

Geavanceerde moleculaire simulaties voor het computationeel modelleren
van de fasestabiliteit en thermische eigenschappen
van metaal-organische roosters

Advanced Molecular Simulations to Computationally Model
Phase Stability and Thermal Properties of Metal-Organic Frameworks

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Proefschrift ingediend tot het behalen van de graad van
Doctor in de ingenieurswetenschappen: toegepaste natuurkunde



UNIVERSITEIT
GENT

Vakgroep Toegepaste Fysica
Voorzitter: prof. dr. ir. C. Leys
Faculteit Ingenieurswetenschappen en Architectuur
Academiejaar 2019 - 2020

ISBN 978-94-6355-294-3

NUR 928

Wettelijk depot: D/2019/10.500/102

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This research has been conducted at the **Center for Molecular Modeling**, in collaboration with:

- The Dynamics and Adsorption in Porous Materials (DAMP) group at the Institut Charles Gerhardt Montpellier, University of Montpellier (Prof. G. Maurin, Prof. P. G. Yot).
- The Computational Materials Physics (CMP) group at the University of Vienna (Prof. G. Kresse).
- The Laboratory of Computational Science and Modelling (COSMO) at the École Polytechnique Fédérale de Lausanne (EPFL) (Prof. M. Ceriotti).
- The Adsorption and Advanced Materials Laboratory (AAML) at the Department of Chemical Engineering and Biotechnology, University of Cambridge (Prof. D. Fairen-Jimenez, dr. P. Z. Moghadam).
- The Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions (cMACS) at the University of Leuven (Prof. D. E. De Vos).
- The Center for Ordered Materials, Organometallics and Catalysis at Ghent University (Prof. P. Van Der Voort).
- The Department of Solid State Sciences at Ghent University (Prof. H. Vrielinck).

Voorwoord

It's the journey. Not just the destination!

Dragoman

Starten met een inspirerende reisquote over de lange weg naar dit doctoraat vond ik bijzonder toepasselijk. Niet alleen omwille van de verre bestemmingen die ik de afgelopen jaren heb mogen ontdekken, neen, vooral vanwege de boodschap die deze zin bevat. Een doctoraat is de eindbestemming van een individuele zoektocht waarin je jezelf bewijst als zelfstandig onderzoeker. Het vergt tijd om er te geraken en het eindpunt is mooi, maar het is de weg ernaartoe die herinneringen heeft gecreeërd voor de rest van het leven.

Centraal in deze herinneringen zijn mijn collega's van het Centrum voor Moleculaire Modelleren. Eerst en vooral wil ik mijn promotor, Veronique, bedanken. Bedankt voor alle kansen die ik heb gekregen en blijf krijgen om aan wetenschappelijk onderzoek te doen. Bedankt voor de mogelijkheid om deel te kunnen nemen aan interessante samenwerkingen en mij te laten groeien in mijn rol als onderzoeker, maar boven alles, bedankt om mij vanaf dag één het vertrouwen te geven. Als gids waakte u ervoor dat ik steeds vooruitgang maakte, en even belangrijk, dat onderzoek op de gepaste tijd afgerond en gecommuniceerd werd. Ik ben dankbaar dat ik zo'n gedreven en ambitieus persoon achter mij had, want zonder u was dit doctoraat nooit mogelijk geweest.

Bedankt ook aan Michel. Mijn eerste stapjes in de kwantummechanica heb ik gezet in uw allerlaatste lessen, en het is hier dat de wetenschappelijke interesse is ontstaan die mij uiteindelijk bij het CMM gebracht heeft. Zonder uw noodzakelijke bijdrage hadden verschillende projecten tijdens dit doctoraat nooit zo vlot kunnen afgerond worden. Naast uw passie voor wetenschap, deel ik ook uw interesse in sport en reizen wat steeds de aanleiding was voor aangename gesprekken. Een match van de Rode Duivels zal nooit meer hetzelfde zijn zonder een nabespreking, en ik hoop op een dag evenveel van de wereld gezien te hebben als u (al ben ik inmiddels goed op weg).

Bedankt aan mijn bureaugenoten Arthur, Steven en Sven. Bedankt Arthur om op regelmatige basis leven in de brouwerij te brengen. Het was een onvergetelijk avontuur om met jou een kantoor te delen, en ik zal er nog lang met positieve gevoelens op terugblikken. Bedankt Steven voor het oplossen van allerlei problemen en mijn werk een stuk gemakkelijker te maken. Een kantoor delen met een fervent sporter en sportliefhebber zoals jou nodigde altijd uit tot leuke gesprekken. Bedankt Sven voor de vele vruchtbare samenwerkingen. Veel van het werk in dit doctoraat was niet mogelijk geweest zonder jouw oog voor detail en jouw persoonlijke zoektocht naar actuele en uitdagende problemen. Ik hoop in de toekomst nog te kunnen samenwerken met even gedreven onderzoekers.

Bedankt Louis en Kurt om mij op te vangen als bureaugenoten tijdens de laatste maanden van mijn doctoraat. Jullie zijn gestart als begeleiders van mijn masterthesis en jullie zijn doorheen de jaren steeds aandachtige en geduldige klankborden gebleven bij mijn vele vragen en ideeën. Bedankt voor de vele toffe babbels op en naast het werk/voetbalveld.

Bedankt Aran, Alexander, Sander en Maarten. Initieel was ik veel in jullie bureau te vinden in mijn rol als begeleider, maar doorheen de jaren veranderde dit. Meer en meer kwam ik jullie mening vragen over bepaalde problemen, en bleef ik al eens plakken in jullie bureau omdat het er steeds aangenaam vertoeven was.

Bedankt Sam, Simon, Merlijn en Chiara. We zijn op hetzelfde ogenblik aan onze doctoraten begonnen, en finaal er in geslaagd om met z'n allen min of meer gelijktijdig af te ronden. Jullie waren lotgenoten van hetzelfde jaar en zeker gedurende de afgelopen maanden was onze gezamenlijke kennis over de afrondingsprocedure van een doctoraat een grote hulp voor mij.

Verder wil ik al mijn collega's op het CMM die ik doorheen de jaren heb leren kennen zowel op als naast het werk nog eens uitdrukkelijk bedanken. Ik wens ieder van jullie alle goeds voor de toekomst. Speciale dank ook aan de jonge generatie doctoraatsstudenten die er het afgelopen jaar in geslaagd zijn het leven op en naast het CMM te verfrissen met hun vele initiatieven. Tot slot, bedankt aan alle leden van FC MolMod (spelers, supporters en sponsor!) voor de leuke avonden in het GUSB.

Uiteraard heeft mijn leven zich de afgelopen jaren niet enkel op het CMM afgespeeld. Hoewel onderstaande personen misschien geen directe bijdrage aan de wetenschap in dit doctoraat hebben gebracht, waren het zij die zich ontfermden over mij op de moeilijke momenten en waren het zij die zorgden voor amusement en verstrooiing op andere dagen.

Lander, Jef, Bart en Ruben, bedankt om er gewoon altijd te zijn. We hebben de afgelopen jaren elkaar nog beter leren kennen op onze vele reizen, en ik

hoop dat we elkaar nooit uit het oog gaan verliezen. Dries, bedankt voor de jarenlange vriendschap en de vele gezellige fietstochtjes. Jens, bedankt om mij weer op te nemen in de KSV Melsen familie waar ik m'n passie voor sport volledig kwijt kan.

Bedankt aan mijn familie. Uitleggen wat ik nu ook al weer aan het doen was, was steeds een relevante oefening voor mezelf. Uitleggen of ik nu eigenlijk al iets verdiende of toch gewoon studeerde, iets minder. Bedankt aan mijn ouders, mijn zus en mijn broer om mij te steunen in alle keuzes die ik tot nog toe gemaakt heb. Het is een cliché, maar daarom niet minder waar.

J. Wieme
Gent, 10 december 2019

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Samenvatting

De ontwikkeling van innovatieve technologieën is sterk gelinkt met de beschikbaarheid en het ontwerp van geschikte materialen. Metaal-organische roosters (metal-organic frameworks of MOFs) zijn een recentelijk ontwikkelde klasse van poreuze materialen die aan veel populariteit hebben gewonnen. De keuze voor een bepaald materiaal hangt uiteraard af van de toepassing die men voor ogen houdt, en net daarom wordt er veel aandacht gespendeerd aan onderzoek naar MOFs. Deze materiaalklasse is naar voren geschoven voor een brede waaier aan hedendaagse toepassingen gaande van gasseparatie tot mechanische energieopslag. MOFs worden gesynthetiseerd door afzonderlijke anorganische en organische moleculaire bouwstenen te combineren met behulp van coördinatieverbindingen in poreuze kristallijne roosters. De ruime beschikbaarheid van moleculaire bouwstenen geeft aanleiding tot nagenoeg oneindig veel mogelijke structuren en verschillende interessante fysische en chemische eigenschappen. Deze grote verscheidenheid maakt het mogelijk om materiaaleigenschappen te gaan tunen binnen de familie van MOFs. Echter, er is een beter begrip van deze materialen nodig om ontwerp op de moleculaire schaal te realiseren.

We leven momenteel in een tijdperk met een schijnbaar onbeperkte computerkracht. Deze rekenkracht kan aangewend worden om moleculaire simulaties uit te voeren. Moleculaire simulaties zijn uitgegroeid tot een onvermijdbare techniek om inzicht te verkrijgen in materialen vanuit een microscopisch standpunt. Het is complementair aan experimenteel onderzoek, en is uitermate geschikt om de beste materialen te zoeken in de ruime klasse van MOFs. In **Hoofdstuk 1** worden MOFs geïntroduceerd als belangrijke poreuze materialen voor de toekomst. Hun exceptionele fysische en chemische eigenschappen worden toegelicht samen met een aantal potentiële toepassingen. Initieel focuste het onderzoek naar deze materialen zich voornamelijk op hun gasadsorptie-eigenschappen, maar de studie van hun intrinsieke fysische eigenschappen is steeds belangrijker aan het worden als antwoord op kritische bedenkingen voor praktische toepassingen zoals hun beperkte stabiliteit en matige warmtetransporteigenschappen.

Het doel van dit doctoraatsonderzoek is de studie van het gedrag van MOFs met behulp van moleculaire simulaties en het verkrijgen van een beter inzicht in de thermische eigenschappen en de fasestabiliteit om de industrialisering van deze materialen te bespoedigen. In **Hoofdstuk 2** wordt er een overzicht gegeven van de verschillende simulatietechnieken die toegepast zijn om MOFs op een accurate wijze te modelleren. Het centrale concept van deze technieken is steeds het potentiële-energieoppervlak (potential energy surface of PES). Dit is de wiskundige link tussen de energie van het moleculaire systeem en de geometrische coördinaten van de atoomkernen. De keuze tussen een kwantummechanische beschrijving of een klassieke krachtveldbeschrijving van het PES bepaalt in sterke mate de nauwkeurigheid die kan behaald worden. Even belangrijk zijn echter ook de tijd- en lengteschaal die kunnen bereikt worden met de huidige computerkracht. In vele gevallen is een kwantummechanisch model gelimiteerd tot zogenaamde statische methodes, terwijl krachtveldsimulaties het mogelijk maken om realistische experimentele condities te benaderen door middel van moleculaire dynamica (MD) simulaties. De keuze van de geschikte simulatietechniek wordt bepaald door de specifieke casestudy.

Twee verschillende topics werden behandeld in dit werk. Het eerste fenomeen dat onderzocht werd is het merkwaardige gedrag van zogenaamd ademende MOFs. Deze MOFs vertonen een structurele transformatie als reactie op verschillende stimuli zoals temperatuur, druk en gasadsorptie. Flexibele MOFs kunnen zo'n stimuli-responsief gedrag vertonen. Er bestaan verschillende vormen van flexibiliteit en afhankelijk van de structurele transformatie zijn er verschillende termen geïntroduceerd in de literatuur. In deze thesis ligt de focus op ademend gedrag van flexibele MOFs. In zulk geval vindt er een faseovergang plaats tussen een open (lp of large-pore) en gesloten (np of narrow-pore) toestand. Dit opmerkelijk gedrag is vergezeld van een substantiële verandering van het materiaalvolume en dit aspect zou bijvoorbeeld kunnen gebruikt worden in slimme schakelaars.

In **Hoofdstuk 3** wordt er aangetoond dat het nauwkeurig beschrijven van london-dispersie-interacties in moleculaire simulaties noodzakelijk is om resultaten in overeenstemming met experiment te verkrijgen. Dit werd gevonden voor het flexibele MIL-53(Al) materiaal dat ademt onder invloed van temperatuur. Dichtheidsfunctionaaltheorie (density-functional theory of DFT) is een populaire methode om een kwantummechanische beschrijving van een materiaal te verkrijgen. Deze methode is alomtegenwoordig in de vastestof-fysica omwille van de computationele efficiëntie voor grote systemen. Echter, in vele gevallen, faalt deze techniek in het modelleren van de zwakke london-dispersie-interacties en moet er een additief dispersiemodel bijgeteld worden. Deze beschrijving wordt ook vaak blind toegepast op flexibele MOFs, en wij

wijzen in deze thesis op een aantal belangrijke beperkingen van deze aanpak. Om dit te illustreren, in samenwerking met professor Kresse (Universiteit van Wenen), hebben we gebruik gemaakt van een veeldeeltjestechiek genaamd de willekeurige-fasebenadering (random phase approximation of RPA) die toelaat om erg nauwkeurige resultaten te verkrijgen voor een flexibele MOF. Deze geavanceerde methode combineert naadloos korte- en lange-dracht interacties, en resulteert in een excellente overeenkomst met experimentele data voor verscheidene systemen. Op deze manier toonden we voor het eerst het belang aan van een nauwkeurige beschrijving van veeldeeltjeseffecten in ademende MOFs.

Bovendien werd er in deze thesis ook een thermodynamisch model voorgesteld dat toelaat om flexibele MOFs te classificeren op basis van gesimuleerde Helmholtz vrije-energieprofielen in functie van het volume. Dit thermodynamisch protocol laat overigens ook toe om ademend gedrag van materialen te voorspellen. Dit model werd vervolgens toegepast op verschillende flexibele MOFs zoals een reeks van MIL-47 en MIL-53 materialen, waar er voornamelijk geconcentreerd werd op het verklaren van de intrinsieke flexibiliteit in afwezigheid van gastmoleculen. Dit resulteerde in de formulering van een aantal eenvoudige ontwerpregels voor MOFs die ademen onder invloed van temperatuur. Twee cruciale factoren werden geïdentificeerd: enerzijds de lange-dracht london-dispersiekrachten die de gesloten np fase stabiliseren en anderzijds de vibrationele entropie die de open lp fase domineert. Deze delicate balans verklaarde waarom voornamelijk de organische moleculaire bouwblokken (nl. de linkers) het geobserveerde gedrag domineren in MOFs zoals MIL-47, MIL-53, COMOC-2/3, DUT-4/5 en DMOF-1.

