and standard practice. As improvements in fastener failure modeling become available, the hierarchical framework can readily adapt to them.

In our second example, we estimated the cdf for E_{app} for a polycrystalline, aluminum plate. Uncertainty in this problem was introduced by the random orientation of the grains in the plate. Hence, we demonstrated the use of SROM to efficiently propagate the uncertainty due to crystallography, thereby illustrating the developments for a vector-valued random field, and we explored the accuracy compared with 10,000 FE calculations to establish “truth.” Here, a piecewise-constant form of SROM-based surrogate was employed, and we developed means to approximate the output cdf via MLE by modifying the SROMs likelihood function.

The MLE-based estimates derived from the $m = 50$ SROM provided reasonable accuracy, *c.f.*, Fig. 15.22. We further attempted to illustrate the potential hazard in a standard Monte Carlo approach by demonstrating the variable outcomes in error. In Fig. 15.25, we plotted the percent of relative error, relative to the truth simulations, for estimates of the first 6 moments of E_{app} . While some samples of 50 standard MCS performed well, in fact better than the SROM-based approach, there were others that doubled the error. In practice, if using only MCS, the engineer has no way (no truth available) of knowing if their 50 samples are twice better or twice worse than an SROM-based approach. In our hierarchical approach, we can improve the SROMs estimates of output statistics by refining the SROM based on the low-fidelity estimates, in a manner analogous to importance sampling, and with only minimal additional cost, a topic of future work.

In the final example, we performed concurrent multiscale UP to determine the probability of fracture of a second-phase particle embedded in a matrix of polycrystalline AA 6061-T6. To achieve this, we followed our hierarchical formulation, first identifying the hotspot with engineering-scale calculations. The final estimates of fracture were somewhat at odds with available validation data, predicting the particle fractured at considerably lower strain levels with relative high probability. All of the most immediate reasons for this discrepancy can be considered deficiencies in the current state of the deformation and fracture models used herein, which are currently open topics of research. There are a number of immediate and obvious improvements to be made with the models: improved MNMs, better crystal-plasticity models, dissipative models for the second-phase particles, improved dissipation and treatment of dislocations at grain boundaries, and larger volumes of materials containing statistically relevant samples of particles accurately distributed, *etc.* However, the hierarchical UP and SROM-modeling tools are immediately applicable with any and all of the aforementioned improvements.

15.6 Conclusions

In summary, the primary goal of this research was to develop efficient tools and capabilities for multiscale UP using FEs. We proposed a hierarchical methodology for multiscale UQ. Each level in the hierarchy consumed a set of random inputs and computed a probabilistic prediction of system performance. The random inputs can include all known sources of uncertainties, but we focused on materials' properties and boundary conditions. Other uncertainties, e.g., a parametric description of geometric tolerances, can easily be included in the method. Each successive level in the hierarchy had two additional inputs: the prediction from the preceding model and model-specific parameters. The prediction from the preceding level was used to focus the higher-fidelity model on specific hotspots, and outcomes of the performance predictions from each level were synthesized with the law of total probability. The intent of the hierarchy is to start with relatively low-cost computational tools and gradually increase the fidelity by improving the physical models and compromising cost. Our examples developed the framework with two hierarchical levels.

Ideally, we would use the fine-scale model everywhere within the domain and perform direct MCS by drawing many random samples of the fine scale. Our method assumes that this is not possible for two reasons. First, the computational cost associated with using the fine-scale material model is so great that its use must be limited to a small spatial subset of the domain containing the fine-scale model. Second, performing this type of calculation thousands of times as needed for traditional Monte Carlo exceeds the available computational budget. To address the first concern, multiscale calculations utilizing the fine-scale material model at a carefully chosen and finite number of spatial subdomains were employed. To address the second issue, we used SROMs and derived surrogate models from them so that function evaluations for MCS were within budget.

The framework further assumed that the low-fidelity model was sufficiently robust to capture the predominant failure mechanisms. Certainly, our methodology will not account for the lack of essential physics in the low-fidelity model, and caution to build an appropriate relationship between the low- and high-fidelity modeling scheme was recommended. Ideally, validation of this assumption via direct numerical simulation with the fine-scale calculations throughout the domain would always be conducted. However, our previous concern precludes this.

We presented three example applications. In the first application example, we demonstrated the overall hierarchical approach with a bolted housing, where the fine-scale model improved the local geometric representation. In this case, we developed a “truth” model, which used the fine-scale model throughout and our framework provided very reasonable estimates of performance at a fraction of the computational cost. In the second application example, we demonstrated UP for random crystallography, and we developed the likelihood function for the SROM method to generate best-fit probability distributions by the method of MLE. Here again we compared to direct numerical simulation and the framework using MLE provided the most accurate and least expensive estimates. In the final application example, the focus was on the variability associated with random grain orientation in a 3D microstructure, including spatial correlation to capture grain misorientation, and including a second-phase particle. The method developed the probability of crack nucleation due to particle fracture. The estimates were askew from the limited observed data, but we conjectured the discrepancies were caused by the present state-of-the-art physics and mechanics and not our framework.

Nomenclature

ϵ_p	Equivalent plastic strain
Γ	Range of Θ , Θ
Γ_k	k^{th} partition of Γ
$\mathcal{D}$	Spatial domain of body
$\mathcal{D}_k$	k^{th} non-overlapping region in $\mathcal{D}$
$\mathcal{D}_M$	Subdomain of $\mathcal{D}$
F_k	Event that failure occurs in region $\mathcal{D}_k$
$\mu(b)$	b^{th} moment of Θ
Pr_H	High-fidelity estimate of the probability of failure
Pr_L	Low-fidelity estimate of the probability of failure
σ_e	Effective stress
σ_y	Initial yield stress
Θ, Θ	Random variable, vector with uncertain inputs
$\tilde{\Theta}, \tilde{\Theta}$	SROM of Θ, Θ
$\tilde{\theta}_k$	SROM sample associated with Γ_k
d	Stochastic dimension of Θ
$F(x)$	Distribution of Θ
h	Hardening modulus
M	Fine- or microstructural-scale model

m	SROM sample size
n	Number of non-overlapping regions in $\mathcal{D}$
p_k	Probability of $\tilde{\theta}_k$
Q	Random variable for failure load
r	Recovery parameter
S	Engineering-scale model
AA 6061-T6	Aluminum alloy 6061-T6
EBS	Electron backscatter diffraction
FE	Finite element
MCS	Monte Carlo simulation
MNM	Multiscale numerical method
MPC	Multipoint constraints
SROM	Stochastic reduced-order model
UP	Uncertainty propagation
UQ	Uncertainty quantification

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Bayesian Global Optimization applied to the design of shape-memory alloys

16

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16.1 Introduction

The Materials Genome Initiative in the United States is aimed at accelerating the process of materials discovery to reduce in half the time and costs [1]. The major challenge in developing new materials with better properties is the huge search space due to the complexity associated with chemistry, composition, crystal structure, microstructure, and processing conditions [2–4]. Considerable effort has been devoted to generating large-scale databases with crystal structures and chemistries using high throughput first principles calculations [5–7]. Based on the calculated data, promising new materials are downselected for subsequent experiments or further calculations. A number of studies have also used inference models, such as on-the-shelf regression and classification learning tools, including deep neural networks for large datasets of microstructures, to make predictions [8–22]. The approach has been employed to suggest new Heusler alloys [23], polymers [24,25], and thermoelectrics [26,27], to name a few examples.

Experimentally, within the high-dimensional space of all possible materials, only a few have been synthesized and characterized experimentally. Many of these have been documented in the Inorganic Crystal Structure Database [28]. What can be used for training machine learning models is a fairly small dataset containing several tens of labeled data points. These data usually cannot ensure a very predictive machine learning model to offer accurate inference to the unexplored data. In addition, predictions from the mere use of machine learning models can often be suboptimal. A Bayesian optimization or active learning or adaptive design framework that uses a machine learning model [29], such as a Gaussian process, together with experimental design algorithms, offers a robust approach as it makes general assumptions on the prior, such as smoothness and locality, together with design algorithms that sample the unexplored space efficiently [30–32]. Often the sampling is designed to reduce overall uncertainties [33]. Engineers often adopt surrogate models if the engineering model is computationally expensive, especially involving large-scale optimization tasks. The surrogate models are trained on a relatively small number of points, and Bayesian

Global Optimization (BGO) has been used extensively in industry in dealing with large-scale computational tasks. The work of Jones et al. who introduced the Efficient Global Optimization (EGO) method [30], which was based on earlier work of Kushner's [34] on the optimization of unknown functions, as well as the work of Mockus and Zilinskas [35], has been key in the widespread use of these ideas in the engineering context. The notion of maximizing the probability of improvement from the "best-so-far" was introduced in these studies and BGO has been adopted for design applications, especially for time-consuming computer experiments [36].

The problem is to find the solution for $\max_x f(x)$, that is, to find x maximizing $y = f(x)$ and BGO offers a means for searching for the extreme of functions for which convexity properties and derivatives are not known. Prior belief in the form of smoothness and locality of $f(x)$ guides the sampling and active learning. Thus, if $D = \{x_i, f(x_i)\} (i = 1:n)$ denotes the observations, then according to Bayes' rule, the posterior distribution can be written as $P(f|D) \propto P(D|f)P(f)$, where the posterior gives the updated distribution or belief for the unknown $f(x)$ given how likelihood is the data seen so far, $P(D|f)$, combined the prior information about f . This step can be thought of as providing an estimate for $f(x)$ with a response surface or a surrogate model, such as a Gaussian process or a machine learned model. The prior can be chosen from several possibilities including a Wiener or Gaussian process. However, a Gaussian process, an extension of the multivariate Gaussian distribution with an infinite number of variables, has been shown to be better suited if we allow for a number of simplifying assumptions [37,38], and unlike a Gaussian distribution with a mean and variance, a GP is a distribution over functions with a mean function, m , and covariance function, k , i.e., $f(x) \sim \mathcal{GP}(m(x), k(x, x'))$. A common choice for k is the squared exponential $k(x, x') = \exp\left(-\frac{1}{2}\|x - x'\|^2\right)$ which converges to 1 as data points x and x' become closer and 0 if they are far apart.

The Bayesian optimization approach we will consider, which we have implemented to accelerate the process of finding new shape-memory alloys (SMAs) with targeted response, is schematically shown in Fig. 16.1. It is an iterative feedback loop, including two key steps: (i) a surrogate machine learning model to relate the material descriptors or features to the property with the associated uncertainties and (ii) a utility or acquisition function with input from the surrogate model dictating the next experiment or calculation to be performed. The surrogate model can be an inference model or a physics-based or reduced order model (ROM). Means should exist that allow the physics-based or ROM to be improved.

From a practical point of view, the key ingredients of the loop of Fig. 16.1 include (i) a training dataset of alloys, each described by features and with a desired property that has been measured; (ii) an inference model that uses the training data to learn the feature–property relationship, with associated uncertainties; (iii) the trained model is applied to the search space of unexplored alloy compositions (for which the property has not been measured), to predict it with uncertainties; (iv) design or global optimization that provides the next candidate alloy for experiment by balancing the trade-off between exploitation (choosing the material with the best predicted property) and

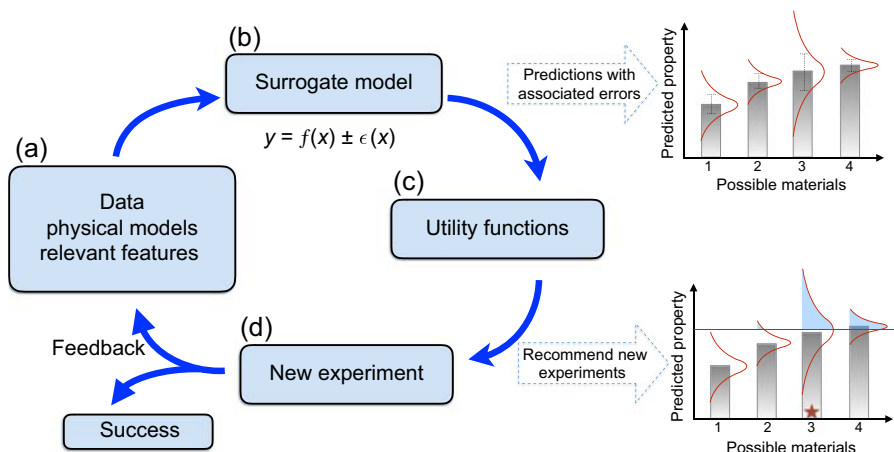


Figure 16.1 The adaptive design loop. (a) Prior knowledge, including data from previous experiments and physical models, and relevant features serve as input. (b) This information is used within a machine learning framework to make predictions that include error estimates. (c) The results are used by an experimental design tool to recommend new experiments via a utility function with the dual goals of model improvement and materials discovery. (d) The recommended experiment (synthesis and characterization) is performed in this work and the new results augment the database for the next iteration. The iterative design loop is applied several times until new materials with better property are obtained.

exploration (using the predicted uncertainties to study regions of search space where the model is less accurate); and (v) feedback from experiments allowing the subsequent iterative improvement of the inference model. The approach is unique in that most of the work done in the field essentially involves one or two of these steps, such as setting up the data, building a model, making predictions, and validating them with calculations or experiments without experimental design.