Onze theoretische toolbox bestaande uit krachtveldontwikkeling, thermodynamische modellen en moleculaire dynamica (MD) simulaties is in grote mate toegepast in samenwerking met verschillende experimentele partners. We onderzochten het gedrag van verscheidene MOFs (DMOF-1(Cu/Zn), MIL-53-FA(Al/GA)) onder mechanische druk met als doel MOFs te ontwikkelen voor mechanische energieopslag in samenwerking met onderzoekers van de DAMP groep (Universiteit van Montpellier). Voor het prototypische MIL-53(-FA) materiaal, hebben we de invloed van de anorganische bouwblok (het metaalion) op het ademend gedrag onder druk geëxploreerd. Hier vonden we dat het ademend proces irreversibel wordt (i.e. de structuur blijft in de gesloten np toestand na het verwijderen van de mechanische druk) wanneer aluminium vervangen wordt door gallium. In een tweede experimenteel-theoretische studie voorspelden we met behulp van ons thermodynamisch protocol de mogelijkheid tot een volumecontractie in DMOF-1, die alleen kan gevonden worden door middel van het uitoefenen van mechanische druk. De voorspelde excellente eigenschappen voor opslagtoepassingen (i.e. een hoge

mechanische transitiedruk en volumeverandering) van DMOF-1 inspireerde onze experimentele partners om dit materiaal effectief experimenteel te testen en hun metingen bevestigden het potentieel van DMOF-1. Tot slot, beide samenwerkingen toonden ook duidelijk aan dat theoretische modellering van MOFs een erg uitdagend domein is, waar technieken op de rand van moleculaire en vastestoffysica modellering noodzakelijk zijn.

De karakterisatie van thermische eigenschappen van MOFs is het tweede topic bestudeerd in dit werk. De thermische geleidbaarheid, de warmtecapaciteit en de uitzettingscoëfficiënt zijn belangrijke ingenieursparameters voor praktische toepassingen, maar ze zijn nauwelijks onderzocht voor MOFs. Ze zijn nochtans noodzakelijk in industriële toepassingen van MOFs als adsorptiemiddel voor gasopslag en gasseparatie. Zulke materialen worden blootgesteld aan thermische fluctuaties omdat adsorptie en desorptie van gasmoleculen het vrijkomen of verbruiken van energie impliceert. De vrijgekomen adsorptiewarmte moet snel gedissipeerd kunnen worden aangezien temperatuursveranderingen een negatieve invloed hebben op de prestatie van het materiaal.

Om de thermische eigenschappen van MOFs te kunnen berekenen in **Hoofdstuk 4**, hebben we een krachtveldbeschrijving van het potentiële energieoppervlak gecombineerd met MD simulaties. Bij MD simulaties worden de posities en snelheden van de atomen geëvolueerd door middel van de Newtoniaanse bewegingsvergelijkingen. Deze aanpak laat toe om het systeem te volgen op experimentele condities (nl. realistische drukken en temperaturen), en includeert op een correcte wijze anharmonische bewegingen van de atoomkernen. Echter, een belangrijk nadeel van deze methode is het verwaarlozen van de kwantumeffecten van de atoomkernen. Het behandelt ze als klassieke deeltjes en deze benadering is alleen van toepassing op voldoende hoge temperaturen en voor voldoende zware atomen onderhevig aan niet al te sterke interatomaire interacties. Desalniettemin moeten kwantumeffecten in rekening gebracht worden wanneer de thermische energie $k_B T$ van een gelijkaardige grootteorde is als het energieverval tussen de gekwantiseerde energieniveaus van de atomaire vibraties. Aangezien deze kwantumeffecten het verloop van de warmtecapaciteit domineren – en mogelijks ook de andere thermische eigenschappen beïnvloeden – werd er gebruik gemaakt van padintegraal moleculaire dynamica (PIMD). Deze techniek is de uitverkoren methode om thermodynamische eigenschappen te evalueren inclusief de nucleaire kwantumeffecten, maar het vereist erg veel rekenkracht. Bijvoorbeeld, de berekening van de warmtecapaciteit met PIMD is honderdmaal de computationele kost van standaard MD simulaties. Daarom hebben we in samenwerking met Prof. Ceriotti (EPFL) een nieuw efficiënt PIMD schema ontwikkeld dat de anharmonische bewegingen en kwan-

tumeeffecten van de atoomkernen beschrijft en dat toelaat om de thermische expansie en de warmtecapaciteit op een accurate wijze te berekenen. Deze aanpak werd zorgvuldig getest op MOF-5 met en zonder de aanwezigheid van geadsorbeerde methaanmoleculen waar we bovendien een intrigerend minimum detecteerden van de warmtecapaciteit op lage temperaturen.

Vervolgens hebben we de thermische eigenschappen bestudeerd van een diverse verzameling van MOFs met onder andere de gekende MOF-5, UiO-66, HKUST-1 en Al-soc-MOF-1 materialen. Dit resulteerde in de eerste systematische studie van deze eigenschappen, wat ons toeliet een overzicht te geven van de thermische prestaties en beperkingen van MOFs. Eerst en vooral vonden we een erg lage warmtegeleidingscoëfficiënt ten gevolge van de poreuze opbouw van deze materialen met veel lege ruimte. Dit illustreerden we door middel van enkele IRMOF materialen die een sterke positieve correlatie vertoonden tussen de massadichtheid en de warmtegeleidingscoëfficiënt. Dit bleek bovendien relatief onafhankelijk te zijn van de onderliggende chemische structuur van de MOFs in onze verzameling. De warmtecapaciteit toonde in tegenstelling een tegengestelde trend. De meest poreuze materialen – degene met de laagste massadichtheid – bezitten de grootste specifieke warmtecapaciteit. Onze simulaties bewezen ook dat alle onderzochte MOFs krimpen in volume met stijgende temperatuur, maar de grootte van de negatieve uitzettingscoëfficiënt is sterk afhankelijk van het specifieke materiaal. Om deze eigenschappen te kunnen vergelijken met andere materiaalklassen, hebben we materiaaleigenschapdiagrammen opgesteld voor de verschillende thermische eigenschappen. De gesimuleerde eigenschappen van de onderzochte MOFs lagen op het kruispunt van keramieken, polymeren en hybride materialen (natuurlijke materialen en composieten), en impliceerden bovendien dat het moeilijk wordt om de eigenschappen van deze klasse fundamenteel te verbeteren. Op basis van deze voorbeelden was het duidelijk dat de intrinsieke thermische karakteristieken en adsorptie-eigenschappen van MOFs zorgvuldig gebalanceerd moeten worden.

Daarenboven hebben we door middel van een hypothetische thermodynamische cyclus de temperatuurstijging van deze materialen onderzocht wanneer CH_4 en CO_2 geadsorbeerd worden. Afhankelijk van de gastmolecule, brachten deze thermodynamische beschouwingen grote potentiële temperatuurspieken aan het licht van dezelfde grootteorde als de ontbindings-temperatuur. De temperatuurstijging op zichzelf is een relevante materiaalparameter die bepaald wordt door zijn thermische en gastafhankelijke adsorptie-eigenschappen. Onze simulaties toonden aan dat het selecteren van een MOF met een hogere warmtecapaciteit om de temperatuurstijging te beperken slechts een uitvoerbare strategie wordt als er sterk verbeterde MOFs worden ontwikkeld.

Samenvattend werden voor beide onderzochte thema's belangrijke stappen gezet richting het betrouwbaar simuleren van deze complexe materialen. Computationale onderzoekers kunnen met behulp van de methodologie die ontwikkeld en besproken werd in deze thesis op een verbeterde wijze aan computationeel materiaalontwerp doen. Dit is van cruciaal belang om deze materialen eindelijk te gaan exploreren richting high-tech industriële toepassingen. Bovendien, dragen de verschillende individuele studies in het kader van deze thesis bij aan het stijgende inzicht in de nanoscopische interacties die het gedrag van deze fascinerende materialen bepalen.

Summary

The development of novel technologies founded on fundamental scientific advancements has always been intimately associated with the accessibility and design of suitable materials. Evidently, there is not a single class of materials that is ideally suited for all applications and purposes. Within this context, metal-organic frameworks (MOFs) have emerged as attractive porous materials for a multitude of contemporary applications ranging from gas separation to mechanical energy storage. These materials are synthetically produced and can be made by linking inorganic and organic molecular building blocks by coordination bonds into porous crystalline frameworks. The abundance of building blocks in combination with different ways of organizing them gives rise to an almost unlimited number of possible structures. This large diversity results in a wide range of intriguing and promising physical and chemical features. Especially the modular nature of MOFs allows to tune the material characteristics, and opens up many opportunities for molecular and crystal engineering. A better molecular-level understanding of MOFs is highly needed to tailor them at the nanoscale.

We live in an era with access to enormous computing power that can be harnessed to reliably model materials such as MOFs. Molecular simulations have become an indispensable tool to acquire insight into the functioning of materials from a microscopic perspective. It yields complementary insight into various phenomena, and is particularly suited to screen the large chemical space of MOFs for the best materials. In **Chapter 1**, MOFs are introduced as important porous materials for the future. Their exceptional physical and chemical properties are highlighted together with potential applications. The research on these advanced tailor-made materials has long been focused on their tunable porosity and resulting exceptional adsorption properties. Lately, however, the study of their intrinsic physical properties has gained increasing interest as a response of the community on important engineering considerations such as stability and heat management for practical applications.

The overall aim of this PhD research is to study the behavior of MOFs using computational techniques and to provide a deeper insight into their phase stability and thermal properties. Modeling of these materials is inevitable to guide the experimental design, and aid in the transition from academic research to industry. To accurately model MOFs, a wide range of molecular simulation techniques was used as discussed in **Chapter 2**. The central concept is always the potential energy surface (PES), which is the mathematical link between the energy of the system and the geometrical coordinates of the nuclei. The choice between a quantum mechanical (QM) or classical force field (FF) description of the PES determines to a large extent the accuracy that can be obtained. However, equally relevant are the time and length scales that can be reached with current computational power. While in many cases a QM model is limited to static methods, FF simulations enable to access realistic experimental conditions via molecular dynamics (MD) simulations. Selecting the proper computational technique depends on the specific case study and a deliberate choice has to be made. With constantly evolving computational power, more and more groups even start to combine a QM description with lengthy MD simulations.

Two major topics were tackled in this work. A first phenomenon that was investigated is the intricate, unique behavior of breathing MOFs. Some MOFs display cooperative structural transformability as a response on different stimuli such as temperature, pressure and guest adsorption. MOFs capable of stimuli-responsive behavior are considered to be flexible, and are also referred to as soft porous crystals. Flexibility can express itself in many ways, and depending on the type of structural response and atomic displacements different terms have been introduced. In this work, the focus lies on breathing, where a phase transition takes place between an open, large-pore (lp) state and a closed, narrow-pore (np) state. This peculiar behavior is accompanied by a substantial change in volume, which could be exploited in novel temperature-controlled switches or in nanoshock absorbers.

First, it was shown in **Chapter 3** that accurately modeling the long-range dispersion interactions is crucial to obtain information in agreement with experiment. This was found for the well-known flexible MIL-53(Al), which displays temperature-responsive breathing. A popular approach to work on the QM-level is density-functional theory (DFT), which is ubiquitous in solid state science because of its computational efficiency for large systems. In many cases, however, it fails in capturing long-range effects and therefore relies on an additive dispersion scheme. Such a description is often used in the case of flexible MOFs, but we were able to highlight important deficiencies in commonly applied electronic structure methods. To illustrate this, a many-electron method, i.e. the random phase approximation (RPA),

was applied for the first time on a flexible MOF to yield highly accurate theoretical benchmark results in collaboration with Prof. Kresse (University of Vienna). This state-of-the-art technique seamlessly combines long-range dispersion effects with short-range interactions and results in an excellent agreement with experimental data for various systems, and now revealed the importance of many-body long-range dispersion effects for the adequate modeling of breathing MOFs.

Furthermore, flexibility was explored in a general context within this thesis. To that end, a thermodynamic model was proposed that enables a classification of flexible MOFs based on the construction of Helmholtz free energy profiles in terms of the volume. In addition, this protocol allows to unravel and predict breathing. We utilized this idea on flexible MOFs ranging from wine-rack-type frameworks to pillared-layered MOFs, where we concentrated on the intrinsic flexibility of the structures in absence of guest molecules. By probing the isoreticular MIL-53 and MIL-47 series, we were able to bring forward some simple design rules for thermo-responsive MOFs, where we emphasized the two factors influencing the phase transition: long-range dispersion stabilizing the dense np phase and vibrational entropy favoring the lp phase. This delicate balance explained why mostly the organic building blocks, i.e. the linkers, dominate the observed flexibility in various MOFs such as MIL-47, MIL-53, COMOC-2/3, DUT-4/5 and DMOF-1.

Our theoretical toolbox consisting of force field development, thermodynamic models and molecular dynamics (MD) simulations was used to a large extent in collaboration with different experimental partners. More specifically, we investigated for various MOFs (DMOF-1(Cu/Zn), MIL-53-FA(Al/Ga)) their behavior under influence of mechanical pressure in an attempt to use MOFs in mechanical energy storage devices in collaboration with researchers from the DAMP group (University of Montpellier). For the prototypical MIL-53(-FA) material, we explored the influence of the metal ion in the inorganic part of the MOF on the nature of the breathing transition. We found that by changing aluminum with gallium, the pressure-induced breathing process becomes irreversible, i.e. the structure remains in a closed state after removing the mechanical pressure. In a second joint experimental-theoretical exploration, we discovered through our thermodynamic protocol a massive volume contraction in DMOF-1 – a pillared-layered MOF – that could be triggered by exerting a large mechanical pressure. The excellent characteristics for storage applications, i.e. a large transition pressure and volume change, inspired our experimental collaborators to measure and confirm its promise for these applications. Both collaborative efforts also demonstrated that theoretical simulations remain very challenging for MOFs, as techniques are required at the crossroads of molecular and solid-

state modeling.

The characterization of the thermal properties of MOFs is a second major topic covered in this work. Thermal conductivity, heat capacity and thermal expansion are important engineering parameters for practical applications, but they have hardly been investigated for MOFs. This is especially relevant in view of their industrial potential as adsorbent materials for gas storage and separation. Adsorbents are exposed to thermal fluctuations, because the adsorption and desorption of guests implies the release or consumption of energy. The released heat of adsorption during charging needs to be dissipated quickly as small temperature changes can have a detrimental influence on the performance.

To properly extract thermal properties of MOFs in **Chapter 4**, a force field description of the PES was combined with MD simulations, where the atomic positions and velocities are followed over time via the Newtonian equations of motion. This approach allows to track the system at operating conditions, i.e. realistic pressures and temperatures, and captures the anharmonicities of the nuclear motion. However, this technique treats the nuclei as classical particles. This approximation reasonably holds at sufficiently high temperatures and for sufficiently heavy atoms subjected to moderate inter-atomic interactions. Nevertheless, nuclear quantum effects (NQE) need to be taken into account when the thermal energy $k_B T$ has a similar order of magnitude as the difference between the quantized energy levels of the nuclear vibrations. As NQEs typically dominate the behavior of the heat capacity, and potentially influence other thermal properties, we had to resort to path integral molecular dynamics (PIMD), which is an ideal simulation method for the evaluation of thermodynamic properties influenced by NQEs. Unfortunately, a high cost is associated to this technique. This is especially true for the evaluation of the heat capacity, which can easily cost more than hundred times the simulation cost of standard MD. To tackle this issue, a new PIMD scheme was developed in collaboration with the group of Prof. Ceriotti (EPFL) to accurately model the interplay of NQEs and anharmonic atomic motions on properties such as the heat capacity and the thermal expansion. This approach was benchmarked on the prototypical MOF-5 with and without methane molecules in the pores, where we detected an intriguing heat capacity minimum at low temperatures.

Subsequently, we investigated the thermal properties of a diverse set of guest-free MOFs including popular frameworks such as MOF-5, UiO-66, HKUST-1 and Al-soc-MOF-1. In this way, we presented the first systematic study of these characteristics, enabling a broader view on the thermal performance of MOFs and their associated limitations. On the one hand, we found that MOFs display a low thermal conductivity, which mainly stems from

the large empty voids in their porous frameworks. Through an isoreticular series of IRMOFs, we showed how this quantity is highly positively correlated with the mass density of the framework, and that it appears to be relatively independent of the underlying chemical structure in our larger set. On the other hand, the specific heat capacity displayed the inverse trend. The most porous frameworks – the ones with the lowest density – possess the largest specific heat capacity. Our simulations also showed that the MOFs under study shrink with increasing temperature, but the magnitude depends on the structure. Moreover, to put things into perspective, we compared the thermal properties of MOFs with standard materials in a materials property chart. Our simulated data shows that MOFs have thermal properties at the crossing of the ceramics, polymers and hybrid materials (natural materials and composites), and that it will be difficult to fundamentally improve the material's properties. On the basis of these examples, it was clear that a careful trade-off between the intrinsic thermal characteristics and adsorption properties will have to be made.

In addition, we investigated the temperature rise of the bulk material when adsorbing CH_4 and CO_2 by mimicking the adsorption process with a hypothetical thermodynamic cycle. These thermodynamic considerations reveal significant potential temperature increases at the material's level on par with the thermal decomposition temperature depending on the adsorbate. The temperature increase itself is a relevant material's parameter balancing both thermal and adsorption properties in MOFs. Our simulations predict that choosing a MOF with a higher heat capacity only could become a viable strategy to limit temperature spikes if new and improved MOFs are synthesized.

In summary, for both investigated topics, important steps toward reliably simulating these complex materials were taken. Using the methodology developed and outlined in this thesis, computational researchers are provided with improved tools to target predictive design, which is vital to explore these materials for high-tech industrial applications. Moreover, the wide range of studied materials and the various case studies contributed to the rising insight into the nanoscopic interactions that govern the behavior of these fascinating materials.

List of Symbols

Throughout this dissertation, italicized variables indicate scalars, italicized and bold-faced variables indicate vectors, and bold-faced variables are matrices or tensors. The sole exception to this latter are the matrices and tensors indicated with Greek symbols, which are bold-faced and italicized.

Alphanumeric symbols	
a	Length of the first unit cell vector
b	Length of the second unit cell vector
c	Length of the third unit cell vector
C	Heat capacity
C_P	Isobaric heat capacity
C_V	Isochoric heat capacity
$C_n^{AB(C)}$	n -th order dispersion coefficient
E	Energy
E_c	Correlation energy
E_i	Per-atom energy of atom i
F	Helmholtz free energy
$\mathbf{F}_i$	Total force exerted on atom i
H	Enthalpy
$\hat{H}$	Total energy or Hamiltonian operator
$\mathbf{J}$	Local heat flux density
k_B	Boltmann constant
n	Electron density
P	Pressure or number of replicas
$P_{\max}$	Mechanical transition pressure from an open framework to a closed framework
P_{NT}	Mechanical equation of state
q	Partition function

Q	Heat
$\mathbf{r}$	Electronic coordinates
r_{AB}	Interatomic distance between A and B
$\mathbf{r}_i$	Position of atom i
$\mathbf{R}$	Nuclear coordinates
S	Entropy
T	Temperature
$\hat{T}$	Kinetic energy operator
T_{cross}	Crossing temperature
$\hat{T}_e$	Kinetic energy operator of the electrons in a molecular system
$\hat{T}_N$	Kinetic energy operator of the nuclei in a molecular system
U	Internal energy
U_{bond}	Force field interactions between two-atom bonds
U_{bend}	Force field interactions between three-atom bends
U_{cov}	Force field covalent interactions
U_{cross}	Force field cross terms
U_{ei}	Force field electrostatic interactions
U_e	Potential energy surface (electronic ground state)
U_i	Per-atom potential energy of atom i
U_{oopd}	Force field interactions between three-atom out-of-plane distances
$U_{torsion}$	Force field interactions between four-atom dihedral angles
U_{vdW}	Force field van der Waals interactions
$U_{e,n}^{BO}$	n -th potential energy (or Born-Oppenheimer) surface
$U_e^{\tilde{F}F}$	Force field approximation of the potential energy surface
$\mathbf{v}_i$	Velocity of atom i
V	Volume
$\hat{V}$	Potential energy operator
V_0	Equilibrium volume
v_{xc}	Exchange-correlation potential
V_{ee}	Coulomb repulsion between the electrons in a molecular system
V_{Ne}	Coulomb attraction between the electrons and the nuclei in a molecular system
V_{NN}	Coulomb repulsion between the nuclei in a molecular system
Z	Quantum mechanical partition function in the canonical ensemble

Greek symbols

α	Polarizability
β	$\frac{1}{k_B T}$
β_l	Lattice thermal expansion coefficient
β_P	$\frac{\beta}{P}$
β_V	Volumetric thermal expansion coefficient
θ_a	Internal angle formed by r_{AB} and r_{CA}
κ	Second-order thermal conductivity tensor
ν	Vibrational frequency
ϕ_e	Electronic wavefunction in a molecular system
Φ	Nonlocal kernel
ψ_N	Nuclear wavefunction in a molecular system

List of Abbreviations

ACFDT	Adiabatic-connection fluctuation-dissipation theorem
AIM	Atom-in-molecule
ATM	Axilrod-Teller-Muto
B3LYP	Becke three-parameter Lee-Yang-Parr
bdc	1,4-benzenedicarboxylate
bdp	1,4-benzenedipyrazolate
BJ	Becke-Johnson damping
bpd	Biphenyl-4,4'-dicarboxylate
BO	Born-Oppenheimer
BUT	Beijing University of Technology
CAU	Christian-Albrechts-Universität zu Kiel
CMM	Center for Molecular Modeling
COMOC	Center for Ordered Materials, Organometallics and Catalysis
CoRE	Computation-ready, experimental (database)
COSMO	Laboratory of Computational Science and Modelling
cp	Closed pore
D2	Grimme D2 dispersion
D3	Grimme D3 dispersion
dabco	Diazabicyclo[2.2.2]octane
DAMP	Dynamics and Adsorption in Porous Materials group
DFT	Density-functional theory
DMOF	Dabco MOF
DUT	Dresden University of Technology
EOS	Equation of state
EXX/cRPA	Combination of the exact exchange energy with the random phase approximation to the correlation energy
FA	Fumaric acid
FF	Force field
GCMC	Grand canonical Monte Carlo
GGA	Generalized gradient approximation
GLE	Generalized Langevin equation

HCACF	Heat current autocorrelation function
HF	Hartree-Fock
HKUST	Hong Kong University of Science and Technology
HO	Harmonic oscillator
HPC	High-performance computing
HSE	Heyd-Scuseria-Ernzerhof
IR	Infrared
IRMOF	Isorecticular MOF
IUPAC	International Union of Pure and Applied Chemistry
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LDA	Local density approximation
lp	Large pore
M06-L	Minnesota '06 (local)
MBD	Many-body dispersion energy method (MBD@rsSCS)
MBD/FI	Many-body dispersion energy method with a fractionally ionic approach to polarizability (MBD@rsSCS/FI)
MBIS	Minimal Basis Iterative Stockholder
MC	Monte Carlo
MD	Molecular dynamics
MM3	Molecular mechanics force field
MIL	Matériaux de l'Institut Lavoisier
MOF	Metal-organic framework
MTS	Multiple time stepping
ndc	Naphthalene-2,6-dicarboxylate
NMA	Normal mode analysis
NOTT	University of Nottingham
np	Narrow pore
NU	Northwestern University
NQE	Nuclear quantum effect
op	Open pore
PAW	Projector-augmented wave
PBE	Perdew-Burke-Ernzerhof
PBEsol	Perdew-Burke-Ernzerhof revised for solids
PCP	Porous coordination polymer
PES	Potential energy surface
PIMD	Path integral molecular dynamics
QHA	Quasi-harmonic approximation
QM	Quantum mechanics
RPA	Random phase approximation
RPC	Ring polymer contraction
rVV10	revised Vydrov-Van Voorhis van der Waals correlation
SC	Suzuki-Chin

SCAN	Strongly constrained and appropriately normed
SE	Single-excitation contributions
SPC	Soft porous crystal
TS	Tkatchenko-Scheffler method
TS-SCS	Tkatchenko-Scheffler method with self-consistent screening
tpdc	<i>p</i> -terphenyl-4,4''-dicarboxylate
UFF	Universal force field
UMCM	University of Michigan Crystalline Material
UiO	Universitetet i Oslo
VASP	Vienna Ab initio Simulation Package
vib	Vibrational
vdW-DF2	van der Waals density functional 2
XC	Exchange-correlation
XRPD	X-ray powder diffraction
yaff	Yet Another Force Field code
ZPE	Zero-point energy

Part I

Advanced Molecular Simulations to Computationally Model Phase Stability and Thermal Properties of Metal-Organic Frameworks

1

Introduction

The physician or herbalist who is ignorant of the virtues of herbs, or who knows the virtues of some but does not seek to know the virtues of all, knows little or nothing. He must work until he knows them all, whether useful or injurious, in order to deserve the title he claims.

Attributed to Pachacútec (1438 – 1471)

Human curiosity and imagination are in many cases the driving force behind the stepwise progression of society. Evolution and the search for prosperity, however, have also lead us up to this point where we face global issues such as food scarcity, climate change and the quest for sustainability. While these major problems demand a political vision and strategy, the scientific community should contribute to the identification and understanding of their underlying causes, and provide fitting solutions in the form of technology, for example. The development of new technologies founded on fundamental scientific advancements has always been critically dependent on the availability of suitable materials.

A historical example is the development of the transistor. This crucial building block revolutionized electronics and laid the foundation of the modern computer. Although semiconductor materials were already experimentally observed and empirically described, it was only when quantum mechanics provided a solid understanding of the flow of electrons that a major step forward could be taken. The intimate relation between fundamental science

and suitable materials has inspired the European Union to invest in major research programs (e.g. the Graphene Flagship¹) to drive the search for the most innovative materials.

The development of novel materials also plays a key role in tackling the mounting environmental concerns and climate-related problems with new technological innovations. As we need to move away from fossil fuels, alternative ideas such as electric cars for transportation are being explored. Nevertheless, their success hinges on the development of adequate battery materials capable of delivering the necessary power.² Another example is the use of membranes capable of reducing greenhouse gas emissions in a wide range of current applications. These membranes are based on porous materials that could capture and store harmful molecules instead of releasing them into the atmosphere.³ Numerous other examples exist where progress depends on the availability of well-designed materials toward specific applications.

Hence, research on the improvement of these advanced materials is a highly active and multidisciplinary field. This PhD thesis is located at the intersection of materials science and physics, where concepts and techniques based on quantum mechanics, thermodynamics and statistical mechanics are combined through molecular modeling. In this way, a fundamental understanding of the nanoscale behavior can be acquired together with the associated macroscopic characteristics. This has been accomplished in a virtual laboratory by performing molecular simulations of materials on a high-performance computing infrastructure. By harnessing the massive increase in computing power, computational materials science has become an indispensable tool that contributes to materials innovation.^{4–7}

Of course there does not exist a single class of materials that is ideally suited for all purposes. A judicious choice has to be made depending on the envisioned application domain. In this work, the focus lies on metal-organic frameworks (MOFs).^{8,9} Much fundamental research effort has been devoted to these porous frameworks because of their promising properties for a variety of applications such as clean energy technologies,³ catalysis,¹⁰ biomedical drug delivery,¹¹ etc. For that reason, they have become one of the most exciting and investigated material classes of the last decades.

Before stating the goal in Section 1.2, this specific class of advanced functional materials will be introduced in Section 1.1.

1.1 Metal-organic frameworks

Porous materials are a class of low density materials possessing pores. Depending on the size of these voids, different categories exist such as microporous (< 2 nm), mesoporous (between 2 nm and 50 nm) and macroporous (> 50 nm) materials.¹² The porous family contains a large number of representatives including zeolites, MOFs, and porous organic polymers.⁹ MOFs are a relatively new class of materials, but have attracted attention from scientists in various research areas. As will be discussed later in this chapter, they possess captivating physical and chemical properties, owing to their hybrid inorganic-organic nature.⁸

1.1.1 Physics and chemistry of MOFs

Definition. MOFs are an emerging class of advanced materials that can be made by linking inorganic and organic molecular building blocks by coordination bonds into crystalline frameworks. According to the IUPAC recommendations, a MOF is a coordination polymer (or alternatively coordination network) with an open framework containing potential voids.¹³

Although various groups were working in the nineties on such hybrid organic-inorganic crystalline frameworks,^{14–17} the field only started gaining widespread attention when Yaghi and co-workers synthesized a framework (i.e. MOF-5) with unprecedented surface area, porosity and stability.¹⁸ The discipline of rationally assembling these porous crystals from well-defined molecular fragments with a specific connectivity and a simple geometrical shape into periodic nets is now called reticular chemistry, which actually lies at the crossroads between molecular chemistry and solid-state physics. This building block approach is illustrated in Figure 1.1.

The intelligent design of new MOF structures stems from the wide richness of possible topologies and periodic structures that can be targeted.¹⁹ Nevertheless, the origin of the explosive growth of MOF chemistry is the abundance of available molecular building blocks in combination with different topologies. This gives rise to an almost unlimited number of possible structures,⁸ which is exemplified by the more than 50 000 experimentally reported MOFs to date.²⁰ Snurr and co-workers highlighted this by generating more than 100 000 hypothetical structures by combining experimentally available building blocks into a limited number of topologies.²¹ This modular nature of MOFs allows to tune the chemical and physical properties of the material, and opens up many opportunities for molecular and crystal engineering. Some MOF structures that were studied in this thesis are displayed in Figure 1.2 to give an impression of the large structural and chemical space that they cover.