In this chapter, we further briefly discuss the Bayesian approach to inference and design in [Section 16.2](#) with its focus on incorporating prior information and data to predict the property or objective using a Gaussian process. However, other approaches to inference based on machine learning methods, such as kernel methods or those based on trees, including ensemble methods, can also be used for this purpose. The Gaussian process method is an attractive choice as it includes an uncertainty estimate via a distribution. Other approaches do not typically estimate uncertainties, and we need to use a bootstrap approach to obtain uncertainties associated with model predictions. For simplicity, the Gaussian process is employed. Here, we also discuss methods for estimating uncertainties and how these can depend on the datasets. We consider two high-quality experimental datasets that we generated and examine the behavior of the standard deviation and Infinitesimal Jackknife estimates for uncertainties. We show that for one dataset related to piezoelectric materials the two uncertainty measures are consistent with each other, whereas one severely estimates the other for the alloy dataset. The concept of utility function was previously introduced in decision theory in relation to the theory of the value of information

[39,40], and this provides us with a selection and ranking criteria to make decisions about where to optimally sample next. We review a number of these functions, such as the widely studied expected improvement, which provides a criterion that balances exploitation and exploration for making choices. In [Section 16.3](#), we discuss applications of this two-stage approach, also widely known as BGO, to show how we can discover new compositions of SMAs with very small hysteresis, as well as high temperatures. We will consider multicomponent NiTi-based alloys, which undergo a B2 to rhombohedral (B2 to R), as well as a B2 to orthorhombic and/or monoclinic (B2 to B19 or B19') transformation. As we are targeting an alloy with hysteresis as small as possible, we expect that our approach toward this problem will largely seek out alloys undergoing the B2 to R transformation, which we know to have small strains and therefore small hysteresis. These results are from experiments carried out in previously published work, but we review these in the context of BGO, as these were the methods which were employed to discover these alloys. We conclude in [Section 16.4](#) by summarizing the essential elements of BGO discussed in this chapter, especially the new results related to how uncertainties are calculated when the data comes from experiments and is relatively small in size.

16.2 Bayesian Global Optimization

Machine learning algorithms are often hindered by small datasets and extrapolation to a vast unexplored chemical space with little or no experimental feedback to validate the predictions. They are also prone to be suboptimal, because they only exploit the model outcome and therefore are liable to become conned to local minima, without sampling points in the search space where the uncertainties are larger. This can be important in the early design stages where uncertainties are the greatest. Hence, an approach as shown by the iterative design loop in [Fig. 16.1](#) provides the means to reduce uncertainties in the objective adaptively as new experiments are performed. The first step in BGO is to establish a model, $f(x)$, that predicts a given value or provides a posterior distribution of the targeted property based on available data $(x_i; y_i)$ with $i = 1, 2, \dots, n$. The second step is the decision-making step to direct future sampling so that the next experiment or calculation, x_t , is chosen by maximizing a utility function, $u(x|D_{1:t-1})$, over all the data in the sampling domain, that is, $x_t = \operatorname{argmax}_x u(x|D_{1:t-1})$.

16.2.1 Surrogate model with uncertainties

The machine learning algorithm learns a map connecting features or independent variables x to a specific material property Y , that is, $Y = f(x)$. As what is measured is subject to noise, we write $Y = f(x) + \varepsilon$, where the noise ε is distributed normally. The effect of noise is that the posterior distribution no longer interpolates the data points but the credible or confidence interval has positive width at all data points.

The features can be constructed and selected by either using domain knowledge or by feature selection methods, such as gradient booting, which ranks many possible features according to their relative importance. Given the features, the learning

algorithm estimates f using a training dataset, which includes the measured targeted property. The empirical or surrogate model, f , can be applied to predict or estimate the targeted property over the set of unexplored, possible materials whose targeted material properties have not been measured.

Training the model is an important part of the process until the model achieves a desired level of accuracy on the training and test data. Here various machine learning algorithms can potentially be used including decision trees or random forests, support vector machines, and neural networks. In contrast to a Gaussian process that provides a probability distribution and variance, it is often necessary to use bootstrap methods for ensemble sampling to estimate uncertainties of the surrogate model, especially in the limit of relatively small data sizes. These algorithms contain hyperparameters, such as the penalty term, insensitive loss function term, and coefficient of the kernel function, that control model complexity and help balance the bias–variance trade-off. In general, the hyperparameters are tuned to optimize the cross-validation (CV) error, such as leave-one-out error obtained by successively leaving out in turn each data point so that it becomes a test point. The leave-one-out error is the average of the residual of these out-of-training samples. For a Gaussian process, the hyperparameters can be chosen from the training data by minimizing the log marginal likelihood with respect to the hyperparameters and the noise. Samples are normally drawn randomly from a prior distribution such as a normal or uniform distribution. For support vector regression, for example, a model is constructed with the best combination of hyperparameters leading to the smallest CV error. The model performance is given by tracking two errors: the CV error and the mean squared error (MSE) between the predicted and measured values. For the MSE, bootstrap sampling on all the training data with replacement is used. For the selected bootstrap sample, a model is constructed with the hyperparameters fixed by 10-fold CV, and then applied on the training data. In total, 1000 bootstrap samples give rise to 1000 models giving 1000 predictions, from which the uncertainty can be calculated.

Bayesian models such as the Gaussian process model predict the posterior and accompanying variance. Usually with experimental data in materials science, we typically have a training dataset of samples from an unknown population. In our case for the SMA problem, we have 57 samples well characterized from the same laboratory. Therefore, we use nonparametric bootstrap sampling with replacement (and other variants of this) to generate many training datasets to form a distribution from which we can make predictions. The idea underlying this is that a distribution such as this is a way to simulate the original population and allows us to train 1000s of models of training datasets in order to make robust predictions with measures of uncertainties. Now uncertainties may be estimated using different methods. In general, the accuracy of the uncertainty estimates will be affected by several factors, such as the size of the bootstrap samples, the size and variety of the training data, and also the surrogate model. In the limit of large datasets, many of the estimates are expected to essentially give similar results. One method to obtain an uncertainty is based on the standard deviation (σ), which is a measure to quantify the amount of variation or dispersion within a set of data point values and is given by $\sigma^2 = \frac{1}{n} \sum_{i=1}^n (y_i - \mu)^2$, where y_i is

the value of each data point and μ is the mean of all the data point values. For the random forest algorithm, a popular extension of bagged trees aims at variance reduction by estimating the uncertainty using the Jackknife, Infinitesimal Jackknife (and their variants) method [41–44]. These methods estimate the standard error or variance based on the preexisting bootstrap samples. The Jackknife after-bootstrap estimate is given by $\hat{V}_J^\infty = \frac{(n-1)}{n \sum_{i=1}^n (\bar{t}_{-i}^*(x) - \bar{t}^*(x))^2}$, where $\bar{t}_{-i}^*(x)$ is the average of $t^*(x)$ over

all the bootstrap

samples not containing the i -th example and $\bar{t}^*(x)$ is the mean of all the $t^*(x)$, $t^*(x) = t(x, Z_1^*, \dots, Z_n^*)$ and Z_i^* is an element of one bootstrap sample. Compared to Jackknife, the estimate of variance using Infinitesimal Jackknife converges more rapidly and can

be calculated from the following equation: $\hat{V}_{IJ}^\infty = \sum_{i=1}^n \text{Cov}_*[N_i^*, t^*(x)]^2$, where

$\text{Cov}_*[N_i^*, t^*(x)]$ is the covariance between $t^*(x)$ and the number of times N_i^* the i -th training example, appears in a bootstrap sample.

In Fig. 16.2, we compare the uncertainty calculated from the Infinitesimal Jackknife with that from standard deviation. For an SMA alloy dataset [18], 50,000 trees were trained using bootstrap sampling with replacement from the whole training data (57 alloy compounds), and then the models were applied on the out of bag samples. Fig. 16.2(a) shows that the standard deviation overestimates the uncertainty compared to that calculated from Infinitesimal Jackknife for this particular dataset. However, the estimates are very data dependent. To emphasize this point, we compare in Fig. 16.2(b) the standard deviation with Infinitesimal Jackknife for a dataset for piezoelectrics. This dataset of 61 compounds was previously studied to identify new piezoelectrics with large electrostrains [10]. For this dataset, the standard deviation and Infinitesimal Jackknife estimates are quite consistent with each other. Hence, it is important to consider different methods for estimating uncertainties, particularly if the data sizes are small, and this remains an active area under study.

16.2.2 Utility functions

The utility function (u) is a means to steer the decision-making process. Maximizing the utility function selects the next point to be sampled at $\text{argmax}_x u(x|D)$. Given a surrogate model, $f(x)$ and assuming that the response surface or allowed data points are normally distributed with mean (μ), and standard deviation (σ), the utility function u can be defined in several ways. A few examples include the following:

- Max-prediction: $f(\mu, \sigma) = \mu$: greedily chooses the material with maximum predicted value.
- Max-SD: $f(\mu, \sigma) = \sigma$: choose the material with maximum variance on successive iterations.
- Min-SD: $f(\mu, \sigma) = -\sigma$: choose the material with minimum variance on successive iterations.
- Expected improvement: maximize the “expected improvement” $f(\mu, \sigma) = \sigma[\varphi(z) + z\Phi(z)]$, where $z = (\mu - \mu^*)/\sigma$ and μ^* is the maximum value observed in the training set. $\varphi(z)$ and $\Phi(z)$ are the standard normal density and distribution functions, respectively. Expected improvement with Gaussian process is often referred known as efficient global optimization or EGO.

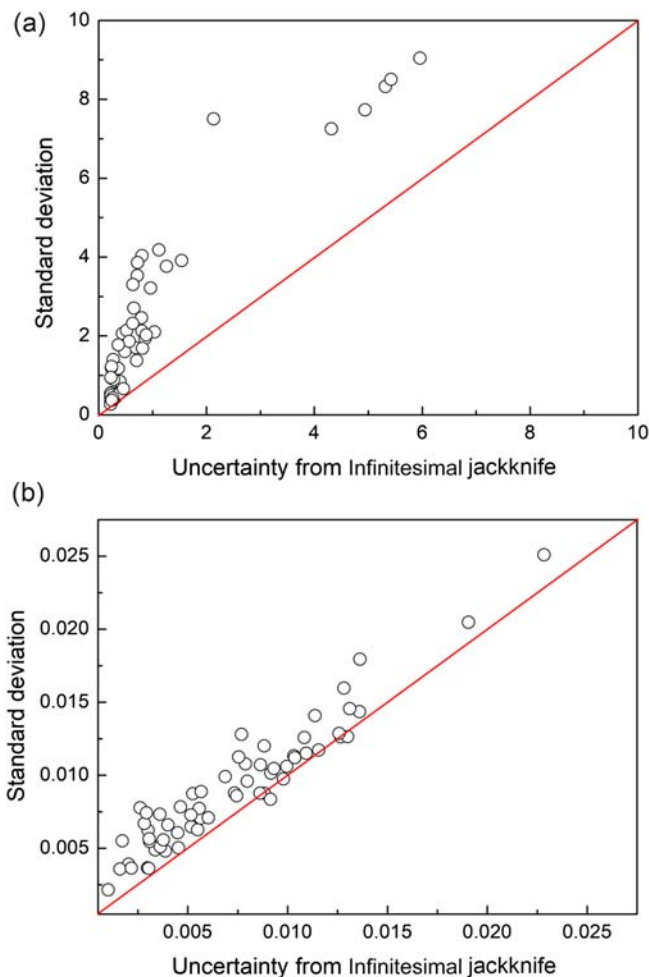


Figure 16.2 Estimates of uncertainties as calculated using standard deviation and Infinitesimal Jackknife from two different datasets: (a) for 57 SMA compounds with thermal hysteresis as targeted property and (b) for 61 piezoelectric compounds with electrostrain as targeted property.

(a) Data from D. Xue, P.V. Balachandran, J. Hogden, J. Theiler, D. Xue, T. Lookman, *Nat. Commun.* (2016) 711241. (b) Data from R. Yuan, Z. Liu, P.V. Balachandran, D. Xue, Y. Zhou, X. Ding, J. Sun, D. Xue, T. Lookman, *Adv. Mater.* (2018) 1702884.

Fig. 16.3 shows a simple example on the efficacy of the above listed utility functions for a one-dimensional optimization problem for a function $f(x) = \sin(20(x - 0.3)^2)x^2 + (x - 0.9)/2$ for which we seek the x value at which y is a maximum. Fig. 16.3 compares the behavior of two utility functions, namely Max-SD ((a) and (b) in Fig. 16.3) and EGO ((c) and (d) in Fig. 16.3). The dotted lines

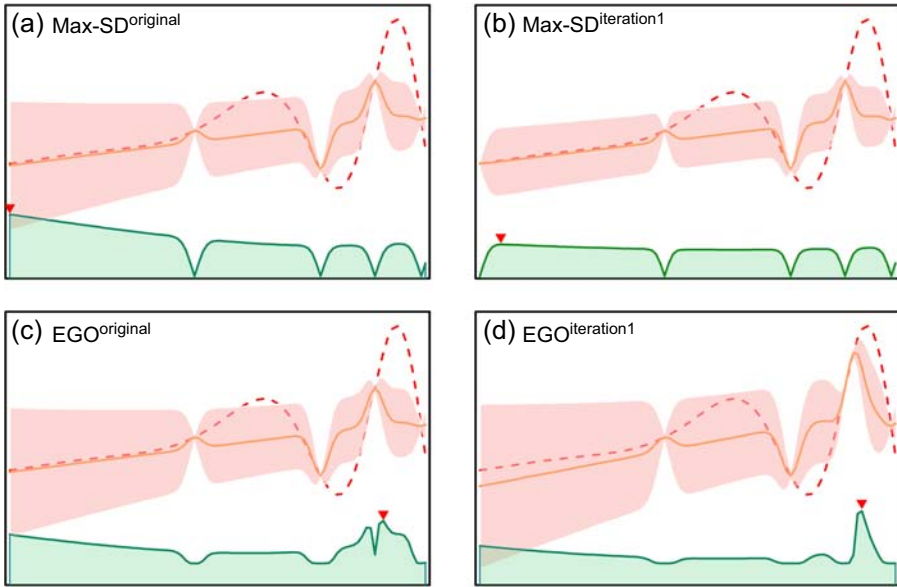


Figure 16.3 Example illustrating model prediction and decision by maximizing the utility function (in green) for the function $f(x) = \sin(20(x - 0.3)^2)x^2 + (x - 0.9)/2$. The *dotted line* is the actual solution to the function whose maximum we seek, and the *solid line* and *shadow* are the values and associated uncertainties estimated from a Gaussian process model. Panels (a) and (b) show the sampling due to choosing the next point by maximizing the standard deviation; (b) the opportunity cost is defined as the difference between the true value of the selected candidate and the true value of the best candidate, as a function of new measurements.

in Fig. 16.3 show the actual function. We utilize a Gaussian process model to estimate the predictions and associated uncertainties as shown by the solid line and shadows, respectively. Four randomly chosen points on the function $f(x)$ ((a) and (c)) were chosen as the training dataset for both utility functions, thus no uncertainties are associated with these data points. Shown in green for (a) and (b) is the standard deviation and expected improvement, $f(\mu, \sigma)$ for EGO, for (c) and (d). After selecting the data point with the maximum standard deviation in (a) (red arrow), (b) shows the updated predictions. We clearly see that the “footballs” of uncertainties are now smaller; however, there appears little improvement in the maximum prediction for the function. On the other hand, for EGO, after choosing the point with the maximum $f(\mu, \sigma)$ (red arrow) in (c), the prediction for the maximum in the function has considerably improved. However, it is at the expense of the overall uncertainties, which have increased in (d). This emphasizes the difference in the two utility functions; EGO is designed to seek optima of functions, whereas standard deviation reduces the overall uncertainty by sampling data points with maximum uncertainty.