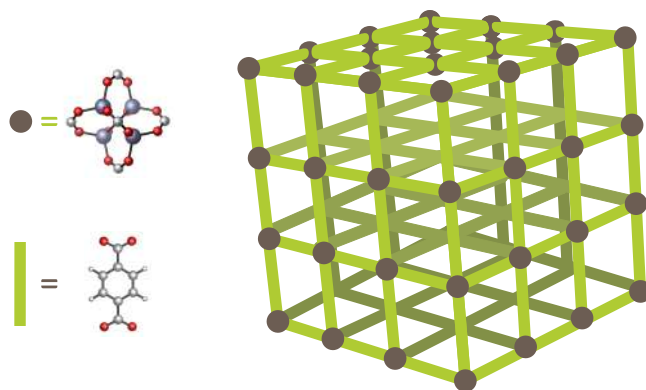


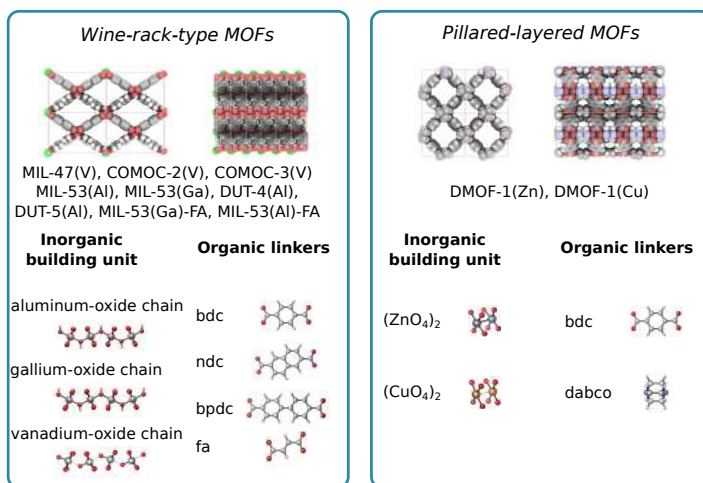
Figure 1.1: Metal-organic frameworks are constructed by linking inorganic and organic molecular building blocks by coordination bonds into crystalline frameworks.

Synthesis. These materials do not occur in nature and are produced in a laboratory. Several synthetic procedures exist to yield MOFs under a wide range of thermodynamic and chemical conditions.^{36–38} A supplemental technique that greatly contributed to the construction of MOFs is postsynthetic modification, which allows to prepare topologically equivalent MOFs with different chemical functionalities.³⁹ It is notable that conventional synthesis methods do not yield large single crystals such as silicon wafers in the electronics industry, but rather loose powders of micrometer-sized polycrystals. For some MOFs, however, specific procedures can result in single crystals of a few millimeters, but in general this is rather exceptional.⁴⁰ They can also be grown as thin films of polycrystalline and randomly oriented crystals with a thickness ranging up to several tens of micrometers.⁴¹ The crystal size itself can play an important role in different phenomena such as flexibility.⁴²

Stability. An often-expressed concern is the stability of these materials.⁴³ This includes thermal, mechanical and chemical stability. Thermal degradation and stability is heavily linked with the strength of the bond between the metal node and organic linker. Therefore, carboxylate-based organic linkers and high-valency metal ions often lead to stable structures and can result in MOFs that remain stable above 500°C (e.g. UiO-66³⁵). Most MOFs are nevertheless limited to 350–400°C.

A high resistance to partial collapse of the pores or amorphization under a mechanical pressure is incompatible with intrinsic ultrahigh porosity, but it

Chapter 3: Understanding Flexibility in Stimuli-Responsive MOFs



Chapter 4: Thermal Properties of MOFs

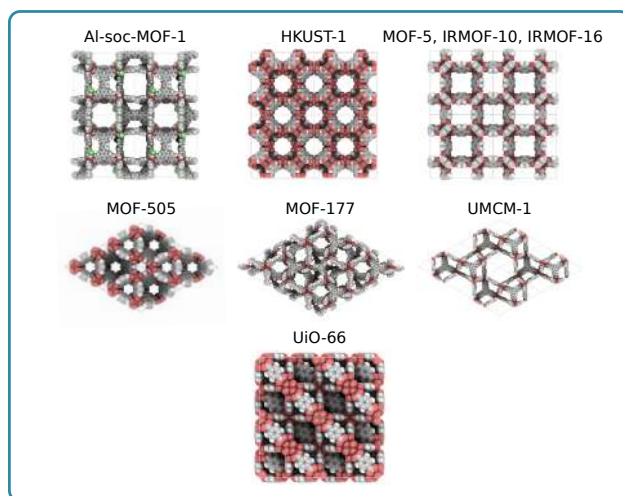


Figure 1.2: An overview of the materials studied in this work: MIL-47(V),²² COMOC-2(V),²³ COMOC-3(V),²⁴ MIL-53(Al),²⁵ MIL-53(Ga),²⁶ MIL-53(Al)-FA,²⁷ MIL-53(Ga)-FA,²⁸ DUT-4(Al),²⁹ DUT-5(Al),²⁹ Al-soc-MOF-1,³⁰ HKUST-1,¹⁷ MOF-5,¹⁸ IRMOF-10,³¹ IRMOF-16,³¹ MOF-505,³² MOF-177,³³ UMCM-1³⁴ and UiO-66.³⁵

is – together with the bond strength – greatly determined by the connectivity of the metal nodes and the underlying topology.⁴⁴

The chemical stability of MOFs depends on the nature of the environment but also on the exposure time.^{45, 46} Not surprisingly, various studies have shown that MOFs are mainly vulnerable at the weakest connection between the molecular building blocks, but numerous MOFs exist that show an acceptable chemical stability. Farha and co-workers⁴³ mentioned in their review that it is difficult to envisage MOFs with a stability beyond the current limits, and that the challenge now lies in obtaining routine synthetic access to such robust frameworks.

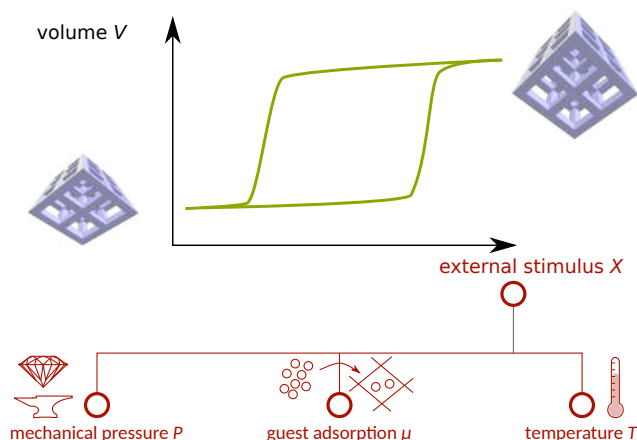


Figure 1.3: Hypothetical flexible MOF that displays a hysteresis loop. The volume is displayed as a function of the external stimulus (i.e. temperature T , mechanical pressure P or guest adsorption μ). Adapted from Ref. 47 with permission of Springer Nature, copyright 2018.

Properties. Tunable ultrahigh porosity and surface area were originally the unique selling points of MOFs in comparison to other porous materials. For example, DUT-60, a recent MOF, has the world's highest specific surface and the highest specific pore volume among all known crystalline materials, and consists of 90 percent free volume.⁴⁸ The size, shape and surface of these pores are the key parameters that determine to a large extent the potential applications of MOFs. These structural properties control the adsorption properties that make MOFs attractive.^{49–52} The last decade, as MOFs are slowly progressing toward industrial applications,^{53, 54} more and more attention is being spent on other relevant physical characteristics such as their thermal, mechanical and electronic properties.^{55, 56}

Finally, certain MOFs display cooperative structural transformability while preserving their crystallinity without breaking chemical bonds as a response to physical or chemical stimuli.^{47, 57–59} Various triggers such as temperature, pressure and guest adsorption have been used to initiate a transformation in a limited number of frameworks (e.g. Refs. 60–62). MOFs capable of such stimuli-responsive behavior are considered to be flexible, and are also referred to as soft porous crystals.⁶³ Flexibility can express itself in many ways, and depending on the type of structural response and atomic displacements different terms have been introduced.⁵⁷ When flexibility is discussed in the remainder of this thesis, we will focus on the special case of breathing. Here, the material undergoes a phase transition accompanied by a substantial change in unit cell volume and thus porosity. In many cases, a hysteresis loop – which is still not fully understood – is found for this kind of flexibility as schematically shown in Figure 1.3.

1.1.2 Potential applications of MOFs

The list of potential applications that scientists have envisioned for MOFs is nonexhaustive and excellently illustrates the great promise that they have:^{53, 54} carbon capture;⁶⁴ fuel storage in vehicles (Figure 1.4);⁶⁵ capturing water from air in desert environments;⁶⁶ biomedical drug delivery;¹¹ rechargeable batteries;⁶⁷ high-performance gas sensors;⁶⁸ molecular motors;⁶⁹ capturing nuclear waste;⁷⁰ destruction of chemical warfare agents;⁷¹ confidential information encryption;⁷² food safety;⁷³ and so on.

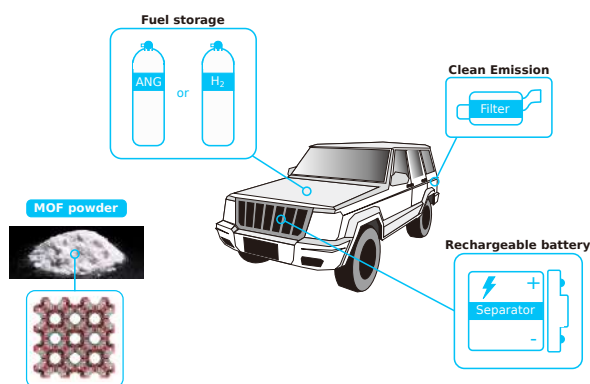


Figure 1.4: Illustration of MOF applications as adsorbent in the automotive sector.

During recent years, much progress has been made in guiding this field of research toward industrial applications. While some major chemical compa-

nies (e.g. BASF) already sell MOFs, and pioneers (e.g. NuMat Technologies,⁷⁴ novoMOF,⁷⁵ MOF Technologies,⁷⁶ MOFWORX,⁷⁷ etc.) start to enter the market, we have yet to witness the commercial breakthrough. The main reasons for this slow entrance within industrial applications are the stability of most MOFs as mentioned above, the cost of the raw materials and the synthetic challenge of cost-effectively achieving an industrial-scale production of MOFs.^{37, 53} Furthermore, from an engineering point of view, loose powders need to be densified, shaped or even processed toward MOF composites to be usable in real applications.^{78–80}

On top of that, fundamental materials research is required to improve the intrinsic properties of the materials. An excellent example is the volumetric storage target set by the US Department of Energy for vehicular on-board storage of natural gas in solid adsorbents, which is still a difficult challenge to reach.^{80, 81} Moreover, enhancement of other properties such as mechanical rigidity and heat transfer characteristics are essential for many applications.^{82, 83}

1.1.3 Computational modeling of MOFs

Computational modeling of MOFs is a broad and ever-changing topic that has been reviewed several times.^{84–88} Very recently, it was for the first time the central theme of an international conference at this university (i.e. MOFSIM2019).⁸⁹ Modeling studies of MOFs can differ in the number of materials under study (from detailed case studies to large-scale screenings), the investigated time scale (static or dynamic simulations), the size of the model (from a number of atoms to multiple crystallographic unit cells) and the level of detail of the structure (atomic-level representation or continuum models). However, a theoretical assessment only becomes viable when a sufficiently accurate methodology is used. Some properties necessitate a quantum mechanical treatment of the whole system consisting of nuclei and electrons, whereas others only require the description of the atomic degrees of freedom through force fields. It should be clear that a more accurate description of the system and longer time and length scales require more computational resources, and that a careful choice needs to be made.

Given the enormous number of imaginable MOFs, synthesizing and characterizing all possibilities is unfeasible. The large structural versatility may in that regard be seen as a practical disadvantage, and finding the best material becomes a daunting task. Fortunately, a computational high-throughput screening of materials can significantly reduce the number of possible candidates for a desired application, allowing to target the most promising ones in a later experimental stage.⁵ Computer-aided detection of valuable materials

in this high-dimensional space is progressively becoming a proven strategy for MOFs.^{21, 81, 90}

Besides, these large-scale computational investigations are needed to acquire insight into the underlying structure-property relations and the materials genome in general.^{91, 92} The latter aims to unravel the fundamentals of materials science,^{81, 93} analogous to uncovering the human genome.⁹⁴ A prerequisite for a valuable computational screening is the availability of computationally cheap, but sufficiently accurate, simulation procedures for the relevant materials properties. For MOFs, this is especially true for gas adsorption properties where the application of generic force field models and structural descriptors can indicate better performing structures with reasonable predictive power.^{21, 91} Another important aspect of screening are the development of databases with MOF structures, which has become an active topic of research.^{20, 21, 95}

In contrast, detailed theoretical investigations of specific materials and/or phenomena are necessary to improve our understanding.^{96–100} Such studies are complementary to experiment and can provide molecular-level insight into the nanoscale behavior.¹⁰¹ In this work, we illustrate this by several experimental-theoretical collaborations.^{28, 102–106}

Finally, modeling of defects and structural heterogeneity is gaining attention due to the recent understanding that MOF properties might actually be dominated by them.^{107–109} For example, we investigated how linker defects in UiO-66 influenced the high-pressure behavior.¹¹⁰ Efforts are underway to develop new models to adequately model longer length scales.^{111–113}

1.2 Goals of this PhD thesis

The overall aim of this PhD thesis is to provide a fundamental understanding of the phase stability and thermal properties of MOFs, which is mandatory to further explore these materials for high-tech industrial applications. The research on these advanced tailor-made materials has long focused on their tunable porosity and resulting exceptional adsorption properties for gas storage and separation applications. Lately, however, the study of their intrinsic physical properties has gained increasing interest. For instance, thermal engineering issues such as thermal stability and heat management are bound to become important as the adsorption of guests implies the release of energy, which needs to be dissipated. Insight into the underlying thermal properties is therefore a very topical theme of research. The intrinsic flexibility of MOFs is another example that requires an improved understanding of the

	RPA	DFT	FF	Exp.	Paper(s)	Topic(s)
Chapter 3						
Wine-rack-type MOFs						
MIL-47(V)			✓		I	Flexibility (P, T)
COMOC-2(V)			✓		I	Flexibility (P, T)
COMOC-3(V)			✓		I	Flexibility (P, T)
MIL-53(Al)	✓	✓	✓		I, III-V, VII	Flexibility (T)
MIL-53(Ga)		✓	✓		I, III, V	Flexibility (T)
DUT-4(Al)		✓			I, V	Flexibility (T)
DUT-5(Al)		✓			I, V	Flexibility (T)
MIL-53(Al)-FA		✓	✓	✓	II, V	Flexibility (P, T)
MIL-53(Ga)-FA		✓	✓	✓	II	Flexibility (P, T)
Pillared-layered MOFs						
DMOF-1(Zn)		✓	✓	✓	III, IX	Flexibility (P, T)
DMOF-1(Cu)		✓		✓	IX	Flexibility (P)
Chapter 4						
Al-soc-MOF-1			✓		X	Thermal properties
HKUST-1			✓		X	Thermal properties
MOF-5			✓		VI, VIII, X	Thermal properties
IRMOF-10			✓		X	Thermal properties
IRMOF-16			✓		X	Thermal properties
MOF-505			✓		X	Thermal properties
MOF-177			✓		X	Thermal properties
UMCM-1			✓		X	Thermal properties
UiO-66			✓		X	Thermal properties

Figure 1.5: An overview of the materials that were investigated, together with the respective papers and topics. The different levels of theory (RPA = random phase approximation, DFT = density-functional theory and FF = force field) will be discussed in Chapter 2.

nanoscopic interactions and transition mechanisms. In this thesis, we particularly focus on the response of the material to temperature and mechanical pressure.