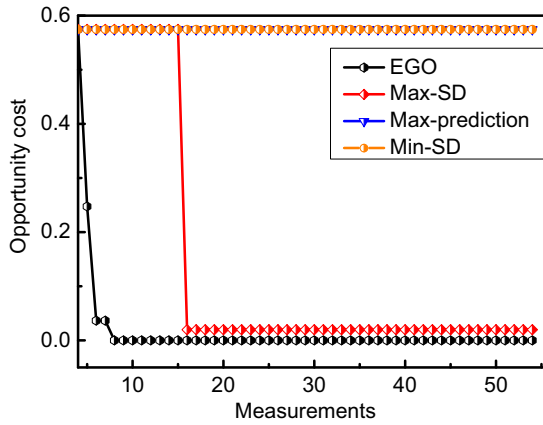


Figure 16.4 The opportunity cost, defined as the difference between the maximum of the function and the best value in the training data used to construct the Gaussian process model, as a function of the number of iterations. EGO requires fewer iterations than standard deviation or using the best value from the Gaussian process model or ranking based on choice of data point with the smallest uncertainty.

To compare the performance of the various utility functions, Fig. 16.4 plots the opportunity cost, defined as the difference between the maximum of the function and the best value in the training data used to construct the Gaussian process model, as a function of the number of iterations. We see that EGO finds the maximum in fewer iterations than standard deviation. However, merely choosing the best value from the Gaussian process model or the data point with the smallest uncertainty performs very poorly and thus emphasizes the importance of selection and ranking via utility functions.

16.3 Design of new shape-memory alloys

SMA find wide applications as sensors and actuators due to their superelasticity (SE) and shape-memory effect (SME) [45]. The SME and SE originate from the temperature-induced or stress-induced martensitic transformation, a displacive transition characterized by rapid change of crystal structure at the transformation temperature [46]. Such a solid-to-solid phase transformation is typical of a first-order phase transition with large thermal hysteresis, ΔT , the difference in transformation temperatures on heating and cooling. Usually the transformation temperature and hysteresis are two key factors that impact applications of SMAs. The former determines the operation temperature window for devices made from SMAs, and the latter gives rise to large energy dissipation and consequent functional fatigue. We review here how we have utilized BGO to rapidly optimize the properties of transformation temperature [14] and thermal hysteresis in NiTi-based SMAs [18].

16.3.1 Searching for NiTi-based shape-memory alloys with high transformation temperature

It is well known that the transformation temperatures of SMAs are affected by their composition [46–48]. We thus define a search space for NiTi-based SMAs to encompass alloys with the formula $\text{Ni}_{50-x-y-z}\text{Ti}_{50}\text{Cu}_x\text{Fe}_y\text{Pd}_z$. The compositions x , y , and z vary in steps of 0.1% with constraints $50-x-y-z \geq 25\%$, $x \leq 20\%$, $y \leq 7\%$, and $z \leq 25\%$. This gives a total number of 1,652,470 possible alloys. Our aim is to find the SMA with transformation temperature as high as possible within this search space.

We prepared a training dataset of 53 alloys for which the transformation temperature T_p was measured experimentally in our own lab. In the present study, we did not consider the uncertainties from the experimental measurement. Each sample in our dataset is represented by a feature vector, X_p , which contains information on the structure, chemistry, and bonding. We synthesized a number of features based on our knowledge of SMAs. These include the effects of elastic constants or local strains on the transformation temperature. The feature vector, X_p , is calculated from composition using the mole fraction of the elemental features, that is, $X = f_{\text{Ti}}X^{\text{Ti}} + f_{\text{Ni}}X^{\text{Ni}} + f_{\text{Cu}}X^{\text{Cu}} + f_{\text{Fe}}X^{\text{Fe}} + f_{\text{Pd}}X^{\text{Pd}}$, where f is the mole fraction and X is the feature for each element. We then subjected these features to a correlation filter to retain features not highly correlated. Further down selection was performed by identifying a subset of the features, from all possible combinations of pair and triples, that best fit a polynomial regression model. The best subset of three features included Pauling electronegativity (en), the valence electron number (ven), and the Waber–Cromer’s pseudopotential radii (dor). Except for the known training data, the remaining unexplored search space still contained 1,652,417 potential alloys without transformation temperatures measured. This is where we utilized BGO to find the highest transformation temperature.

Our first step was to develop a predictive machine learning surrogate model, $T_p = f(\text{en}, \text{ven}, \text{dor})$, to predict the transformation temperature for unknown samples. We estimate f by using different regression methods including linear (LIN) and polynomial regression (POLY), support vector regression with a linear kernel (SVR.lin), polynomial kernel (SVR.poly), and radial basis function kernel (SVR.rbf). The comparison and selection of the models were performed by evaluating the training error and the test error. The former can be calculated by comparing T_p measured and T_p predicted for the data in the training set. The latter was estimated by the above-mentioned CV or bootstrap resampling with replacement. The standard deviation (σ) is given by $\sigma^2 = \frac{1}{n} \sum_{i=1}^n (y_i - \mu)^2$, where y_i is the value of each data point and is the

mean of all the data point values. The bootstrap results for different models are shown in Fig. 16.5. The predicted T_p or y axis is the end error bar is from 1000 bootstrap predictions. We found that SVR.rbf and the polynomial model outperformed all other models in terms of the test error. However, SVR.rbf is a kernel-based model and not often easy to interpret. In order to glean physical insight in the

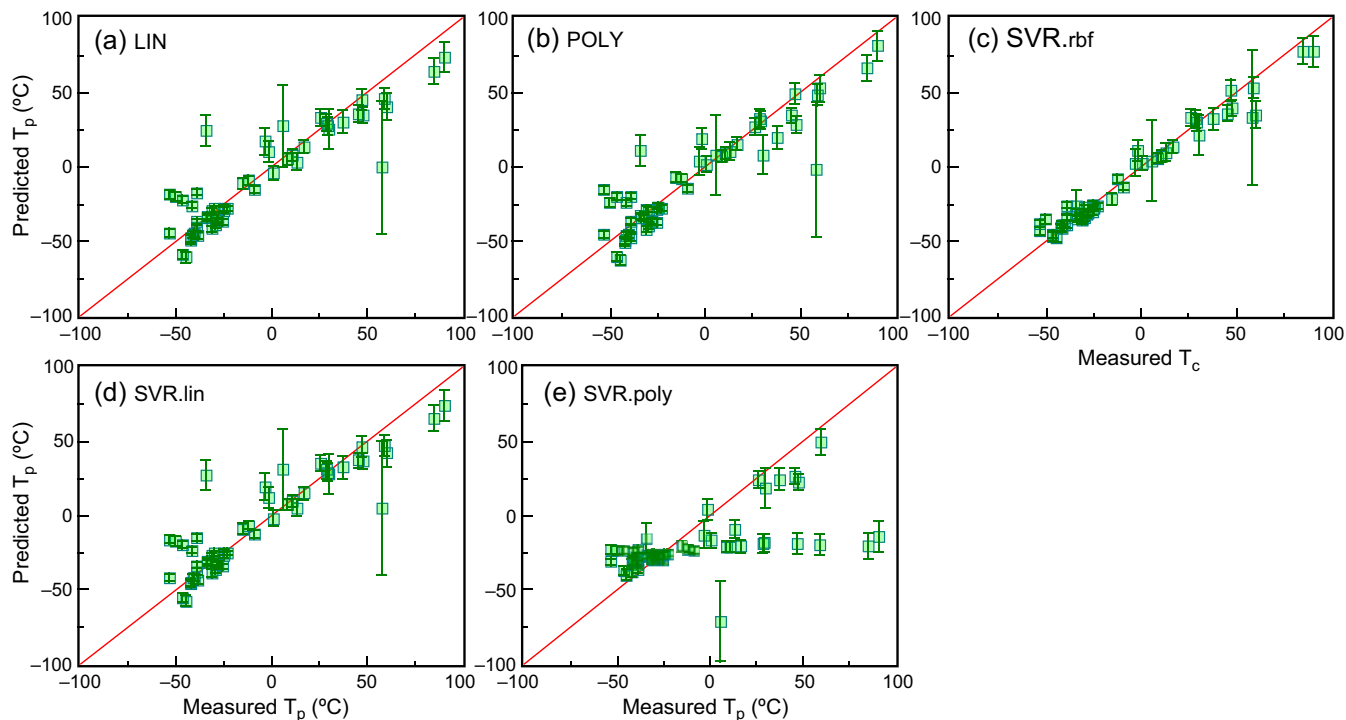


Figure 16.5 The predicted T_p from the surrogate model versus measured values are plotted for different models: (a) linear regression (LIN); (b) polynomial regression (POLY); (c) support vector regression with radial basis function kernel (SVR.rbf); (d) support vector regression with linear kernel (SVR.lin); and (e) support vector regression with polynomial kernel (SVR.poly). The scatters and error bars correspond to the mean (μ) value and standard deviation (σ) obtained by bootstrap resampling.

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transformation temperature for SMAs, we chose the polynomial model: $T_p = \beta_0 + \beta_1^{en} en + \beta_1^{dor} dor + \beta_1^{ven} ven + \beta_2^{dor} dor^2$. The polynomial model is trained by the least square method and utilized to estimate the T_p and associated uncertainty for unexplored alloys.

The next experiment was designed via utility functions to find the alloy with the highest transformation temperature among all unexplored alloys. We employed the polynomial model to predict T_p and utilized 1000 bootstrap models built on 1000 different resampled training datasets for all 1,652,417 potential alloys to estimate the uncertainties associated with predictions. We used two utility functions MAX-prediction and EGO to choose the next experiment for searching for the highest T_p alloy from our search space of allowed alloys. The results are shown in Table 16.1. The MAX-prediction recommended $Ti_{50}Ni_{49.9}Cu_{0.1}$ as the best candidate, whereas EGO found that $Ti_{50}Ni_{25}Pd_{25}$ had the highest expected improvement and should be the alloy to be synthesized next. The compound selected by EGO is physically meaningful as it is known that adding Pd will increase the transformation temperature. Thus, $Ti_{50}Ni_{25}Pd_{25}$ was synthesized and its T_p determined to be 182.89°C. The predicted value from the polynomial model was 189.56°C, showing good agreement with the measured value. The result of the new compound augmented the training dataset, and the polynomial model was retrained with the updated training dataset.

The retrained polynomial model provided updated predictions on the unexplored alloy dataset. The two functions MAX-prediction and EGO then all recommended the same alloy $Ti_{50}Ni_{25}Pd_{25}$ for synthesis, indicating no further room for improvement of T_p . The predicted value from our polynomial model was 183.41°C, indicating an improvement on the previous value. In summary, two iterations of the adaptive design loop were executed to find SMAs with highest transformation temperatures. It is noted that the uncertainty in experiment measurement is considered. Bayesian models such as Gaussian process are better choice to assess a surrogate model as the uncertainty can be an input parameter to the models. During the decision-making process, the utility functions that consider the uncertainty associated with measurement such as knowledge gradient should be employed.

16.3.2 Search for very low thermal hysteresis NiTi-based shape-memory alloys

We have also demonstrated how BGO can be used to find NiTi-based SMAs with very low thermal hysteresis ΔT [18]. Although the binary $Ni_{50}Ti_{50}$ alloy represents the best-known SMA for practical applications, it is prone to fatigue due to large temperature/stress hysteresis. To reduce fatigue, it is common to chemically modify $Ni_{50}Ti_{50}$ by substitutions at the Ni site. A severe obstacle to the development of narrow hysteresis SMAs is the large search space because a vast majority of transition metal elements in the periodic table can be alloyed with $Ni_{50}Ti_{50}$. We considered the alloy family $Ni_{50-x-y-z}Ti_{50}Cu_xFe_yPd_z$, and following similar composition control and constraints used in the previous transformation temperature problem, there are a total of $N = 797,504$ potential alloys. Only $n = 22$ were experimentally synthesized with

Table 16.1 Comparison of the performance of different utility functions, MAX-prediction and EGO, on a surrogate model of polynomial regression (POLY).

Data	Model:POLY		MAX-prediction		EGO		Prediction
	mse	CV error	Alloy	Mean	Alloy	EI	Ti ₅₀ Ni ₂₅ Pd ₂₅
Initial	13.7	356.2	Ti ₅₀ Ni _{49.9} Cu _{0.1}	81.2	Ti ₅₀ Ni ₂₅ Pd ₂₅	258.5	189.56
Updated	13.5	224	Ti ₅₀ Ni ₂₅ Pd ₂₅	125.5	Ti ₅₀ Ni ₂₅ Pd ₂₅	113.5	183.41

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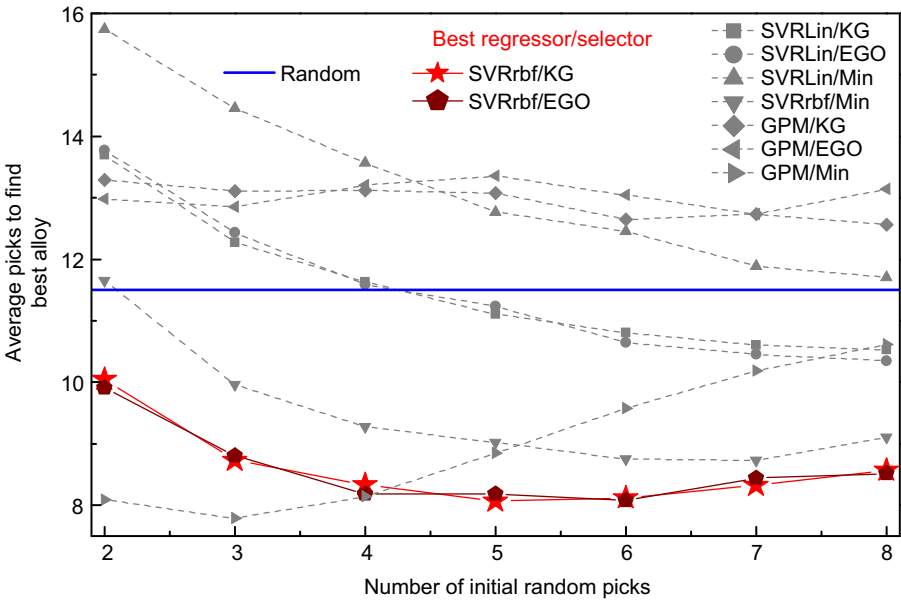


Figure 16.6 Comparison of various surrogate model:utility function combinations. The average number of picks required and the best alloy in the training set were plotted as a function of the number of initial random picks from the training data. The best surrogate model:utility function combination is SVRrbf:KG or SVRrbf:EGO.

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measured ΔT values, serving as our training dataset. Based on our domain knowledge, the features were chosen to be Zunger's pseudopotential radii, Pauling electronegativity, metallic radius, valence electron number, Clementi's atomic radii, and Pettifor chemical scale, which have been utilized in the past for classification and prediction problems involving transition metal elements. Similarly, each alloy in our composition space was uniquely described as a mole fraction of each of these features.

In Fig. 16.6, we show the relative performance of various combinations of the surrogate machine learning model and the utility function on the initial 22-alloy NiTi SMA training dataset. Three surrogate models used in this study include a Gaussian process model (GPM), a support vector regression with a radial basis function kernel (SVRrbf), and a support vector regression with a linear kernel (SVRLin). Besides EGO, we also employed the knowledge gradient (KG) as an utility function, which defines $f(\mu, \sigma) = \sigma[\varphi(z) + z\Phi(z)]$, where $z = (\mu - \mu^{**})/\sigma$, μ^* is the maximum value observed so far in the training set, μ^{**} is the maximum value of either μ^* or μ' , and μ' is the maximum predicted value in the virtual set. Since it is a minimization problem, the utility function of MIN chooses the material with minimum predicted value. The goal here is not to find the best material in the unexplored dataset, but to evaluate which combination of the surrogate machine learning model and the utility function should be used for this particular dataset. Our results indicate that SVRrbf:KG is the

best combination for modeling the NiTi SMA dataset and all data presented are based on these rigorous tests. After four initial random picks, SVRrbf:KG and SVRrbf:EGO outperformed every other combination. We thus chose the SVRrbf:KG combination for adaptive design.

In contrast to the earlier transformation temperature example, where at the end of each iteration loop we identified one new composition for validation, here we predict four alloys using the “Kriging believer” algorithm as our experimental setup allowed for the synthesis of four compounds at a time. This involved choosing the first alloy as before but the second choice was made after augmenting the training set with the predicted value of the first alloy, treating it as the actual measurement. This procedure was repeated for the third and fourth choices. Samples in the training set without martensitic transformation were given a ΔT value of 30, which is near the worst value found in the 22 measured alloys. Samples were synthesized with the predicted compositions and their ΔT values measured following heating and cooling protocols using differential scanning calorimetry (DSC).

The results of nine design iterations are shown in Fig. 16.7. Fig. 16.7(a) shows how the experimental and predicted ΔT change with successive iterations. The range of ΔT , $\max(\Delta T) - \min(\Delta T)$, is large in the first two iterations, suggesting the exploration of the algorithm. It becomes smaller in iteration 36, indicating that a global minimum is possibly reached. But it increases from the seventh iteration onward, which means the occurrence of reexploration. From the third iteration onward, we found new alloys (nine in total) with ΔT smaller than 3.15K (the best value in our original training set in every iteration). One of the alloys, $\text{Ti}_{50.0}\text{Ni}_{46.7}\text{Cu}_{0.8}\text{Fe}_{2.3}\text{Pd}_{0.2}$, discovered in iteration 6 had a ΔT of 1.84K, surpassing the best value in the training data by 44%. Fig. 16.7(b) shows how the measured ΔT distributed along with the average valence electron number (one of the features used). There are two local minima in the valence electron number, one at 6.95 and the other at 7.13. The new alloys after iteration 3 are coned to an apparent minimum in the narrow interval around 6.95. Thus, SVRrbf:KG predominantly explores the minima for the valence electron number at 6.95, which eventually led to the discovery of the $\text{Ti}_{50.0}\text{Ni}_{46.7}\text{Cu}_{0.8}\text{Fe}_{2.3}\text{Pd}_{0.2}$ alloy. In addition to a very low ΔT , the transformation temperature of the best alloy found M_S (282.6K) is 60K higher than that of the smallest reported alloy, AuCuZn. The decrease in ΔT also improves the fatigue properties and shows good thermal stability with relative shifts of the transformation temperature 0.02K after 60 thermal cycles.

The outcome of the machine learning allows us to gain insight into the mechanism underlying a low ΔT . Guided by Fig. 16.7(b), we selected three alloys, $\text{Ti}_{50}\text{Ni}_{34}\text{Cu}_{16}$, $\text{Ti}_{50}\text{Ni}_{34}\text{Pd}_{16}$, and $\text{Ti}_{50}\text{Ni}_{46}\text{Fe}_4$ with valence electron numbers 7.16, 7, and 6.92, respectively, and for which ΔT is already known. We performed DFT calculations to compare the total energies of NiTi-based martensite (M) and austenite (A) phases as a function of Cu, Pd, and Fe substitutions. The $\text{Ti}_{50}\text{Ni}_{34}\text{Cu}_{16}$ and $\text{Ti}_{50}\text{Ni}_{46}\text{Fe}_4$ alloys fall in the two minima (in Fig. 16.7(b)) and $\text{Ti}_{50}\text{Ni}_{34}\text{Pd}_{16}$ corresponds to a data point away from the minima. In addition, the SME in $\text{Ti}_{50}\text{Ni}_{34}\text{Cu}_{16}$ and $\text{Ti}_{50}\text{Ni}_{34}\text{Pd}_{16}$ arises from the B2 $\rightarrow$ B19 transformation, in contrast to $\text{Ti}_{50}\text{Ni}_{46}\text{Fe}_4$ which undergoes a B2 $\rightarrow$ R transformation. Our $\text{Ti}_{50.0}\text{Ni}_{46.7}\text{Cu}_{0.8}\text{Fe}_{2.3}\text{Pd}_{0.2}$ has a valence electron number of 6.95, which is in close proximity to $\text{Ti}_{50}\text{Ni}_{46}\text{Fe}_4$. We find that as the energy difference between the martensite (M) and austenite (A) phases (ΔE^{M-A}) in the three alloys

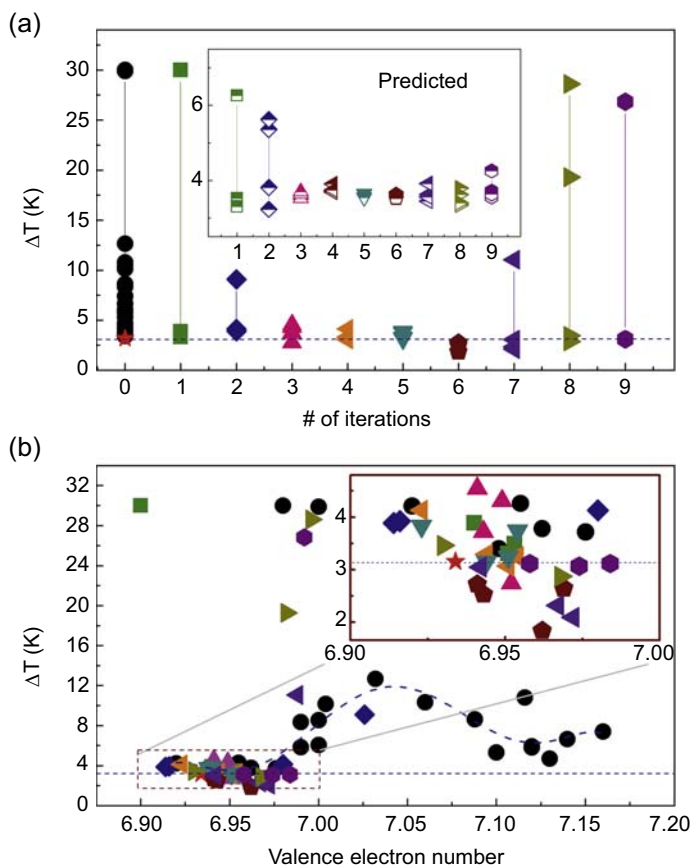


Figure 16.7 (a) The experimentally measured values of thermal hysteresis (ΔT) as a function of the number of iterations of the loop of Fig. 16.1. The inset of (a) is the predicted values of ΔT . Iteration 0 is the initial training set of 22 alloys. At each iteration (from one onward), four new predicted alloys are synthesized and their ΔT are measured. The range of ΔT , $\max(\Delta T) - \min(\Delta T)$, is large in the first two iterations, becomes smaller in iteration 36, and increases from the seventh iteration onward. (b) The ΔT as a function of the valence electron number feature shows that the exploration after iteration 3 is connected to an apparent minimum in the narrow interval. The inset of (b) zooms in the range of valence electron number between 6.9 and 7.0.

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decreases, T also decreases and we conjecture that very little activation energy is required to transform between $M \leftrightarrow A$. In the DSC measurements, the origin of the main peak is attributed to the R phase. We hypothesize that the low ΔT in $\text{Ti}_{50.0}\text{Ni}_{46.7}\text{-Cu}_{0.8}\text{Fe}_{2.3}\text{Pd}_{0.2}$ arises from the (near) optimal concentration of Fe (3 at%), which stabilizes the R phase.

16.4 Summary

We have demonstrated how BGO can be applied to accelerate the process of finding materials, such as SMAs, with desired properties using a surrogate model together with a utility function. After reviewing the salient aspects of BGO as a two-step process involving a surrogate model and a utility function, we considered different estimates of uncertainty. In particular, using a random forest model, we compared the Infinitesimal Jackknife estimate of uncertainty to the well-known standard deviation estimate on two sets of high-quality experimental data of similar size. For the piezoelectric data, we find that the two estimates are consistent with each other. However, for the SMA data, the estimates diverge appreciably with the standard deviation being an overestimate compared to the Jackknife. Thus, different estimates for calculating uncertainties behave differently, and clearly this is data dependent. Given that the true estimates of uncertainty for the datasets are not known, this raises a number of questions as to what the appropriate uncertainty measures should be for given datasets with unknown population distributions in cases where different estimates are not consistent with each other. Our work should motivate further studies as uncertainties impact the outcome of experimental design. In this regard, we have considered a number of utility functions and showed how the choice of utility function impacts the number of new measurements or iterations that need to be performed. We have also reviewed applications of BGO to the accelerated discovery of SMAs with the smallest hysteresis and large transition temperatures. Iterative feedback involving synthesis and characterization of materials is costly and emphasizes the need for strategies to minimize the number of experiments that need to be performed. In our review of applications to SMAs, we have shown how new multicomponent compounds with large transition temperatures, as well as those with the smallest hysteresis, can be discovered rapidly with predictions using BGO that are not far removed from the experimental findings. In both cases, the utility function that balances the trade-off between exploration (using uncertainties) and exploitation (using only inference model predictions) gives the optimal criterion for the design of the next experiment. Some of our newly found alloys have both very low ΔT and relatively high MS. But the achievement of the two good properties in one alloy was not by design and methods such as multiobjective optimization [49] could lead to further improvement in optimizing both MS and ΔT (or other properties such as transformation strain, damping capacity, and output work of SME and SE).

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An experimental approach for enhancing the predictability of mechanical properties of additively manufactured architected materials with manufacturing-induced variability

17

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17.1 Introduction

Architected materials derive their unique properties primarily from the arrangement of their constituent material(s) rather than the composition of the materials themselves. Lattice structures and honeycomb materials, for example, arrange material in truss-like networks that offer exceptional trade-offs between density and effective stiffness that are difficult to achieve in any other way. In addition, these materials typically offer high levels of mechanical energy absorption because their cells collapse progressively when the applied mechanical loading exceeds the yield strength of the structure. The same voids that contribute to low density and high levels of energy absorption also promote convective heat transfer, acoustic dampening, and many other properties, such that these materials can be very effective for multifunctional applications.

The surge in recent interest in architected materials can be attributed to the increasing prevalence and maturity of additive manufacturing (AM) processes, which are crucial for fabricating these materials. AM is defined by ASTM as “the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies [1].” AM technology is now available to fabricate architected materials from a variety of metals, thermoplastics, and thermosets, as well as functionally graded combinations of materials and composite precursors loaded with fibers, particles, and other additives.

The most common fabrication route for *metallic* architected materials is metal powder bed fusion (PBF). Metal PBF systems fabricate parts by selectively melting metallic powders, layer-by-layer, in a surrounding powder bed. To fabricate each layer, a laser or electron beam scans the surface of the powder bed to impart enough energy to melt powder in the desired cross section of the part. A powder delivery system delivers another layer of powder, and the process continues with the next layer. The metal PBF machine maintains an inert atmosphere to prevent oxidation. The parts are typically anchored to a build plate via a network of support structures. The support structures serve two primary roles: (1) preventing distortion and warping of the parts due to residual thermal stresses, which are caused by melting and cooling of successive layers and (2) providing favorable, high thermal conductivity boundary conditions for melting of subsequent layers, which prevents vaporization of powder.