To reach these goals, we used and developed a multitude of molecular simulation techniques to reliably model phase transformations in flexible materials and to describe the thermal properties of MOFs. These methods were applied to investigate a large variety of materials on the nanoscale including prototypical examples such as MIL-53, DMOF-1, MOF-5 and UiO-66. Depending on the property under investigation and the material, different methods were

applied to properly account for specific effects such as long-range dispersion or nuclear quantum effects. An overview of the most important materials that were studied is given in Figure 1.2. In this work, various case studies were performed to consider either the phase stability of flexible MOFs (Chapter 3) or the thermal properties of MOFs (Chapter 4) (Figure 1.5).

Within the first topic, namely the flexibility of MOFs, the methodology relied on a thermodynamic protocol that was developed at the Center for Molecular Modeling. It allows to construct the Helmholtz free energy in terms of the volume and facilitates the identification of the factors governing flexible behavior. The main focus was the stimuli-responsive behavior upon temperature (MIL-47-type materials, MIL-53-series) and mechanical pressure (DMOF-1(Zn/Cu), MIL-53(Al/Ga)-FA) triggers. In particular, temperature-induced breathing was shown to heavily rely on a balance of long-range dispersion and entropy. Accurately modeling this phenomenon proved itself to be a challenging computational endeavor which required state-of-the-art techniques beyond density-functional theory (DFT). To validate our findings, we had to resort to the random phase approximation (RPA) in collaboration with Prof. Kresse from the University of Vienna, which inherently captures both short- and long-range interactions in an accurate manner. Flexibility under mechanical pressure was studied for a few materials such as MIL-53-FA and DMOF-1, which were all inspired by collaborations with the experimental DAMP group at the University of Montpellier (Prof. G. Maurin, Prof. P. G. Yot). Such collaborative experimental-theoretical research efforts are essential to obtain a deeper insight into the functional behavior of materials and to validate the computational models.

Starting from this rather fundamental insight into the stimuli-responsive behavior of MOFs, a second goal was to obtain a better understanding of the thermal properties, which are very important for engineering applications. This is covered in Chapter 4. Surprisingly, although the field of molecular modeling of MOFs has expanded substantially, this specific topic received rather limited attention. Furthermore, experimental and computational data regarding thermal properties are mainly limited to a select number of well-known MOFs. Motivated by this, we studied the thermal expansion, thermal conductivity and heat capacity of a diverse set of MOFs with and without guests present in the pores. In this way, we presented the first systematic study of these relevant properties, giving a broader view on the thermal performance of MOFs and their associated limitations. To obtain an accurate characterization, it was necessary to apply force field molecular dynamics (MD) techniques. In collaboration with Prof. Ceriotti and co-workers (COSMO, EPFL), a new advanced MD methodology was worked out to adequately model the interplay of nuclear quantum effects and

anharmonic atomic motions on properties such as heat capacity and thermal expansion. Based on the thermal properties obtained at the molecular level, we furthermore proposed a thermodynamic cycle to estimate how adsorption impacts the thermal performance.

The first and second part of the thesis are connected by the temperature as a central quantity. On the one hand, the temperature may take the role of a stimulus controlling the phase in which a material resides at certain conditions. Thermal properties, on the other hand, are the physical properties of matter related to the transfer of heat. All three studied thermal properties are heavily linked with the temperature of the MOF. When heat is added to a material, its temperature increases depending on the heat capacity. At the same time, its shape will change based on the thermal expansion coefficient. The thermal conductivity determines the rate of heat transfer within a material exhibiting a spatial temperature gradient.

1.3 Outline

The remainder of this PhD thesis is organized as follows:

- In Chapter 2, the computational methods to investigate MOFs in this work are introduced. The theory behind the methods is not discussed in-depth, but an explanation on why they are the methods of choice is provided. Only for the techniques which are less common to the field, a more detailed explanation is given. Most methods are illustrated with examples obtained in the course of this work.
- In Chapter 3, the first part of the major research results obtained during this PhD are presented. Here, the work on the phase stability of flexible MOFs is considered. Both wine-rack-type frameworks (e.g. MIL-47 and MIL-53) and pillared-layered MOFs (DMOF-1) are discussed. Most of these results were published in international peer-reviewed journals, which can be found in **Part II**.
- In Chapter 4, the second part of the major research results obtained during this PhD are presented. This Chapter covers the research on thermal properties of MOFs. Similarly, most of these results were published in international peer-reviewed journals, which can be found in **Part II**.
- In Chapter 5, the main conclusions of this work and an outlook to future research together with my personal perspective are given.

2

Computational Methods to Study Metal–Organic Frameworks

I shall either find a way or make one.

Attributed to Hannibal (247 BC – 183 BC)

As discussed in Chapter 1, computational studies can offer complementary information to experiment and may speed up the detection of optimal materials. In this Chapter, the methods that were used in this work are highlighted and briefly discussed. It is not the intention to provide a general and thorough overview of molecular simulation methods, nor does it explain in depth the theory behind it. Rather, it provides justification for using the various techniques on MOFs for specific case studies. For more information on the different methods, additional references and textbooks will be mentioned in the various sections.

2.1 Modeling the potential energy surface

The central concept of all molecular simulation methods is the potential energy surface (PES). This is the mathematical link between the energy of the system and the geometrical coordinates of the nuclei, and expresses the potential energy felt by the latter. It relies on the Born-Oppenheimer (BO) approximation in quantum mechanics,¹¹⁴ which transforms the Schrödinger

equation¹¹⁵ containing the total molecular Hamiltonian into an electronic and a nuclear Schrödinger equation. The latter provides a relation between the total energy of the system E , the kinetic energy operator of the nuclei $\hat{T}_N$ (containing partial derivatives toward the nuclear coordinates) and the n -th PES (or BO surface) $U_{e,n}^{BO}$ that parametrically depends on the nuclear coordinates $\mathbf{R}$ (a $3 \times P$ -dimensional array with the coordinates of P atoms):

$$\left[\hat{T}_N + U_{e,n}^{BO}(\mathbf{R}) \right] \psi_N(\mathbf{R}) = E \psi_N(\mathbf{R}). \quad (2.1)$$

In the remainder of this thesis, the electronic ground state is always assumed and $U_{e,n}^{BO}$ is replaced by U_e (index n comes from the electronic degrees of freedom). This eigenvalue equation yields the nuclear wave function ψ_N and the total energy E including contributions from the electrons and nuclear motion. The computational power required to analyze a specific problem heavily depends on the model used to describe the PES.

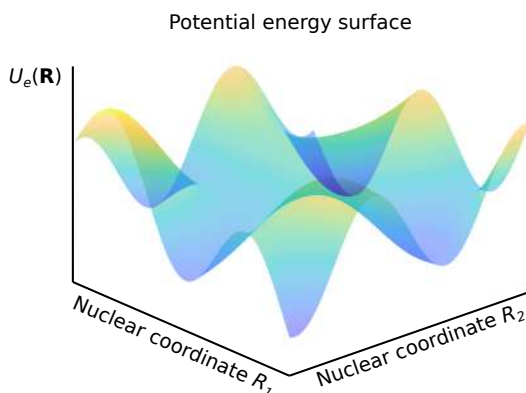


Figure 2.1: An example of a potential energy surface (PES) as a function of two nuclear coordinates R_1 and R_2 . The PES is in general a highly dimensional, complex surface with multiple minima, maxima and saddle points.

2.1.1 Quantum mechanical description of the molecular problem

The most accurate description of the PES can be obtained by solving the electronic many-body problem through the electronic Schrödinger equation

that describes the wave function ϕ_e of the electrons with coordinates $\mathbf{r}$ (a $3 \times l$ -dimensional array with the coordinates of l electrons).

$$\left[\hat{T}_e + V_{ee}(\mathbf{r}) + V_{Ne}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R}) \right] \phi_e(\mathbf{r}, \mathbf{R}) = U_e(\mathbf{R}) \phi_e(\mathbf{r}, \mathbf{R}). \quad (2.2)$$

The potential energy V contains three terms referring to the electrostatic interactions between the electrons and the nuclei via the Coulomb potential. $\hat{T}_e$ is the kinetic energy operator of the electrons. This equation has to be solved for all $\mathbf{R}$ to obtain the PES $U_e(\mathbf{R})$.

I. Density-functional theory

A first approach to handle this expression are called the wave function based methods. They aim to calculate the many-electron wave function ϕ_e , and different classes exist such as (post-)Hartree-Fock (HF) methods. These techniques are computationally expensive, but can deliver highly accurate results. Nevertheless, they are only rarely applied on the crystallographic unit cell of MOFs due to the large system size.¹¹⁶

A second and more popular approach is density-functional theory (DFT), which is ubiquitous in solid state science because of its computational efficiency for large systems. This formalism exploits the Hohenberg-Kohn theorems¹¹⁷ stating that there is a one-to-one mapping between the electron density ρ , the electronic wave function and the external potential v_{ext} (the potential in which the electrons move), and secondly, that the ground state electron density can be obtained variationally given the exact universal density functional. The latter is a functional that yields the electronic energy U_e for a given electron density. Using these theorems, Kohn and Sham transformed the intractable electronic Schrödinger equation to a set of simple uncoupled single-particle equations (i.e. the Kohn-Sham equations), where the electron density becomes the fundamental variable. The particles in these equations are subject to an external potential containing an unknown exchange-correlation (XC) potential v_{xc} .¹¹⁸ This potential captures the many-body quantum effects of the electrons and is the functional derivative of the XC functional to the electron density.

In case the exact v_{xc} would be used, the ground state and energy following from DFT would be exact. There exist a wide variety of approximations to this XC functional that have been found to produce good results in various areas of chemistry and solid state physics, but the development of better functionals is still a hot topic in quantum chemistry.^{119, 120} An interesting

analogy on the accuracy of XC functionals is Jacob's ladder (Figure 2.2). In a Bible story (Genesis 28), Jacob dreams about a stairway resting on earth with its top reaching to heaven, and the angels of God ascend or descend along it. According to Jacob's ladder for XC functionals, one starts with Hartree-Fock theory (earth) and moves along the ladder toward chemical accuracy (heaven). In principle, climbing the ladder implies an increase of accuracy and computational complexity as additional variables are introduced.

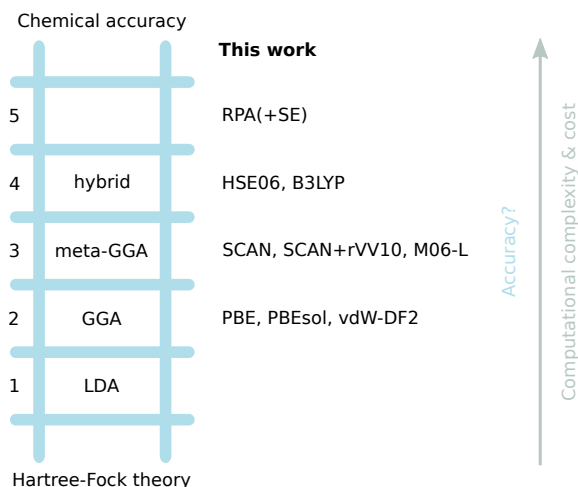


Figure 2.2: Jacob's ladder in DFT for XC functionals: the local density approximation or LDA (first rung), the generalized gradient approximation or GGA (second rung), the meta-generalized gradient approximation or meta-GGA (third rung), hybrid (fourth rung) and the fully nonlocal description (fifth rung). The XC functionals that were used in this work are indicated on the ladder: PBE,¹²¹ PBEsol,¹²² vdW-DF2,¹²³ SCAN,¹²⁴ SCAN+rVV10,¹²⁵ M06-L,¹²⁶ HSE06¹²⁷ and B3LYP.¹²⁸ RPA+SE is a technique that goes beyond DFT.

At the lowest rung, one can find the local density approximation (LDA), where the XC functional only depends on the electron density (e.g. Vosko-Wilk-Nusair¹²⁹). The most popular ones, however, are the so-called generalized gradient approximations (GGAs) in which the XC functional depends on the electron density and its gradient, but much more complicated forms exist along the ladder.^{130–132} The choice of an appropriate XC functional is crucial to obtain accurate results, but has to be balanced with the computational cost. We used XC functionals from the first to the fourth rung (the ones

indicated on the ladder in Figure 2.2), and aimed at the fifth rung by applying the random phase approximation (see further). In this work, we have mainly employed the PBE XC functional (GGA)¹²¹ to characterize flexible MOFs,^{28, 47, 102–106, 133–137} and we have highlighted the critical influence of the XC functional in a study on the phase stability of MIL-53(Al).¹³³ In this particular study, we showed that flexible MOFs are a challenging case for common DFT-based methods, and should therefore be used with caution.

In addition to the XC functional, there are several ways of numerically solving the Kohn-Sham equations.¹³⁸ As MOFs are crystalline materials, simulations are performed on the crystallographic unit cell and periodic boundary conditions are employed. The periodic simulations in this thesis were performed with VASP¹³⁹ in the projector-augmented wave (PAW) formalism.¹⁴⁰

II. Dispersion interactions in DFT

The relative stability of different phases of flexible MOFs can depend on a sensitive balance between long-range dispersion and entropy, which will be discussed in Chapter 3. Dispersion is the attractive interaction between instantaneous multipoles and is part of the van der Waals-type nonbonding interaction. Vibrational entropy is determined by the amount of freedom the atoms have to move. Computationally taking into account both effects is difficult, but necessary to obtain the correct qualitative behavior.^{133, 141} In this section we focus on including the dispersion interactions in DFT.