The layer-based melting of the metal PBF process, combined with the lack of effective feedback control mechanisms in most commercial machines, leads to defects in fabricated parts. Those defects, in turn, affect the mechanical performance of resulting parts. Some of the most common defects include porosity and incompletely melted powder particles. If they occur on the surface, they are typically characterized as surface roughness; if they occur within the part, they are typically characterized as porosity. Porosity and surface roughness correlate strongly with strength and ductility [2–5]. Pores or incompletely sintered holes or channels serve as nucleation sites for crack initiation and growth, thereby limiting the strength and ductility of the part.

These defects are typically associated with process parameters that affect the energy density of the laser/electron beam scan, such as laser power, scan spacing, scan speed, and general scan strategy (i.e., the scan pattern on the surface of the powder bed) [2,6–16]. Insufficient energy density can result in unsintered powder; excessive energy density can result in metal evaporation and ejection of liquid metal from the melt pool, leading to porosity. Furthermore, with the lack of effective feedback control in many commercial metal PBF machines, these processing parameters can vary from vendor-to-vendor, machine-to-machine, and build-to-build, as well as with location within the build chamber [17–19]. In addition, the material composition and morphology can influence these defects. For example, the powder size distribution strongly influences meltability/sinterability, with larger particles requiring more energy to melt, resulting in undesirable segregation of melted/resolidified material and unsintered particles [20,21].

Some of the same process parameters that cause defects also influence the microstructure of the resulting part (cf. [22,23] for comprehensive reviews). The rapid cooling rate during solidification of metal PBF parts typically leads to nonequilibrium microstructures and significant residual stresses. Stress relief heat treatments and/or hot isostatic pressing (HIP) are often performed on parts after removal from the machine. These treatments are important for relieving the residual stresses, and in the case of HIP, reducing internal porosity, thereby increasing the toughness and fatigue strength of the resulting parts. However, even with postprocessing treatments, mechanical properties, especially strength and ductility, typically vary

significantly across machines, as well as across builds and within builds on the same machine. For example, Salzbrenner et al. [24] utilized a high-throughput testing procedure to investigate the yield strength, ultimate strength, and ductility of approximately 100 DMLS (direct metal laser sintering) samples from each of two vendors. They found slightly lower strength and ductility versus wrought samples, on average, but much more variation in the AM samples, which they attributed to factors such as surface roughness and porosity from lack of fusion.

These defects cause not only discrepancies between as-built and as-designed material properties but also between as-built and as-designed *geometry*, especially for small features. In a follow-on study to the work of Salzbrenner et al., for example, the as-built dimensions of batches of high-throughput tensile specimens differed by approximately 4% from their as-designed dimensions of 1 mm by 1 mm [25]. Yan et al. [26] found even greater deviations for SLM (selective laser melting) struts, with the percent deviation from as-designed strut diameter increasing with decreasing strut diameter. Cansizoglu et al. [27] demonstrated that strut diameter and surface roughness increase with decreasing inclination angle (relative to the build platform) for individual struts of equivalent nominal diameter. Weissman et al. [28] found similar size deviations for SLM struts and noted that deviations from a circular cross section worsened with decreasing strut diameter. Similarly, surface roughness and porosity have been found to worsen with decreasing inclination angle [27,29], and porosity of a given size occupies a much larger fraction of the cross-sectional area of a smaller strut, exacerbating the effect of the porosity on strength and ductility [24].

These strut-level defects can have a significant effect on the performance of a lattice structure that comprises periodically repeating arrangements of struts. Wang and McDowell [30] found that effective shear strength and yield strength in compression decrease nonlinearly with the percentage of cell walls that are removed or broken at random locations within the honeycomb and that the sensitivity depends on the cell topology. In contrast, Wang and McDowell found that the effect of defective cell walls on the effective elastic *stiffness* of honeycombs can be linear for stretch-dominated cell topologies, such as triangular cells, and Liu and Liang [31] found that the relationship between the percentage of defective cell walls (in a honeycomb) or struts (in a lattice) and the effective elastic stiffness depends strongly on the spatial arrangement of the defects, such that surrounding cell walls or struts compensate more effectively for multiple defects that align with one another. Other authors have reported similar findings (e.g., [32–34]). In response to some of these findings, Seepersad et al. [35] designed unit cell topologies that are more robust to these defects than standard topologies and demonstrated that different types of defects can place conflicting demands on the cell topology.

Additively manufactured lattice structures exhibit a much broader range of defects than missing cell walls or struts, however, including surface roughness, porosity, warpage, and shrinkage or expansion of dimensions, as described previously. As a result, it is important to investigate the impact of these defects experimentally in additively manufactured samples. Carlton et al. [36], for example, subjected octet

truss unit cells to compressive loading coupled with in situ synchrotron radiation microtomography, which showed that some struts exhibited greater strain than predicted, and they hypothesized that the phenomenon was caused by imperfections in surrounding struts. Cansizoglu et al. [27] fabricated hexagonal lattice structures via electron beam melting and found that compressive strength varied by as much as 10% or more among equivalent samples loaded in the same direction relative to the build direction, but their sample size was small (two to three specimens). Mazur et al. [37] documented significant variations in compressive strength and Young's modulus as a function of the number of unit cells for specimens with 10 or fewer unit cells in each principal direction, thereby confirming theoretical predictions that converged compressive behavior requires a minimum of 7 unit cells per direction [38]. Wauthle et al. [29] fabricated lattice structures with diamond-like unit cells via SLM and found that build direction influenced the compressive stiffness and strength of the lattice structures significantly (35%, on average).

Stochastic variations in the properties and performance of architected materials is a serious challenge to the extent that some companies are hesitant to utilize architected materials, especially for structural applications, because it is difficult to predict their mechanical properties accurately. One approach for addressing this challenge is capturing higher fidelity geometric models of additively manufactured lattice structures to inform structural finite element analysis (FEA). Previous work has demonstrated that the discrepancy between experimental testing and FEA predictions of mechanical properties can be reduced by building three-dimensional finite element models directly from CT scans of an additively manufactured metallic lattice structure or by statistically characterizing each of the geometric defects and building stochastic finite element models of the metallic lattice structure [39–42]. These investigations demonstrated that the discrepancy can be reduced by as much as an order of magnitude, resulting in predictions of effective mechanical stiffness and strength that agree with experimental results within approximately 5%–10%. (Similar approaches have been demonstrated for polymer lattice structures fabricated via material extrusion [e.g., [43]], but the focus in this paper is on metallic lattice structures fabricated via metal PBF, which introduce different types of imperfections.)

The difficulty with the model-based approach, however, is that it is computationally expensive to perform stochastic FEA of large lattice structures and to gather and process the CT data required as input to the stochastic FEA. In this work, a simpler strategy is adopted, focused on mechanically characterizing the struts themselves and then building finite element models of the lattice structures based on the as-built mechanical properties of the struts. The strategy is described in greater detail in the following section. Implementation of the strategy begins by investigating the repeatability and predictability of the mechanical properties of periodic octet truss lattice structures fabricated with DMLS and loaded in compression. Then, variability in strut-level mechanical and geometric properties is characterized experimentally, and the results are utilized to enhance the predictability of the mechanical properties of periodically repeating lattice structures.

17.2 A strategy for predicting the mechanical properties of additively manufactured metallic lattice structures via strut-level mechanical property characterization

The conventional approach to modeling lattice structures is illustrated in Fig. 17.1. In this approach, the design engineer assumes that the AM process fabricates bulk material that is arranged into unit cells, which are organized into lattice structures. The mechanical properties of the bulk material are characterized using standard ASTM testing procedures to evaluate Young's modulus, yield strength, ultimate strength, elongation at break, and other mechanical properties for the base material (e.g., 17-4PH stainless steel, Ti-6-4) and process of interest (e.g., DMLS, SLM). The material properties could be generically agnostic to processing parameters, or they could be distinguished by build orientation, location on the build chamber, or other processing parameters of interest to the designer. However, the primary assumptions are that (1) the properties, as derived from standard tensile bars, are representative of the mechanical properties of the material when fabricated in the form of small struts and (2) the geometry of the struts and their arrangement into unit cells match as-designed specifications precisely. All of the process-induced variability is assumed to be captured in the bulk material properties of the standard tensile bars. This approach is implemented in Sections 17.3 and 17.4, where it is found to overestimate the properties of lattice structures by 30%–40%, which is in agreement with similar studies reported in the literature [40,41].

A refined approach to modeling lattice structures is illustrated in Fig. 17.2. In this approach, the design engineer assumes that the AM process is responsible for variability in not only the base material properties but also the effective mechanical

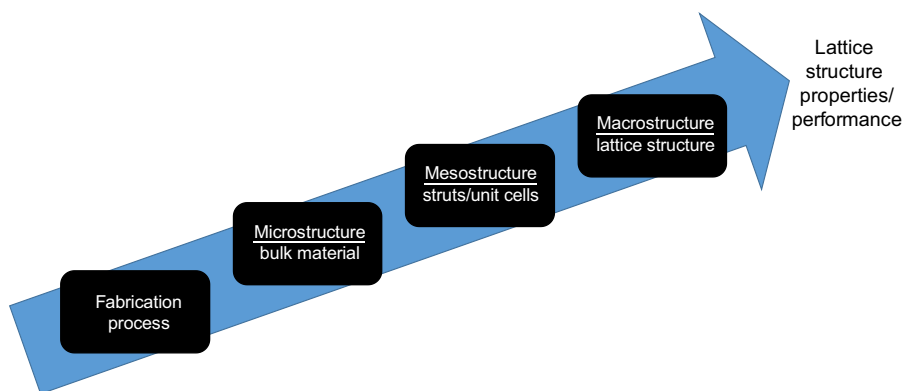


Figure 17.1 A conventional approach for modeling lattice structures. Estimates of bulk material properties for a specific fabrication process serve as input to unit cell models; effective or homogenized unit cell properties serve as input to large-scale lattice structure models. No process-induced variability is explicitly modeled.

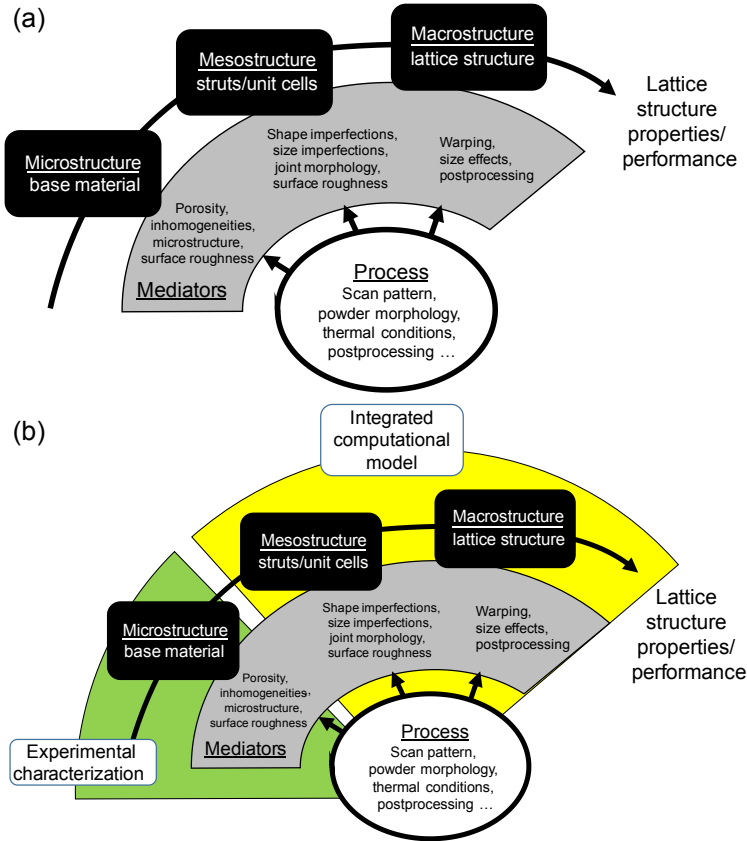


Figure 17.2 (a) A refined approach to lattice structure modeling that explicitly considers the effect of process-induced variation on the behavior of the lattice structure and its fundamental constituents. (b) An integrated computational modeling approach that models struts, lattice structures, and their imperfections concurrently. (c) An upscaling computational modeling approach that creates separate stochastic models of the mesostructure and then utilizes them in macroscale models. (d) The approach utilized in this research in which experimental characterization of struts generates effective strut-level properties that serve as input to the macroscale lattice structure models.

properties of the struts themselves and the unit cells in which they are arranged (i.e., the mesostructure). In this paradigm, small changes in processing conditions can induce significant changes in effective mechanical properties via a wide variety of mediating factors. As shown in Fig. 17.2, those mediators include porosity, inhomogeneities, microstructural changes in the base material, and surface roughness, shape imperfections, size imperfections, and joint morphology in the mesostructure. These mediators, in turn, are affected by processing conditions such as scan pattern, laser power, powder morphology, thermal conditions during the build, postprocessing steps (heat treatment, HIP), part orientation, build density, and feature and part sizes.

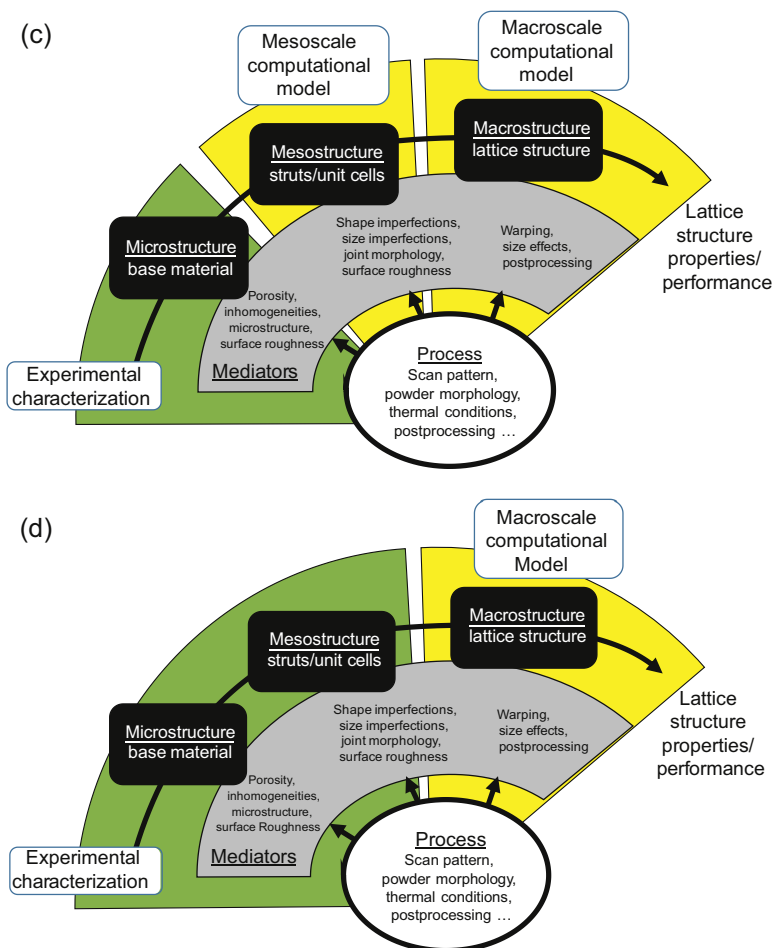


Figure 17.2 cont'd.

Given the wide variety of mediating factors, it becomes very challenging to predict the mechanical properties of a lattice structure accurately. There are at least three categories of approaches to address this challenge, as outlined in Figs. 17.2(b–d). The first approach (Fig. 17.2(b)), discussed briefly in the introduction, relies on integrated computational modeling of individual struts assembled into a large-scale lattice structure [40,41,44]. Mediating factors, such as shape and size imperfections, are characterized typically from CT scans of representative lattices; their statistical distributions are quantified; and those distributions serve as inputs to stochastic FEA of an expansive lattice structure comprised of a large number of “imperfect” struts. The second approach (Fig. 17.2(c)), also known as stochastic upscaling [45], relies on building models of the homogenized or effective mechanical properties of unit cells, which capture the variability in their performance. These statistical effective models are then used to determine the properties of the

overall lattice structure. The deterministic version of this approach is used widely for computationally efficient analysis of lattice structures and honeycomb materials [46,47]. The benefit of this approach is its computational efficiency relative to integrated approaches because it is not necessary to model stochastic fine-scale features directly when evaluating the properties of a complex lattice structure; homogenized or effective models of the struts or unit cells are used, instead. The third approach (Fig. 17.2(d)), which is adopted in this research study, relies on building experimental models of the effective mechanical properties of struts and utilizing those empirical models as direct input to computational models of an overall lattice structure. This approach is more computationally efficient than other approaches because it does not require any simulation of fine-scale features. Significant experimentation is required, however, to build the empirical models of strut behavior. This approach is implemented in Sections 17.5 and 17.6, where it is found to estimate the mechanical stiffness of lattice structures with an order of magnitude less error than the standard approach depicted in Fig. 17.1.

In summary, the focus of this research is to demonstrate the approach depicted in Fig. 17.2(d) and contrast it with the conventional approach illustrated in Fig. 17.1. The conventional approach is implemented in Sections 17.3 and 17.4. Specifically, Section 17.3 describes fabrication and testing of lattice structures and standard tensile bars. Section 17.4 reports the results of FEA of the lattice structures based on the bulk properties derived from the standard tensile bars and compares those lattice structure properties to the experimental results. The approach depicted in Fig. 17.2(d) is implemented in Sections 17.5 and 17.6, which describe experimental testing of strut-level tensile specimens and incorporation of the experimentally derived effective mechanical properties of the struts into a more refined FEA of the lattice structures.

17.3 Experimental investigation of the mechanical properties of DMLS octet lattice structures

To investigate the mechanical properties of DMLS octet truss lattice structures, a test specimen was designed and fabricated. As illustrated in Fig. 17.3, the compression test

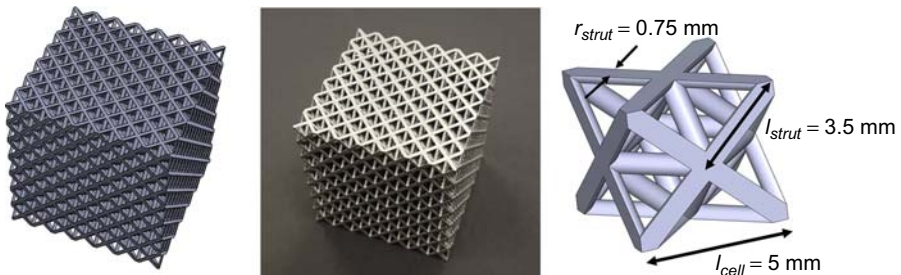


Figure 17.3 Compression test part as-built (left) and as-designed (middle) with as-designed dimensions of a unit cell (right).

specimen comprised $7 \times 7 \times 7$ octet truss unit cells. Each individual strut was 0.75 mm in diameter, and each octet cell was 5.0 mm in height, width, and depth, resulting in a $35 \times 35 \times 35$ mm lattice structure and 22% theoretical relative density. Strut and cell sizes were selected according to the results of a bridge test described in the appendix.

17.3.1 Fabrication of octet truss lattice structures and tensile bars

All compression specimens were fabricated by a commercial vendor, Stratasys Direct Manufacturing, on a single EOS M270 DMLS machine with 17-4PH stainless steel, a 40- μ m layer height, and standard EOS settings for this material. After fabrication, the parts were bead-blasted and solutionized and stress relieved for 1 h at 1900°F prior to removal from the build plate. After removal from the build plate, half of the parts underwent HIP at $2125 \pm 25^\circ\text{F}$ and 14.75 ± 0.25 ksi for 240 ± 60 min and then solutionizing again at 1900°F for 1 h. Then, all parts underwent a precipitation heat treatment at 1150°F for 4 h. Ten compression specimens (5 with HIP and 5 without HIP treatment) were fabricated in one build, followed by a second duplicate build for a total of 20 compression specimens. Four tensile bars were built in the second build, with three of them receiving the standard heat treatment with HIP and one receiving the standard heat treatment without HIP. The fabricated specimens are summarized in Table 17.1.

17.3.2 Dimensional accuracy and relative density analysis of octet truss lattice structures

Prior to testing, the octet truss lattice structures were analyzed for dimensional accuracy and relative density. Ten measurements of strut diameter were collected from

Table 17.1 Summary of fabricated octet truss lattice structures and standard tensile bars.

Octet truss lattice structures				
# Samples (total = 20)			As-designed strut diameter, r_{struts} in mm	Mean as-built strut diameter, r_{struts} in mm
	HIP	No HIP		
Build 1	5	5	0.75	0.76
Build 2	5	5	0.75	0.68
Standard tensile bars (ASTM E08)				
# Samples (total = 4)			As-machined gauge width in mm	As-machined gauge length in mm
	HIP	No HIP		
Build 1	0	0	NA	NA
Build 2	3	1	12.5	50

each specimen. The 10 struts were randomly selected from different faces and strut orientations on each specimen. The measurements were limited to struts on external faces of the cube, so they could be made with digital calipers (0.025 mm resolution). Strut diameters were found to differ significantly ($P < .05$) between builds. Average strut diameter and 95% confidence interval for build 1 was 0.76 ± 0.003 mm versus an average for build 2 of 0.68 ± 0.003 mm. Build 2 strut diameters were much smaller than the strut diameters of 0.75 mm specified in the design. The shift in mean strut diameter is most likely due to small changes in machine tuning from build to build given that the builds were fabricated by the same machine but several months apart. Mean values of as-built strut diameters are recorded in [Table 17.1](#).

Density measurements were collected using the Archimedes method for all compression specimens from build 1; specimens from build 2 were not measured. The measurements were repeated five times and averaged. The results are reported in [Table 17.2](#). The “density” column reports the mass of the lattice divided by its bounding volume. The “relative density” column reports the density of the solid material within the lattice structure itself as determined by the Archimedes method. A t-test reveals a statistically significant difference ($P < .05$) between the density of the HIP specimens and the specimens without HIP, as demonstrated by the mean values and the 95% confidence intervals reported in the table. As expected, the HIP specimens are denser with a relative density of 99% compared to a density of 97% for their counterparts without HIP.

17.3.3 Tension testing of standard tensile bars

In preparation for testing, the tensile bars were machined to the ASTM E08 standard (sheet-type with 12.5 mm gauge section width) from larger blocks fabricated alongside the lattice structures. This procedure is in agreement with ASTM standards for various metallic AM materials (e.g., Section 11 of [48]). Some postbuild machining is required to separate the tensile bars from their support structures/anchors, but postbuild

Table 17.2 Density measurements of build 1 compression specimens.

	Density (kg/m ³)		Relative density (%)	
	No HIP	HIP	No HIP	HIP
	7681	7759	98.12	99.11
	7566	7760	96.65	99.13
	7606	7830	97.15	100.02
	7520	7698	96.06	98.33
	7608	7726	97.18	98.69
	7596	7755	97.03	99.06
Mean				
95% C.I.	±73.8	±61.2	±0.94	±0.78

machining also tends to reduce the effect of surface defects on the bulk material properties [22]. All tensile bars were oriented parallel to the build platform during fabrication.

The tensile bars were tested in uniaxial tension on an MTS 1125 servohydraulic load frame at a displacement rate of 0.855 mm/min. The Young's modulus, 0.2% offset yield strength, and ultimate yield strength were determined from the stress—strain data, and mean values and population standard deviations are recorded in Table 17.3. The modulus was calculated via a linear fit to stress—strain data for stress values in the linear region (300–600 MPa), and the 0.2% offset yield strength was calculated via a 0.2% offset from the linear fit. The yield strength and ultimate tensile strength were remarkably consistent from specimen-to-specimen, as indicated by the small standard deviation, but the modulus demonstrated greater variability. The yield and ultimate strengths showed close agreement with previously reported as-built yield and ultimate strengths of 860 and 886 MPa,¹ respectively, for parts built parallel to the build platform. It is possible that the H1100 precipitation heat treatment could have altered those values relative to the as-built condition.² These results indicate that some deviation in stiffness between different lattice structures could be attributed to variability in the Young's modulus of the base material; however, the base material itself cannot explain significant variability in peak loading.

17.3.4 Compression testing of octet truss lattice structures

Compression specimens were interrogated via compression testing to failure to evaluate the stiffness, peak force, and failure behavior of the specimens. The failure testing was conducted on an MTS C64-206 load frame with a 2000 kN capacity. The test was displacement controlled. Loading was incremented at a displacement rate of 2.0 mm/min and stopped after the load exceeded 200 kN. The compression tests were conducted with the loading applied parallel to the build direction of the lattice structure, such that the individual layers of the additively manufactured lattice structure were oriented parallel to the compression platens. The force—displacement behavior of all specimens is plotted in Fig. 17.4, along with a magnified view of the

Table 17.3 Summary of tensile bar mechanical properties.

	Modulus [GPa]	UTS [MPa]	Yield strength [Mpa]
Mean	151.7	948.5	841.0
Standard deviation	33.95	3.42	5.89

¹ EOS, Material Data Sheet, Industry Line 17-4PH.

² The standard acceptable values of yield and ultimate strength are 790 and 965 MPa, respectively, for H1100 heat treatment of 17-4PH (Source: <https://www.aksteel.com/sites/default/files/2018-01/174ph201706.pdf>).

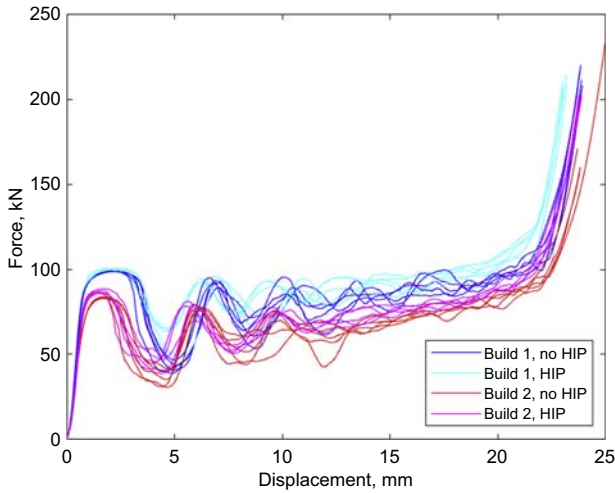


Figure 17.4 Force–displacement behavior of the lattice structures in compression.

initial strut failure event in [Fig. 17.5](#). After the initial failure event, the force–displacement plots exhibit a serrated shape, with each of the local peak forces corresponding to the collapse of an additional band of unit cells. At displacements exceeding 20 mm, densification is observed as opposing cell struts begin to contact one another, resulting in a rapid increase in stiffness. One observation to note is the remarkable consistency in the force–displacement plots of the initial failure events for compression specimens within the same build, indicating that there is much less variation in mechanical properties within builds versus across builds.

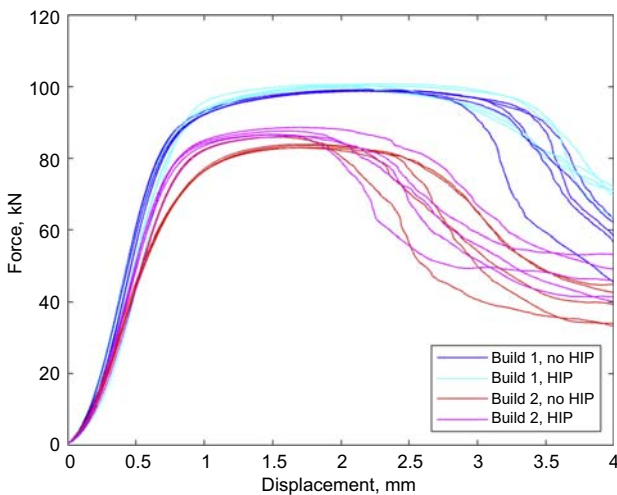


Figure 17.5 Force–displacement behavior of the lattice structures loaded in compression, highlighting the first failure event.