These long-range interactions arise from dynamical electron correlation, i.e. the correlation resulting from the movement of electrons. In contrast, static correlation plays a role when the ground state of the system is degenerate, and tackling this problem is outside the scope of this PhD thesis. Both arise from the Coulomb repulsion between the electrons and are not physically different, but a distinction is made in handling these computationally challenging effects. Simple second-order perturbation theory showed that there should be an attractive part of the energy that asymptotically decays as r_{AB}^{-6} when the distance between interacting molecular fragments A and B increases.¹⁴²

In principle, the XC functional should be able to describe this dynamical correlation and resulting long-range decay. However, most popular approximations of the XC functional only depend on the local electron density and its gradient (second rung on Jacob's ladder). Hence, the XC potential is semilocal by construction and fails to capture the long-range effects of dispersion.^{143, 144} The same is true for well-known hybrid functionals such as B3LYP¹²⁸ and HSE06¹²⁷ (fourth rung), which incorporate to some extent exact

exchange, but remain semilocal. To resolve this issue, dispersion schemes have been developed in the past which add a dispersion energy contribution to the electronic energy found by the XC functional. They are routinely used with a reasonable accuracy in many materials, and are often computationally much cheaper than the corresponding electronic structure calculation. Similar to the XC functionals, there exist several dispersion schemes and approximations. Some of them only include pairwise interactions between the nuclei (e.g. DFT-D3¹⁴⁵), while others also contain many-body effects (e.g. MBD^{146, 147}). Depending on the type of material, the latter are important or not. Finally, another solution are the XC functionals specifically designed to include some long-range dispersion such as vdW-DF2¹²³ and SCAN+rVV10¹²⁵. There exist many recent reviews that provide classifications of these methodologies and that explain the mathematics and physics behind these approaches in much more detail.^{143, 144, 148–150} Below, the methods that are used within this PhD thesis are shortly discussed.

The most popular dispersion method is DFT-D3, developed by Grimme and co-workers.¹⁴⁵ It is an atom-based pairwise method that approximates the correlation energy as

$$E_c = -\frac{1}{2} \sum_{AB} \sum_{n=6,8} \frac{C_n^{AB}}{r_{AB}^n} f_n(r_{AB}). \quad (2.3)$$

In this expression, the sum is taken over pairs of atoms A and B separated by a distance r_{AB} . f_n is a short-range damping function that avoids double-counting of the correlation energy contributions of the short-range interactions (which are captured by the XC functional). The parameters inside this function depend on the XC functional and are estimated by fitting interaction energies to standard benchmark sets. The mathematical form of this term can also significantly affect the accuracy of the dispersion model.¹⁵¹

Only the averaged isotropic 6th- and 8th-order dispersion coefficients for atom pair AB are included in the expression for the long-range correlation energy. The C_6^{AB} coefficients are obtained from accurate precomputed polarizabilities α using time-dependent DFT, and depend on the molecular environment via coordination numbers. The relation between the polarizability of the fragments and the dispersion coefficient can be found via the Casimir-Polder formula¹⁵²:

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty \alpha^A(i\omega) \alpha^B(i\omega) d\omega. \quad (2.4)$$

Grimme and co-workers did not exactly compute this expression for all free atom pairs (as polarizabilities can be strongly influenced by their molecular

environment), but proposed an interpolation scheme based on stable hydride compounds where the atoms could have different coordination numbers. The higher-order C_8^{AB} coefficient can be found recursively.¹⁴⁵ Furthermore, it is important to note that this semi-empirical scheme depends on the geometry of the molecular system (through the coordination numbers), but not on the electron density. The older variant – DFT-D2¹⁵³ – only included the C_6^{AB} coefficients, which moreover did not depend on the molecular environment of the atoms.

More recently, Moellmann and Grimme suggested to include an explicit three-body dispersion term in crystals dominated by dispersion as the long-range part of the interaction between three atoms is not equal to the interaction energies taken in pairs.¹⁵⁴ The leading contribution (as derived from third-order perturbation theory) is called the Axilrod-Teller-Muto (ATM) three-body term,^{155, 156} which is given by

$$E^{ATM} = \frac{C_9^{ABC} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(r_{AB} r_{BC} r_{CA})^3} \quad (2.5)$$

where θ_a , θ_b , and θ_c are the internal angles of the triangle formed by r_{AB} , r_{BC} and r_{CA} , and C_9^{ABC} is the triple-dipole constant. The latter can reasonably be approximated by taking the negative of the geometric mean of the C_6 coefficients of the different atom pairs. The total contribution of the three-body interactions should again be multiplied by a short-range damping function.

A second set of methods that were tested to simulate MOFs are the ones developed by Tkatchenko *et al.*^{146, 157} A first scheme, i.e. the Tkatchenko-Scheffler (TS) approach, utilizes a similar expression as Equation 2.3 to determine the pairwise additive dispersion interactions (typically, only the $n = 6$ coefficients are included). In contrast with DFT-D3, they use the electronic structure as input to determine the C_6^{AB} coefficients. More specifically, a Hirshfeld partitioning of the computed electron density of the system under study¹⁵⁸ is employed to determine the effective volume of an atom inside a molecule or solid. This parameter is linked to the effective polarizability of an atom-in-molecule (AIM), which in turn can be used to construct the C_6^{AB} coefficients and other relevant parameters such as the van der Waals radius of an atom. In this way, they are able to propose a method with less empiricism as the dispersion correction depends on the actual electron density. The only fitted parameter is used to couple the dispersion scheme with an XC functional, for which again an accurate benchmark data set of interaction energies is used.

To include many-body dispersion, Tkatchenko *et al.* developed a new method, which is inspired by the ideas of the TS approach that used AIM parameters derived from the electron density.¹⁴⁶ First, an improved estimate for the polarizability was constructed by solving a self-consistent screening (SCS) equation. In this way, it was possible to include long-range electrostatic screening effects in the C_6^{AB} coefficients that could become important for solids.

They extended in a second step the TS-SCS approach to include a fully nonadditive many-body van der Waals energy correction based on a coupled fluctuating dipole model Hamiltonian.¹⁵⁹ All atoms in the molecular system are replaced by three-dimensional quantum harmonic oscillators for which the AIM parameters (including the improved polarizability) are derived by partitioning the electron density. After solving the Schrödinger equation with this Hamiltonian, the long-range many-body dispersion contribution to infinite order is found. In a later version¹⁴⁷, they used a range-separation technique to split the long-range from the short-range correlation for a more consistent description of the long-range effects. The coupling of this many-body contribution with the XC functional is again handled by a damping function including one fitted parameter.

The nonlocal XC functionals are a last set of methods that were considered. They intrinsically account for pairwise van der Waals interactions, and do not require additional dispersion schemes like the ones previously mentioned. This can be understood from the more general expression of the pairwise correlation energy

$$E_c = -\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' C_6(\mathbf{r}, \mathbf{r}') \frac{f(|\mathbf{r} - \mathbf{r}'|)^2}{|\mathbf{r} - \mathbf{r}'|^6} \quad (2.6)$$

which resembles the additive pairwise model in Equation 2.3. These functionals describe correlation with a two-point dependence on the electron density n by recasting the previous formula in

$$E_c = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}') \Phi[n](\mathbf{r}, \mathbf{r}') \quad (2.7)$$

where Φ is a nonlocal kernel that is specifically constructed to capture the long-range part of the correlation energy.

By applying a more general version of the Casimir-Polder relation (Equation 2.4) with the expression of the correlation energy, the nonlocal kernel Φ can

be written as

$$\Phi(\mathbf{r}, \mathbf{r}') = -\frac{3}{\pi} \int_0^\infty du \left(\frac{1}{\omega[n](\mathbf{r})^2 + u^2} \right) \left(\frac{1}{\omega[n](\mathbf{r}')^2 + u^2} \right) \frac{f[n](|\mathbf{r} - \mathbf{r}'|, u)^2}{|\mathbf{r} - \mathbf{r}'|^6} \quad (2.8)$$

Here, quantum harmonic oscillators are used to model the polarizability at $\mathbf{r}$ in the frequency domain. The differences between different nonlocal functionals reside in the specific functional forms of $f[n]$ and $\omega[n]$. In this work, two nonlocal XC functionals were considered, namely, vdW-DF2¹²³ and VV10.¹⁶⁰ A revision of the latter was used in combination with the SCAN functional.^{124, 125}

Finally, the performance of these dispersion methods has been extensively evaluated and validated for various classes of molecules and solids.^{143, 144, 154, 161–163} It is clear from these studies that some methods perform better for specific materials. Nevertheless, MOFs have never been included in these studies, so a thorough assessment of the performance of dispersion methods was pursued in this work on the model system MIL-53(Al).¹³³ Through a systematic comparison of available experimental and theoretical data on this system with results obtained using different methods in **Paper V**, we were able to pinpoint some deficiencies in popular approaches and propose some good practices for accurately simulating flexible MOFs.

III. Beyond DFT: the random phase approximation

A better way to include long-range dispersion effects is to go beyond DFT. One of the most promising methods to obtain an accurate correlation energy is the random phase approximation (RPA).¹⁶⁴ It is a nonlocal treatment that automatically includes long-range van der Waals interactions. This emerging concept is based on combining the exact exchange energy with the RPA approximation to the correlation energy, and is sometimes denoted as EXX/cRPA.¹⁵⁰ It results in an excellent agreement with experimental data for various systems.^{164–167}

RPA can be derived within the adiabatic-connection (AC) fluctuation-dissipation (FD) formalism,^{164, 166} and relies on the fact that the physical description of electron correlations in the ground state can be retrieved by calculating the coupling of electron oscillations under the influence of a periodic electric field.^{168, 169} The correlation energy can be expressed as a sum over zero-point energies of harmonic oscillators representing collective electronic excitations. The theory behind RPA is complex, but has been discussed several times.^{150, 164, 166} The link between RPA and approximate dispersion

methods has also been reviewed.¹⁴⁴ Unfortunately, the computational cost associated to this state-of-the-art method is enormous, but lower scaling algorithms are being developed for large periodic systems.^{170–172}

Practically, the RPA simulations that were performed on MIL-53(Al) in **Paper V** used a cubically scaling algorithm as implemented in VASP^{170, 171} in collaboration with Prof. Kresse, who is one of the main developers of this code. The simulations combine single-shot non-self-consistent calculations for the HF exchange and the RPA correlation energy on top of DFT Kohn-Sham orbitals. Moreover, single-excitation (SE) contributions were included by calculating the difference between the exact exchange energy calculated using the frozen DFT Kohn-Sham orbitals and the energy obtained by a single diagonalization of the HF Hamiltonian set up using the same orbitals.¹⁷³

2.1.2 Force fields

Molecular mechanics is used to model the nanoscale behavior when a quantum mechanical description of the PES becomes unfeasible due to a large system size or a long simulation length. This is often the case for MOFs as the crystallographic unit cell can easily contain more than hundred atoms. The PES is then approximated by an analytical function of the nuclear coordinates, i.e. a force field. This approach neglects the electronic degrees of freedom completely, which results in a significantly reduced computational cost.

Force fields have been used to model crystals and molecules from biology to physics. They exist in many different functional forms and their parameters can be derived from experiment and/or simulations. Some force fields are designed for a specific molecular system, while others are widely applicable and provide generic parameters to describe a multitude of systems. In the context of MOFs, accurate force fields are highly desired.^{174, 175} On the one hand, there is the notable attempt by Heine and co-workers to improve the accuracy of generic force fields of MOFs with UFF4MOF.¹⁷⁶ On the other hand, Schmid and co-workers initiated the systematic development of more accurate system-specific force fields based on quantum mechanical input through MOF-FF.¹⁷⁷ At the CMM, the QuickFF protocol was developed by Vanduyfhuys *et al.*^{135, 178} Both approaches together with UFF4MOF deliver so-called all-atom flexible force fields with force field parameters for bonding and nonbonding interactions. In most cases in the MOF literature, however, the framework atoms are kept fixed, and only nonbonding interactions between the rigid MOF and its adsorbates are used to model gas adsorption.⁸⁵

In this work, QuickFF was used to parametrize system-specific force fields. Within this protocol, the quantum mechanical PES is approximated by a

sum of analytical functions that describe the covalent (cov) and noncovalent (noncov) interactions.

$$U_e^{FF} = \underbrace{U_{bond} + U_{bend} + U_{oopd} + U_{torsion} + U_{cross}}_{U_{cov}} + U_{ei} + U_{vdW}. \quad (2.9)$$

The covalent interactions – which mimic the chemical bonds between the atoms – are described by different terms as a function of the internal coordinates (bonds, bends, out-of-plane distances (oopd), and dihedrals). The unknown covalent force field parameters are fitted directly with QuickFF based on an optimized geometry and the Hessian. Cross terms (U_{cross}) combining different internal coordinates can easily be added to improve the correspondence with the provided Hessian.¹³⁵ The noncovalent interactions are composed of electrostatic and van der Waals interactions. The electrostatic interactions are modeled by a Coulomb interaction between Gaussian charge distributions.¹⁷⁹ The charges centered on the nuclei are derived with the Minimal Basis Iterative Stockholder (MBIS) partitioning scheme from the electron density of the optimized geometry.¹⁸⁰ The van der Waals interactions are described by the MM3-Buckingham model^{181, 182} up to a finite cutoff and are sometimes supplemented with tail corrections.¹⁸³ The required parameters were not refitted, but were instead taken from the MM3 force field.

The original QuickFF protocol only allowed cluster-based input.¹⁷⁸ It was based on the idea that a force field could be derived for the different molecular building blocks of the MOF. The resulting force fields are then combined into one force field for the crystal structure. This procedure was successfully applied on various MOFs (and their isorecticular variants) such as MIL-47(V) (**Paper I**),¹⁸⁴ UiO-66 with and without missing linker defects,^{44, 110} MOF-5 (**Papers VI, VIII and X**)^{185–187}, Al-soc-MOF-1 (**Paper X**),¹⁸⁷ MOF-177 (**Paper X**),¹⁸⁷ MOF-505 (**Paper X**),¹⁸⁷ and UMCM-1 (**Paper X**).¹⁸⁷ With the latest version of QuickFF¹³⁵ it has become possible to use periodic input data, which especially improved the accuracy of force fields for flexible MOFs such as CAU-13(Al),^{135, 137} MIL-53(Al)-F,¹³⁵ NOTT-300,¹³⁵ and DMOF-1(Zn) (**Paper IX**).¹⁰⁶ The detailed force field energy expressions and parameters are presented in the corresponding papers. An overview of the force fields is given in Table 2.1.