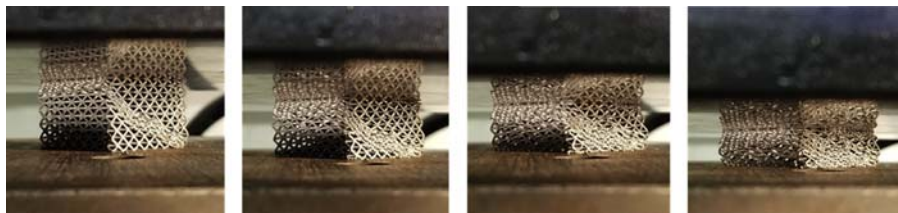


Figure 17.6 Time-lapse images of a representative compression test.

Time-lapse images of a representative compression test are illustrated in Fig. 17.6. A shear band is apparent in the lattice structure following the initial failure event and peak force. The shear band then propagates outward to encompass additional cells. Close inspection of the time-lapse images also indicates that horizontal struts are the first ones to fracture (in tension), indicating perhaps that they are experiencing greater stresses than neighboring struts of different orientations.

For each specimen, stiffness was calculated by interpolating the linear region of the force–displacement plot, and the peak force was identified as the maximum force supported by the lattice structure during the initial failure event, as shown in Fig. 17.7. Table 17.4 documents the stiffness and peak force values measured for each specimen, and Fig. 17.8 plots the mean values and standard errors for each class. An analysis of variance on the data in Table 17.4 with HIP, build, and HIP–build interactions as factors indicated that build and interaction factors are significant (P value $< .05$) for stiffness and that build, HIP, and interaction factors are significant (P value $< .05$) for peak force. The most dominant effect was the difference in stiffness and peak force between builds, with build 1 specimens exhibiting an

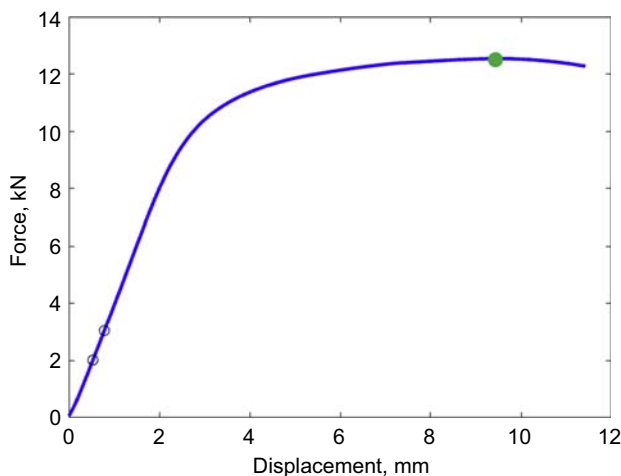


Figure 17.7 Truncated force–displacement response from a single, representative compression test. The green marker indicates the location of peak force, and the black markers indicate the region where stiffness was calculated.

Table 17.4 Compressive stiffness and peak force for all compression specimens.

		Stiffness [kN/mm]	Peak force [kN]
Build 1	No HIP	155	99.2
		157	99.1
		147	98.7
		151	98.8
		158	99.1
	HIP	136	100.5
		150	100.8
		143	99.7
		153	100.2
		134	100.1
Build 2	No HIP	113	83.6
		123	85.9
		113	83.0
		115	83.9
		114	82.9
	HIP	135	87.6
		125	86.2
		136	86.7
		130	86.6
		133	88.6

average of 25 kN/mm more stiffness and 14 kN more peak force than build 2 specimens. As discussed subsequently, the interbuild differences were primarily due to differences in the diameter of the struts. The effect of HIP on peak force was much more minor, with HIP specimens withstanding an average of 2.3 kN more force than those without HIP treatment.

17.4 Finite element analysis of the DMLS octet lattice structures based on bulk material properties

To generate some insight into the observed variability in lattice compressive behavior, an FEA of the lattice structure was performed in Abaqus (version 6.14–1). The simulation was conducted on the same $7 \times 7 \times 7$ unit cell lattice structure specified for

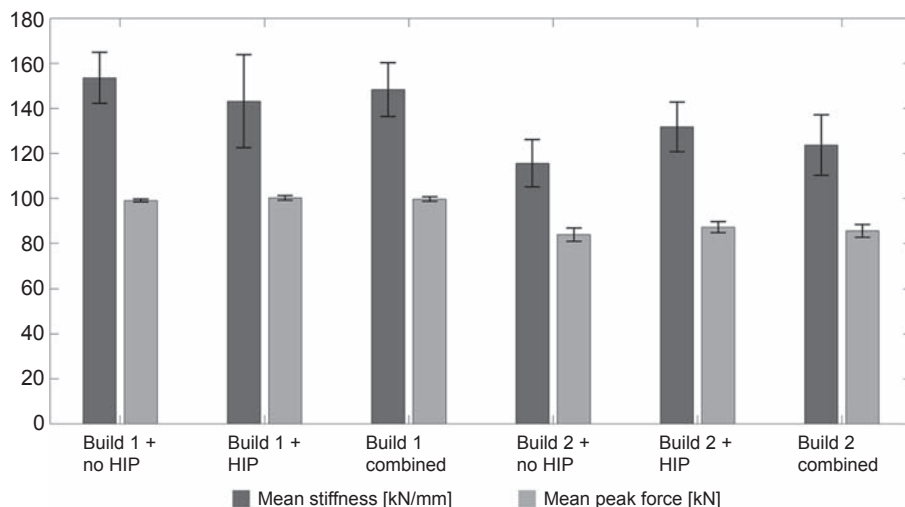


Figure 17.8 Mean values of compressive stiffness and peak force for each build with and without HIP. Error bars correspond to 95% confidence intervals on each sample mean.

fabrication and testing. Material properties were obtained from the solid tensile bars described previously, which provide a mean Young's modulus of 151 GPa. In all simulations, the Young's modulus is assumed to be symmetric in tension and compression. The beam diameters for lattice specimens were based on the average measurements described previously, namely 0.76 mm for build 1 and 0.68 mm for build 2. The boundary conditions included zero vertical displacement along the bottom surface of the lattice structure and zero horizontal displacement on one corner of the bottom surface of the lattice structure. A compressive vertical displacement of 1 mm was applied uniformly to the top surface of the lattice structure. The struts were modeled with Timoshenko (b32) beam elements. The analysis assumed small displacements and linearly elastic constitutive behavior.

A mesh convergence study was completed to determine the appropriate number of beam elements per strut. The mesh study was based on predictions of the effective stiffness of the 7×7 lattice structure, which decreased 0.27% when the mesh was refined from one to two beam elements per strut, but only 0.03% for further refinement to three beam elements per strut. Therefore, two beam elements per strut were utilized in the analysis.

Results of the FEA are reported in Figs. 17.9 and 17.10 and Table 17.5. Fig. 17.9 illustrates contour plots of vertical displacement as the lattice structure is compressed uniformly across the top surface. As expected, the displacement gradient is relatively uniform across the structure with some nonperiodic boundary effects manifesting themselves as curved displacement contours, which are visible under 1 mm of vertical displacement. As shown in Table 17.5, the FEA overpredicts the stiffness of the compression specimens by approximately 30%–40% when the material properties are based on bulk properties derived from the tensile bars. This overprediction is evident in Fig. 17.10, which facilitates comparison of the FEA predictions with the

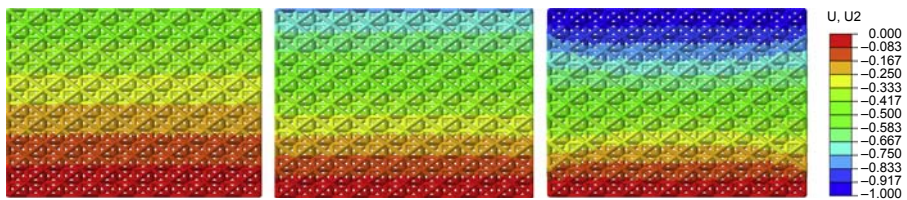


Figure 17.9 Contour plots of vertical displacement for uniform compressive vertical displacements along the top surface of 0.5 mm (left), 0.75 mm (middle), and 1.0 mm (right). In all contour plots, dark blue represents 1 mm of compressive vertical displacement, green represents 0.5 mm, and red represents 0 mm.

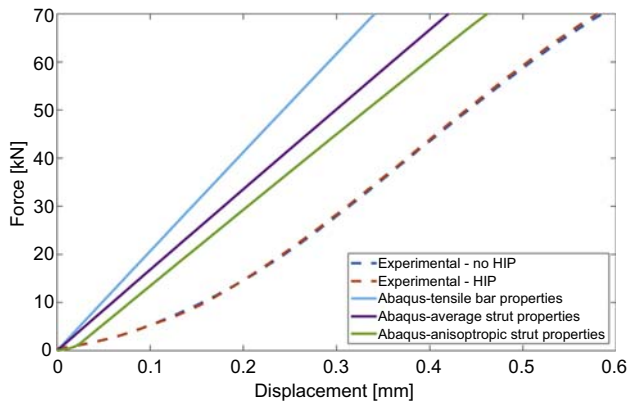


Figure 17.10 A comparison of experimental and simulated force–displacement behavior of a lattice structure. The plots are truncated to focus on the linear regime. Experimental results are based on lattice structures from build 1 with HIP (orange dotted line) and without HIP (blue dotted line).

Table 17.5 Comparison of experimental stiffness to FEA predictions.

	Build 1	Build 2
Mean experimental stiffness [kN/mm]	148	124
FEA prediction of stiffness with strut diameter corrections and ASTM tensile bar Young’s modulus [kN/mm]	208	165
% difference	40.5%	33%
FEA prediction of stiffness with strut diameter corrections and isotropic effective Young’s modulus from strut experiments [kN/mm]	166	129
% difference	12.2%	4.0%
FEA prediction of stiffness with strut diameter corrections and anisotropic effective Young’s modulus from strut experiments [kN/mm]	156	119
% difference	5.4%	–4.0%

experimental results. When comparing the FEA predictions based on material properties derived from the tensile bars (represented by the solid blue lines in Fig. 17.10) and the experimental responses for representative HIP (dashed orange) and no-HIP (dashed blue) specimens, it is evident that the specimens are less stiff than predicted because the FEA-derived force—displacement relationship is steeper than that of the experimental specimens.³

There could be several reasons for the discrepancy between the FEA predictions and the experimental observations of stiffness. As noted by previous authors, additively manufactured lattice structures are subject to a wide variety of imperfections, including under- or oversizing of strut diameters, nonuniform strut cross-sectional areas, waviness along the length of each strut, surface roughness (especially on horizontal struts), and porosity [26–29], which can have size-dependent effects on the mechanical properties of the lattice structure. To investigate this effect in depth, the mechanical properties of the struts were investigated experimentally.

17.5 Experimental investigation of the mechanical properties of DMLS lattice struts

To characterize the properties of the struts, including all of their built-in imperfections, a strut tensile sample was designed, as shown in Fig. 17.11. Multiple struts were

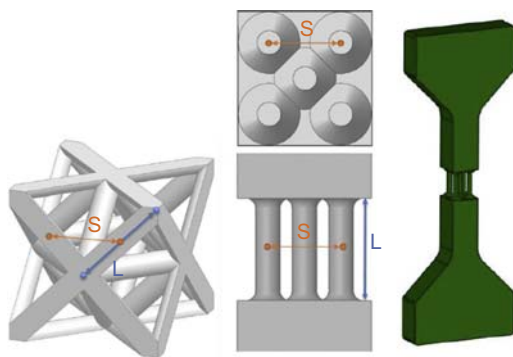


Figure 17.11 A strut tensile sample (right), the arrangement of the five struts in the gauge length (middle), and their relationship to an octet truss unit cell (left).

³ In Fig. 17.10, it is evident that the FEA underpredicts the displacement of the lattice structures. The explanation is due to imperfections in the experimental specimens. Unlike the CAD models on which the FE simulations are based, the DMLS lattice structures are not perfectly flat on the top surface. As a result, the compression platen engages the DMLS lattice structure gradually, as represented by the lower stiffness region near the origin. As the lattice structure is fully engaged, it transitions to a linear force—displacement regime.

included in each strut tensile sample because they are less susceptible than individual struts to damage during fabrication and removal from the build plate. Five struts were arranged in a staggered, symmetric pattern so that dual digital image correlation (DIC) cameras could observe all struts during tension testing; additional struts would have obscured other struts from the view of the dual cameras. The struts were arranged in parallel, as opposed to the octet unit cell arrangement on the left in Fig. 17.11, because individual unit cells are subject to distorted boundary conditions when they are tested in isolation from a periodically repeating lattice structure [49]. The length of each strut was specified as 3.5 mm to match the length of a strut in a unit cell of $5 \times 5 \times 5$ mm, as utilized in the previous lattice structure experiments, and the diameter was specified as 0.82 mm, similar to the 0.75 mm value specified for the lattice structure experiments, to correspond to a lattice structure of approximately 25% relative density.

A combination of horizontally and vertically oriented strut tensile samples were fabricated in two builds with the same machine, material, processing settings, and thermal treatment described previously for the lattice structures, enabling direct comparison with the lattice structures. The only difference was the layer height, which was adjusted from 40 to 20 μm for ease of fabrication of the delicate struts. A total of 17 strut samples were fabricated successfully: 8 oriented horizontally with struts parallel to the build plate and 9 oriented vertically with struts orthogonal to the build plate. 28 additional samples were fabricated with smaller strut diameters and lengths, but the results presented here are based on the 17 samples with dimensions most closely corresponding to those in the lattice structure unit cells. The strut samples are summarized in Table 17.6.

The samples were tension tested to failure using an MTS servohydraulic load frame at a strain rate of approximately 0.0016 s^{-1} for a test duration of approximately 1–2 min. Strain measurement was performed using DIC with software from Correlated Solutions, Inc. The gauge length for the virtual extensometer corresponded to 4x the strut diameter. DIC requires speckle contrast, which was provided by the native roughness of the strut specimens. Prior to destructive testing, all samples were nondestructively evaluated with CT to determine as-built dimensions. During CT scanning, the X-ray tube was operated at 220 kV with a copper plate in front

Table 17.6 Summary of strut tensile samples.

Strut tensile samples				
# Samples (total = 17)			As-designed strut diameter, r_{struts} in mm	Mean as-built strut diameter, r_{struts} in mm
	HIP	No HIP		
Horizontal orientation	8	0	0.82	0.79
Vertical orientation	9	0	0.82	0.79

of it to reduce noise. More than 1000 projections per specimen were collected and reconstructed with Volume Graphics software. The resulting spatial resolution was 11 μm . To determine the as-built cross-sectional area of each strut, slices of CT data were analyzed using the image processing toolbox in MATLAB, and the minimum cross-sectional area of each strut over its gauge length was determined.

The stress–strain response of each strut specimen was evaluated using as-built dimensions. Stress was calculated using the sum of the as-built cross-sectional areas of the five struts, as determined from analysis of CT data. Strain was measured from one of the five struts using DIC. Stress–strain responses for the strut samples oriented in the horizontal and vertical directions are displayed in Figs. 17.12 and 17.13, respectively. As shown, the strut specimens exhibit a region of approximately linear stress–strain response followed by an extended region of nonlinear plastic response. The extended plastic region is associated with successive failure of each of the five struts, which is associated with a series of decreasing stress plateaus.

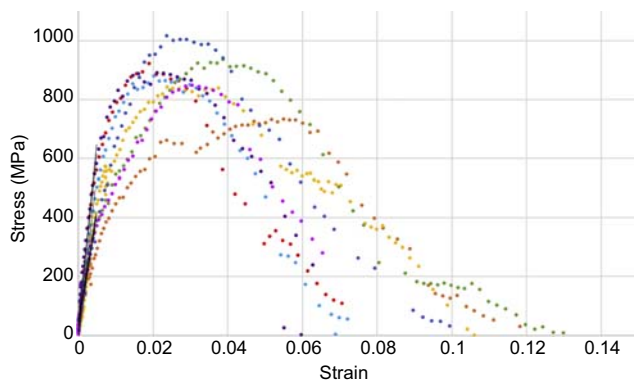


Figure 17.12 Stress–strain responses of strut specimens built in the horizontal direction, with the major axis of each strut oriented parallel to the build platform.

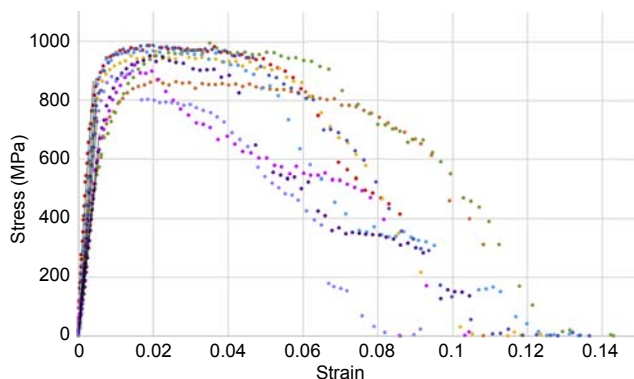


Figure 17.13 Stress–strain responses of vertical strut specimens built vertically, with the major axis of each strut orthogonal to the build plane.

The effective Young's modulus of each strut specimen was calculated via a least squares linear regression to the data in the linear region of the stress—strain response, as represented by the black lines near the origin in each plot. Stress—strain data were included in the regression for strain values less than 0.005 to include a majority of the linear region while excluding the transition out of elastic behavior. This data range resulted in an R^2 value greater than 0.93 for all regressions. The vertical specimens exhibited an average effective Young's modulus of 148 GPa with a standard deviation of 33 GPa. The horizontal specimens exhibited an average effective Young's modulus of 94 GPa with a standard deviation of 21 GPa. The reasons for these differences, along with an investigation of the corresponding differences in ultimate strength, are described fully in a companion paper [50]. In brief, an analysis of CT imaging data and subsequent fractography revealed incomplete sintering, surface roughness and porosity, and geometric waviness, all of which were much more prominent in the horizontal specimens. The effective Young's modulus value for the horizontal specimens is much smaller than the value determined from the ASTM standard tensile bars fabricated alongside the lattice structures, even though all specimens were built on the same machine, with the same material, post-processing, and heat treatment as all of the tensile bars and the same HIP procedures as the tensile bars with HIP. These results indicate that orientation and size effects are very important when determining material properties for DMLS parts.

It is also interesting to note that the stress—strain responses of the strut specimens (Figs. 17.12 and 17.13) are much more highly variable than those of the overall lattice structures (Fig. 17.4). Given that the lattice structures are collections of struts of similar size to those in the strut specimens, strut-level size effects cannot explain this disparity. As demonstrated in previous studies (e.g., [31–35]), lattice and honeycomb structures exhibit network-like effects such that surrounding struts compensate for especially damaged, undersized, or warped struts to some extent. Further research is needed to investigate the combined impact of the spatial distribution, magnitude, and type of strut-level variation on the variability of the mechanical properties of the overall lattice structure.

17.6 Finite element analysis of the DMLS octet lattice structures based on strut-level properties

The effective Young's modulus in the FEA was adjusted to match that of the strut specimens, and the FEA was repeated. First, the average of the experimentally determined effective Young's modulus for the vertical and horizontal strut specimens was utilized as an assumed isotropic value for all of the struts, regardless of orientation. Then, an anisotropic effective Young's modulus was utilized by assigning values for horizontal struts in the FEA according to the average experimental value for the horizontal strut specimen. All other angled struts were assigned an effective Young's modulus corresponding to the average experimental value for the vertical strut specimens, based on the assumption that angled and vertical struts exhibit similarly low

levels of defects, in contrast to the horizontal struts. Results of the analysis are summarized in [Table 17.5](#). As documented, the percent difference between experimental and simulated lattice structure stiffness decreased from extremely high levels (40% or more) for bulk material properties to low levels (4%–12%) for isotropic strut-level properties to extremely low levels (4%) for anisotropic strut-level properties. The improvement in prediction accuracy is illustrated in [Fig. 17.10](#), as well, where it is evident that the gradient of the force–displacement predictions derived from the FE models with updated strut-level mechanical properties (purple and green lines) match the gradient of the linear region of the experimental force–displacement behavior (dotted blue and orange lines) much more closely. The results indicate that incorporating experimentally measured size-dependent and direction-dependent material properties is important for obtaining accurate FEA predictions of DMLS lattice structure stiffness, and that incorporating those refined material properties can lead to highly accurate results.

17.7 Opportunities for expanding the experimental study to better inform the finite element modeling

The strut tensile specimens were fabricated in only one size and two orientations in this study. The study would be more comprehensive if the struts were fabricated in various orientations (e.g., 30 degrees, 45 degrees, 60 degrees) corresponding to the range of potential orientations of struts in lattice structures. It would also be interesting to more closely investigate the effect of strut size on its mechanical properties and repeat the strut-level experiments for a broad range of strut sizes. If these material properties were available, a truly direction-dependent, size-dependent, anisotropic model of strut effective stiffness could be constructed and inserted into FE models of lattice structures. Furthermore, the strut tensile specimens were fabricated in a separate build from the lattice structures. In follow-on studies, build-to-build variation could be eliminated by building all specimens in the same build, thereby isolating only size- and orientation-dependent effects. All of these factors should be varied and included in a database of size-dependent properties for use in subsequent FEA-based modeling.

Similarly, bulk properties were derived from tensile samples fabricated only parallel to the build platform. A more comprehensive study would evaluate bulk properties for various orientations and locations on the build platform. The results of those studies could be used to build an anisotropic (and potentially spatially varying) model of bulk properties to be utilized in the benchmark FE analysis.

Although the lattice structures and strut tensile specimens were loaded through failure, only linear elastic behavior was modeled and compared with experimental results. Subsequent studies should expand the comparison to nonlinear mechanical behavior. Certainly, accurate anisotropic linear models of strut-level material properties would help model the force–displacement behavior prior to failure more accurately, but strut-level elastic–plastic models, coupled with explicit FEA that

incorporates buckling and contact, would be needed to model failure/collapse of the lattice structure. One goal could be to more accurately predict the force plateaus associated with failure events. To obtain accurate failure analysis, it may be necessary to examine unit cell joints and imperfections associated with joints, such as size or shape imperfections, in addition to the strut-level investigations reported here.

17.8 Discussion

Table 17.5 documents dramatic reductions in error levels in FEA predictions of lattice structure stiffness when experimentally measured size- and orientation-dependent strut-level material properties are incorporated into the FEA simulation. These error reductions correspond to similar results reported in the literature for stochastic FEA simulations that account for defects in strut geometry by building probabilistic models of variation in strut geometry from CT imaging of the specimens [39–41]. These stochastic FEA predictions require computationally expensive, repetitive FEA of the lattice structures to sample statistically from probability distributions of the as-built geometry. Moreover, those prior approaches assume all of the deviation in lattice performance is due to geometric imperfections in the struts rather than microstructural variations. In contrast, the approach utilized in this paper utilizes simple, computationally efficient beam-based FEA with effective material properties that represent the as-built geometry more accurately. By utilizing experimentally determined strut-level properties, both geometric and microstructural deviations are combined into the effective material properties. The trade-off is that more material testing is required to obtain the as-built material properties of the struts. However, as demonstrated here, those properties can be obtained with relatively small samples that can be built alongside the lattice structures and tested rapidly and inexpensively with DIC techniques. CT imaging may not be required at all. Furthermore, if build-to-build variation is minimal or limited to geometric scaling (e.g., larger strut diameters in one build vs. another), it may also be possible to characterize the mechanical properties of struts from one build and utilize those properties across multiple builds, especially if the machine, material, build parameters, and postprocessing regimen are consistent.

More broadly, this work reinforces the need for expansive databases of material properties in the AM community. To be useful in FEA simulations, however, the properties must go beyond the bulk properties typically reported for standard engineering materials. The properties must be geometry- and orientation-dependent, ideally spanning size ranges from the smallest features buildable on a machine to large-scale features that could be expected to exhibit bulk properties and spanning a range of orientations, including the horizontal and vertical orientations investigated in this study and angled orientations between the two extremes. Since results can vary with material composition and processing parameters, this information must be reported, as well, including the chemical composition and size distribution of the constituent powders and the full suite of processing and postprocessing parameters utilized to

build the specimens. Even if all of this information is reported, data transferability can be difficult from machine-to-machine or build-to-build due to the lack of feedback control mechanisms. Enhanced monitoring and model-based control algorithms are needed to ensure that different machines build parts under similar conditions to lessen the need for repeated material characterization.

In general, one of the primary concerns among practitioners (e.g., aerospace companies) seeking to utilize lattice structures has been the lack of predictability and repeatability of AM-fabricated specimens. It is the authors' hope that the specimen-to-specimen consistency of the results reported in this chapter combined with the accuracy of the simple FEA simulations reported in [Table 17.5](#) represents a first step toward alleviating these concerns. Lattice structures, indeed, do not behave mechanically as designed, but they do behave mechanically as-built, if the as-built properties of the struts are properly characterized and incorporated into the predictive simulations.

Appendix

Prior to fabrication of the compression specimens, as described in [Section 17.3](#), unit cell and strut dimensions were informed by a bridge test focused on determining the maximum unsupported length of horizontal struts. As shown in [Fig. 17.14](#), bridge specimens were designed and fabricated with strut diameters of 2.0, 1.5, and 1.0 mm and with unsupported bridge lengths of 2.0, 2.5, 3.0, 3.5, and 4.0 mm. The bridge specimens were fabricated on the same EOS M270 DMLS machine with

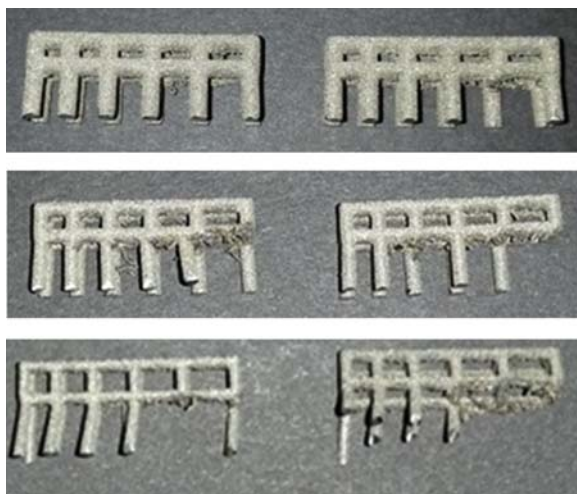


Figure 17.14 Results of bridge tests for 2 mm (top), 1.5 mm (middle), and 1.0 mm (bottom) strut diameters with unsupported bridge lengths of 2.0, 2.5, 3.0, 3.5, and 4.0 mm (left to right). Significant burning is observable for longer bridge lengths.

17-4PH stainless steel, a 20 μm layer height, and standard EOS settings for this material. Significant burn was observed for bridge lengths greater than 3.5 mm for all strut diameters. Burn occurs when struts are fabricated with no supports beneath them, resulting in vaporization and/or ejection of molten material from the melt pool. Burn manifests itself in missing material and/or extremely rough regions on the downfacing surfaces of overhanging features. To avoid significant burn, which would weaken struts, all struts were limited to a length of approximately 3.5 mm, which corresponds to a unit cell height, width, and depth of 5.0 mm.

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UNCERTAINTY QUANTIFICATION IN MULTISCALE MATERIALS MODELING

Edited by

YAN WANG AND DAVID L. MCDOWELL

Uncertainty Quantification in Multiscale Materials Modeling provides a complete overview of uncertainty quantification (UQ) in computational materials science. It provides practical tools and methods along with examples of their application to problems in materials modeling. UQ methods are applied to various multiscale models ranging from the nanoscale to macroscale. This book presents a thorough synthesis of the state-of-the-art in UQ methods for materials modeling, including Bayesian inference, surrogate modeling, random fields, interval analysis, and sensitivity analysis, providing insight into the unique characteristics of models framed at each scale, as well as common issues in modeling across scales.

Key features

- Synthesizes available UQ methods for materials modeling
- Provides practical tools and examples for problem solving in modeling material behavior across various length scales
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