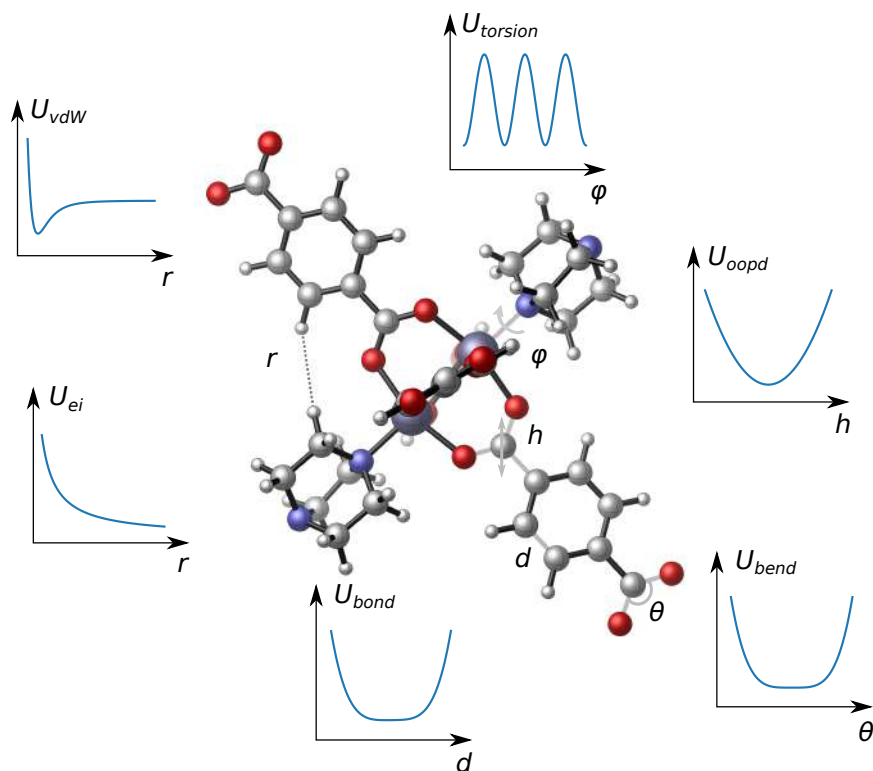


Figure 2.3: Illustration of the force field potentials typically used in this PhD thesis. These force field energy terms describe the van der Waals interactions (U_{vdW}), the electrostatic interactions (U_{ei}), and the covalent interactions. The latter depend on the internal coordinates of the chemically-bonded network: two-atom bonds (U_{bond}), three-atom bends (U_{bend}), four-atom out-of-plane distances (U_{oopd}) and four-atom dihedral angles ($U_{torsion}$).

Table 2.1: Overview of MOFs for which a QuickFF force fields was derived during this PhD thesis. The detailed force field energy expressions and parameters are presented in the associated papers.

MOF	Reference	DFT model input	Applications
Al-soc-MOF-1 ³⁰	187	clusters	thermal properties
BUT-30 ¹⁸⁸	44	clusters	mechanical properties
CAU-13 ¹⁸⁹	137	unit cell	flexibility
	135	unit cell	flexibility
Co(bdp) ¹⁹⁰	47	unit cell	flexibility
COMOC-2 ²³	184	clusters	flexibility
COMOC-3 ²⁴	184	clusters	flexibility
DMOF-1(Zn) ¹⁹¹	106	unit cell	flexibility
DUT-49 ¹⁹²	193	clusters	flexibility
HKUST-1 ¹⁷	187	clusters	thermal properties
IRMOF-10 ³¹	187	clusters	thermal properties
IRMOF-16 ³¹	187	clusters	thermal properties
MIL-47 ²²	102	clusters	structural properties
	184	clusters	flexibility
MIL-53(Al) ²⁵	47	unit cell	flexibility
	135	unit cell	vibrational properties
MIL-53(Al)-F ¹⁹⁴	47	unit cell	flexibility
MIL-53(Al)-FA ¹⁹⁵	47	unit cell	flexibility
MIL-53(Ga) ^{26, 196}	47	unit cell	flexibility
MOF-5 ¹⁸	186	clusters	thermal properties
	187	clusters	thermal properties
MOF-177 ³³	187	clusters	thermal properties
MOF-505 ³²	187	clusters	thermal properties
NOTT-300 ¹⁹⁷	135	unit cell	flexibility
NU-800 ¹⁹⁸	44	clusters	mechanical properties
PCN-111 ¹⁹⁹	44	clusters	mechanical properties
UiO-66 ³⁵	110	clusters	mechanical stability
	44	clusters	mechanical properties
	187	clusters	thermal properties
UiO-67 ³⁵	110	clusters	mechanical stability
	44	clusters	mechanical properties
UiO-68 ³⁵	110	clusters	mechanical stability
	44	clusters	mechanical properties
UMCM-1 ³⁴	187	clusters	thermal properties

2.2 Computationally identifying framework flexibility

Molecular simulations enable to investigate the macroscopic behavior of materials through microscopic information. In Section 2.1, we highlighted the importance of modeling the PES, and in this section we show how this information can be used to understand the framework flexibility in MOFs through thermodynamics and statistical mechanics.

In **Paper III**, we discussed how the knowledge of the thermodynamic potential in terms of the independent variables allows to identify framework flexibility at the macroscopic level. The most interesting thermodynamic potential for flexible MOFs (i.e. MOFs with the ability to undergo breathing transitions) is the Helmholtz free energy F as a function of the volume V and the temperature T . We focus here on the intrinsic flexibility of the framework in absence of any guest molecule, such that the number of particles remains constant.

$$dF = dU - TdS - SdT = -SdT - PdV \quad (2.10)$$

From the second law of thermodynamics, it follows that the MOF is in thermodynamic equilibrium when the system is in a Helmholtz free energy minimum. We can identify (meta)stable states by calculating the Helmholtz free energy as a function of the volume (Figure 2.4). Different methods were used in this work to investigate the Helmholtz free energy starting from the PES.

2.2.1 Static methods

1. Scanning the potential energy surface for stable states

As a first step, the behavior of the system can be investigated at zero kelvin. At the absolute minimum thermodynamic temperature, the vibrational degrees of freedom freeze out and the entropy reaches its minimum value. Obtaining the minima on the Helmholtz free energy surface at 0 K boils down to the minima of the PES, except for the zero-point effects which are typically ignored when constructing an energy profile. For some materials, however, such simulations already give a strong indication to which phases can be found at room temperature.

The PES as a function of the volume can be constructed by fixed-volume relaxations in which the atomic positions and cell shape are optimized.²⁰⁰

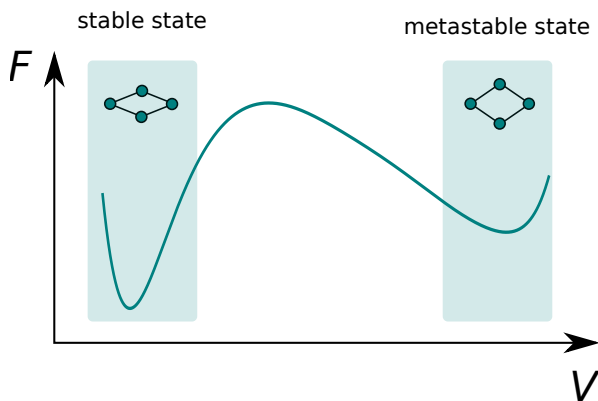


Figure 2.4: Helmholtz free energy F as a function of the volume V to distinguish between possible states of the material. An example is shown of a flexible MOF with a dense narrow-pore and a porous large-pore state.

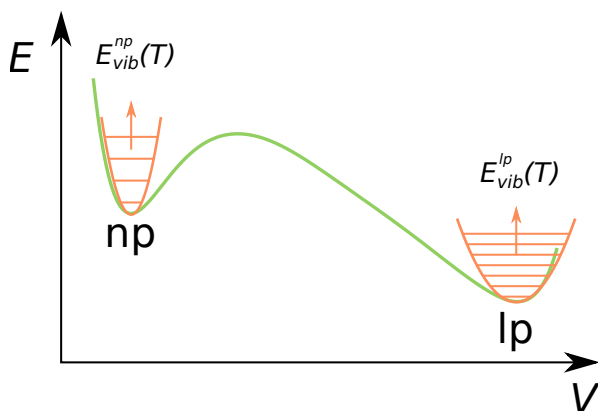


Figure 2.5: Energy E as a function of the volume V to distinguish between possible states of the material. Schematic representation of the harmonic approximation applied on the local minima of the system.

By performing these simulations at different volumes, we can identify the (meta)stable states of the system as shown in Figure 2.5. This strategy was applied on DMOF-1 (**Paper IX**),¹⁰⁶ MIL-53-FA (**Paper II**),²⁸ MIL-53(Al) and some isorecticular variants (**Paper V**),¹³³ and ZrCDC.¹⁰³ These geometry optimizations can be executed with DFT for MOFs with a limited unit cell size. Using a static approach thus allows to obtain insight into the stability

of different phases at the quantum mechanical level.

II. Toward Helmholtz free energies: the harmonic approximation

In order to probe the influence of temperature, we need to include the effects of nuclear motion on the PES by describing the vibrational degrees of freedom. The standard approach for calculating the vibrational Helmholtz free energy starts from a normal mode analysis (NMA) around a minimum on the PES, which is approximated by a second-order Taylor expansion:

$$U_e(\mathbf{R}) \approx U_e(\mathbf{R}_{\text{eq}}) + \frac{1}{2} \sum_{i,j=1}^N \left. \frac{\partial^2 U_e(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right|_{\mathbf{R}_{\text{eq}}} \Delta \mathbf{R}_i \Delta \mathbf{R}_j. \quad (2.11)$$

The second-order term is the Hessian matrix or the dynamical matrix for periodic systems. A crystal containing N atoms in its unit cell can therefore be described as a superposition of $3N-3$ independent harmonic oscillators (the omitted three degrees of freedom are global translations). The frequencies of these harmonic oscillators can be determined by diagonalizing the mass-weighted Hessian. With the knowledge of the partition function of a single harmonic oscillator (HO) with frequency ν ,

$$q_{\text{HO}} = \frac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}}, \quad (2.12)$$

the vibrational partition function of the whole system can be constructed. Analytical expressions for the vibrational free energy (F_{vib}), vibrational energy (E_{vib}) and vibrational entropy (S_{vib}) in the neighborhood of the PES minimum can straightforwardly be derived from this partition function. The Helmholtz free energy of the system is then given by

$$F(T) = U_e + E_{\text{vib}}(T) - TS_{\text{vib}}(T) = U_e + F_{\text{vib}}(T). \quad (2.13)$$

By performing such an analysis in the different minima of the PES, we can approximate the phase stability of a flexible MOF as a function of temperature. This analysis was performed for MIL-53(Al) and some reticular variants (**Papers II and V**).^{28, 106, 136}

Finally, by applying the harmonic approximation at different volumes, it becomes possible to construct the Helmholtz free energy as a function of temperature and volume. This is called the quasi-harmonic approximation (QHA).²⁰¹ It takes some anharmonic effects into account such as thermal

expansion, but the phonons and thus the vibrational free energy and vibrational entropy are still approximated in a harmonic way. This method has only rarely been applied on MOFs, but we demonstrated its applicability on MIL-53(Al) in **Paper VII**.¹³⁴

Numerically, the Hessians were calculated with a finite-differences approach with VASP and post-processing of the vibrational free energies was done with phonopy²⁰² and TAMkin.²⁰³

2.2.2 Molecular dynamics simulations to characterize phase transitions at realistic conditions

A major advantage of static methods is the possibility to describe the PES at the DFT level. Nevertheless, the phase space region which is sampled remains limited to the lowest electronic energy states at fixed volumes. Moreover, when vibrational degrees of freedom are described with the (quasi-)harmonic approximation, anharmonic motions of the nuclei on the PES are not taken into account.

In contrast, molecular dynamics (MD) is a simulations method that allows to explore the phase space at realistic conditions (temperature, pressure, volume) depending on the ensemble. This is done by evolving the atomic positions and velocities over time via the Newtonian equations of motion. The system runs through different configurations on the PES. It is based on the ergodic principle, which states that the time-averaged properties of a system are the same as when these properties are averaged over the system in its different microstates. However, as the forces on the atoms need to be calculated at various time steps (i.e. the electronic Schrödinger equation needs to be solved every step), this technique becomes rapidly unfeasible using a quantum mechanical PES for larger systems such as MOFs. Except for relatively short MD trajectories, one is forced to resort to force fields.

Various algorithms have been developed to perform efficient MD simulations in different ensembles. When dealing with flexible MOFs, however, special care must be taken to correctly sample the phase space.²⁰⁴ Within the scope of this work, the $(NV(\sigma_a = 0)T)$ ensemble is the method of choice for characterizing flexible materials.²⁰⁴ In this ensemble, the number of particles and volume are kept fixed, while the temperature is controlled with a thermostat. Furthermore, the unit cell shape is allowed to change by applying a barostat under the sole constraint of a constant volume. In a similar fashion to constructing the PES along the volume coordinate through fixed-volume optimizations, this ensemble enables to simulate the Helmholtz free energy

profile as a function of the volume via thermodynamic integration (relative to some reference point):

$$F_{NT}(V) - F_{NT}(V_{\text{ref}}) = - \int_{V_{\text{ref}}}^V \langle P_{NT}(V') \rangle dV' \quad (2.14)$$

After a converged MD simulation in the $(NV(\sigma_a = \mathbf{0})T)$ ensemble, the ensemble average of the instantaneous hydrostatic pressure $\langle P \rangle$ can be obtained at a specific temperature and with a fixed number of particles. These simulations are repeated at a series of volumes on a closely spaced volume grid to numerically approximate the integral by a finite sum. In fact, this procedure yields the mechanical equation of state (EOS) $P_{NT}(V)$ from which it is easy to recognize structural transitions due to mechanical pressure. Furthermore, this strategy can also be applied to detect flexibility as a response to other stimuli such as temperature and guests as explained in **Paper III**.

The MD simulations in this work were performed with Yaff²⁰⁵ and LAMMPS²⁰⁶. The thermodynamic protocol of calculating the mechanical equation of state to identify the (meta)stable states of the system was utilized to investigate DMOF-1(Zn) (**Paper IX**), MIL-47(V) and its isorecticular variants (**Paper I**), and many other flexible MOFs (**Paper III**) using QuickFF force fields.

Note that the use of thermodynamic integration may not always lead to the most efficient construction of Helmholtz free energy curves. Other, advanced sampling methods exist to increase the computational efficiency, and to steer the dynamics of the system into the relevant phase space.^{136, 137}

2.3 Characterizing thermal properties

A second major part of this thesis constitutes the characterization of thermal properties of MOFs using molecular simulations. As explained in Section 1.2, a fundamental understanding of the structural and chemical features underpinning their intrinsic thermal properties is a highly topical subject for engineering applications. Nevertheless, only a limited number of experimental and computational studies are available on thermal properties of MOFs. For some properties, well-established molecular simulation techniques and procedures already existed such as the Green-Kubo formalism for thermal conductivity or simulations at different temperatures in the isobaric-isothermal ensemble for the thermal expansion.²⁰⁷ In the course of this work, we developed an advanced molecular dynamics scheme to facilitate the

characterization of complex systems such as guest-loaded MOFs. In this section, we discuss the methods applied during this thesis.

2.3.1 Heat capacity

The heat capacity C is an extensive property of the system, which is defined as the amount of heat Q required to increase the material's temperature T :

$$C = \frac{\delta Q}{dT}. \quad (2.15)$$

Since Q is not a state function, this property depends on the way heat is added to the system. The isobaric specific heat capacity can be found by replacing the heat with the enthalpy

$$C_P(T) = \left(\frac{\partial H}{\partial T} \right)_{P,T}, \quad (2.16)$$

where H is the enthalpy of the system ($= E + PV$). The isochoric specific heat capacity is similarly given by

$$C_V(T) = \left(\frac{\partial E}{\partial T} \right)_{V,T}. \quad (2.17)$$

For most crystals, however, the difference between the isobaric and isochoric heat capacity tends to be small at room temperature.

I. Harmonic approximation

A first method to estimate the isochoric heat capacity directly follows from the harmonic approximation introduced earlier in this chapter. The heat capacity of a single harmonic oscillator in the canonical ensemble can easily be found from the partition function (Equation 2.12). The heat capacity of the crystal is the sum of the heat capacity contributions from all $3N-3$ vibrations. The contribution from the conduction electrons can safely be neglected as only insulating materials were investigated in this work.

$$C_V(T) = k_B \sum_{\nu} \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{\frac{h\nu}{k_B T}}}{\left(e^{\frac{h\nu}{k_B T}} - 1 \right)^2}. \quad (2.18)$$

This expression is analogous to the Einstein model of the solid²⁰⁸ and yields $(3N - 3)k_B T$ in the high-temperature limit corresponding with the Dulong-Petit law.²⁰⁹ It deviates from experiment in the limit of very low temperatures.

It can be evaluated using DFT frequencies,¹³⁴ and is sometimes used to validate new force fields for MOFs.¹³⁵

II. Path integral molecular dynamics

MD is an indispensable tool to simulate many different properties. Using the classical partition function of the canonical ensemble, the heat capacity can be found via following relation

$$C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T} = \frac{\sigma_E^2}{k_B T} \quad (2.19)$$

where the brackets $\langle \cdot \rangle$ denote an ensemble average. It shows that we only need to track the fluctuation of the energy in a regular NVT MD simulation to compute the heat capacity of the system. MD has provided invaluable insight into the behavior of stimuli-responsive MOFs,⁴⁷ but – as mentioned in Section 2.2.2 – the atoms are treated as classical particles. This approximation reasonably holds at sufficiently high temperatures and for sufficiently heavy atoms subjected to moderate interatomic interactions. Nevertheless, nuclear quantum effects (NQEs) need to be considered when the thermal energy $k_B T$ has a similar order of magnitude as the difference between the quantized energy levels of the nuclear vibrations (in case of a HO: $h\nu \ll k_B T$). For example, the thermal energy at room temperature is 2 kJ/mol. For a carbon-hydrogen bond with frequency 3200 cm^{-1} , a difference between subsequent energy levels of approximately 6 kJ/mol is found, which is larger than the thermal energy. As MOFs contain a lot of light atoms such as hydrogen and carbon, it is clear that the energy spectrum cannot be treated as a continuum and that nuclear vibrations possess to a large extent a quantum nature. Hence, treating the atoms in a classical way will not yield the correct energy fluctuations.

Path integral molecular dynamics (PIMD)²¹⁰ provides an ideal simulation method for the evaluation of thermodynamic averages influenced by NQEs. Similar to the harmonic approximation, it correctly describes the nuclear vibrations of the atoms. However, this method also allows to sample larger regions of the phase space as was the case with standard classical MD. Hence, it seamlessly captures both the NQEs and the anharmonic motion of the nuclei. It is therefore the second method that was looked into to characterize the heat capacity of MOFs.

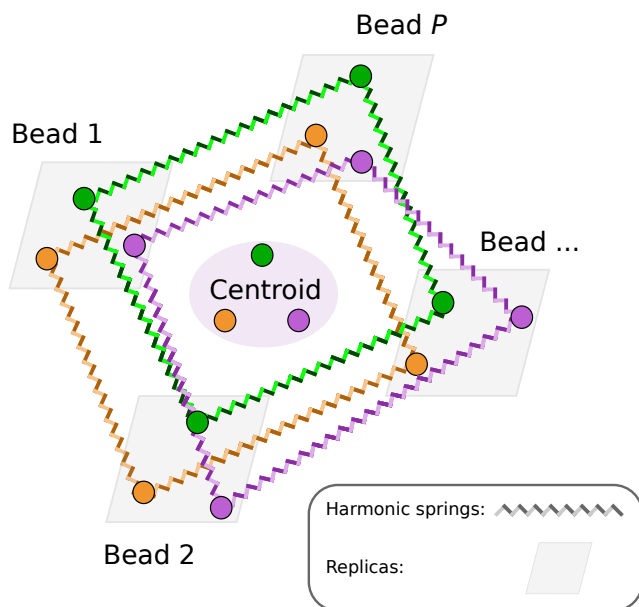


Figure 2.6: Illustration of a path integral simulation of a three-body system. The quantum system is modeled by a set of adjacently interacting classical replicas.

The technique is based on the path integral formulation of quantum mechanics proposed by Feynman.²¹¹ It exploits the equivalence between the thermodynamics of a quantum system and a classical ring polymer by mapping the quantum onto the classical partition function of an extended system composed of P replicas (Figure 2.6). These replicas interact with each other through harmonic springs with force constants determined by P , the mass of the atom and the targeted temperature. This mapping systematically improves for increasing P values, and becomes exact in the limit to infinity. A high computational cost is typically associated with PIMD as the system is replaced by P interacting systems.

Path integral techniques have been used to study the heat capacity of various systems under constant-volume conditions.^{212–218} These studies have shown that a large number of replicas is essential as the heat capacity is a derivative of the energy. For instance, 128 beads were necessary to accurately calculate the heat capacity of water in gas, liquid and solid state.²¹⁶ An application on complex crystals has not yet been reported. This is mainly because of the large computational overhead. Efficient algorithms and methodological advances^{186, 218–223} are increasing the scope of PIMD toward larger systems such as MOFs.²²⁴ A possible approach to decrease the number of replicas

is by using a higher-order expansion of the quantum partition function in contrast to the standard second-order Trotter splitting. In case of the latter, the quantum mechanical partition function in the canonical ensemble ($Z = \text{tr} [e^{-\beta \hat{H}}]$, $\beta = \frac{1}{k_B T}$) is decomposed as

$$e^{-\beta \hat{H}} \approx \left[e^{-\beta_P \frac{\hat{V}}{2}} e^{-\beta_P \hat{T}} e^{-\beta_P \frac{\hat{V}}{2}} \right]^P, \text{ with } \beta_P = \frac{\beta}{P} \quad (2.20)$$

with $\hat{T}$ and $\hat{V}$ the kinetic and potential energy operators, and it is accurate up to second order in β_P . This expression can be shown to lead to a classical-like partition function, which is used in PIMD.

During this PhD thesis, an improved and efficient PIMD scheme was developed in collaboration with Ceriotti and co-workers that enables to predict the isobaric heat capacity of challenging systems such as guest-loaded MOFs (**Paper VIII**).¹⁸⁶ It is based on the fourth-order Suzuki-Chin (SC) decomposition,^{225, 226}

$$e^{-\beta \hat{H}} \approx \left[e^{-\beta_P \frac{\hat{V}_e}{3}} e^{-\beta_P \hat{T}} e^{-\beta_P \frac{4\hat{V}_o}{3}} e^{-\beta_P \hat{T}} e^{-\beta_P \frac{\hat{V}_e}{3}} \right]^{\frac{P}{2}}, \quad (2.21)$$

where

$$\hat{V}_e = \hat{V} + \frac{\alpha}{6} \beta_P^2 [\hat{V}, [\hat{T}, \hat{V}]], \quad (2.22)$$

$$\hat{V}_o = \hat{V} + \frac{1-\alpha}{12} \beta_P^2 [\hat{V}, [\hat{T}, \hat{V}]], \quad (2.23)$$

and $\alpha \in [0, 1]$ is an arbitrary parameter. It can be shown that this again leads to a classical partition function of an extended system, propagating through the SC ring-polymer Hamiltonian.²²³ Kapil *et al.* overcame a challenging hurdle to enable constant-volume PIMD on large systems with this Hamiltonian by showing that the cumbersome terms in the algorithm could be evaluated cheaply in a finite-differences way.²²³ This scheme was extended in **Paper VIII**¹⁸⁶ to allow for constant-pressure simulations by using a PIMD version of the Bussi-Zykova-Parinello barostat,^{227, 228} and implemented in i-PI.^{228, 229}

The computational effort was further reduced by combining this high-order scheme with other accelerating methods relying on the separation of the force field potential into a computationally cheap short-ranged and a more expensive long-ranged part.²²² To this end, we applied ring polymer contraction (RPC)²²⁰ and multiple time stepping (MTS)²³⁰. On the one hand, in RPC, the long-ranged terms are computed separately on a smaller number of

replicas, which are extrapolated to the case of P beads without a significant loss of accuracy. On the other hand, MTS reduces the frequency at which the long-ranged interactions are computed. A *BAOAB* type²³¹ MTS scheme is used to evolve the dynamics of our systems. For our simulations on MOFs in a temperature range from 100 K to 600 K, the computationally cheap short-range terms of the force field are computed on 64 replicas and integrated with a time step of 0.25 fs. The remainder of the interactions, i.e. the expensive long-range interactions, are computed on 8 replicas using RPC and integrated with a time step of 1 fs.

Estimators need to be derived to compute quantum mechanical observables from (SC) PIMD.²¹⁹ The standard estimators for the heat capacity in the path integral formalism tend to be complex and suffer from numerical imprecision due to a large variance.^{186, 213, 217} As the focus lay on calculating the heat capacity of MOFs in a wide temperature range, a different approach was pursued. The enthalpy H was constructed as a function of temperature by evaluating the energy (using a specific SC estimator)²²³ and the volume. The heat capacity C_P (Equation 2.16) can then be found by analytically (after a polynomial fit) or numerically deriving the enthalpy to the temperature.¹⁸⁶ Figure 2.7 displays the simulation results for the heat capacity of MOF-177.

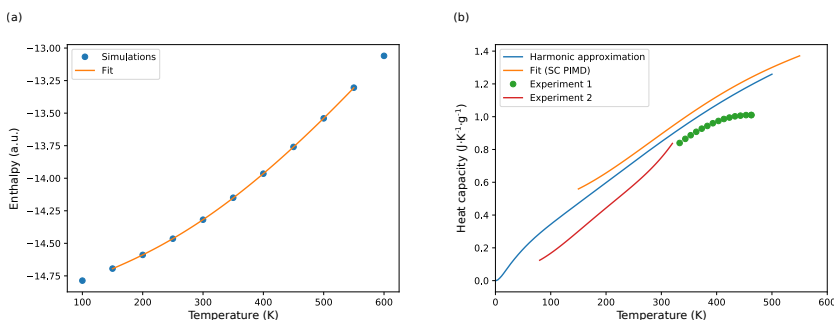


Figure 2.7: (a) Enthalpy of MOF-177 as a function of temperature obtained with SC PIMD simulations. (b) Heat capacity of MOF-177 as a function of temperature obtained by analytically deriving a polynomial fit to the enthalpy and by the harmonic approximation. Two experiments are added for comparison.^{232, 233}

2.3.2 Thermal expansion

A second thermal property that needs to be dealt with in applications is the thermal expansion behavior. This is characterized by a volumetric thermal

expansion coefficient β_V :

$$\beta_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,T} = \left(\frac{\partial \ln V}{\partial T} \right)_{P,T}. \quad (2.24)$$

It gives information on how the volume will evolve when the temperature changes at constant pressure. For some MOFs, it is also interesting to look at the lattice expansion coefficient β_l :

$$\beta_l = \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_{P,T} = \left(\frac{\partial \ln l}{\partial T} \right)_{P,T}. \quad (2.25)$$

The relation between both coefficients for isotropic expansion is given by $\beta_V = 3\beta_l$.

Early work already suggested that a good correspondence with experiment could be obtained with force field MD.^{234–238} Additionally, it can be studied with DFT by applying the QHA method. This was used in the past by Zhou *et al.*²³⁹ to unravel the origin of the negative thermal expansion of MOF-5. We also tested this approach on MIL-53(Al) and retrieved the coefficients of the different (meta)stable phases as a byproduct (**Paper VII**).¹³⁴ However, in this PhD thesis, the focus lay on predicting thermal expansion using force field (PI)MD simulations.

I. Molecular dynamics

The most straightforward method to calculate thermal expansion with MD is by obtaining the equilibrium volume as an ensemble average of an MD trajectory at different temperatures. This can be done with constant-pressure simulations. Subsequently, the natural logarithm of the MD volume is fitted as a function of temperature to a linear polynomial:

$$\ln \langle V \rangle_{NPT} \approx \beta_V T + \ln V_0. \quad (2.26)$$

V_0 is the equilibrium volume at zero temperature. This is the way most computational MOF studies have acquired the thermal expansion coefficient,^{135, 174, 185, 186, 234–238, 240} and it is often a good approximation as the volume almost linearly depends on the temperature.²⁴¹ There also exists a fluctuation formula based on the enthalpy and the volume, which facilitates the calculation of the thermal expansion coefficient as a function of temperature. As this property converges much slower than the equilibrium volume, we opted for the first approach.²³⁴ In summary, we can conclude

that the extraction of thermal expansion coefficients from MD simulations is well-known in the MOF community.

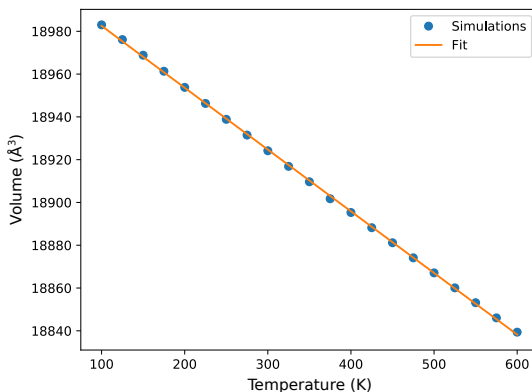


Figure 2.8: Volume of HKUST-1 as a function of temperature obtained with SC PIMD simulations. The fitted thermal expansion coefficient is $-15.3 \cdot 10^{-6} \text{ K}^{-1}$, which is in a good agreement with experiment ($-12.3 \cdot 10^{-6} \text{ K}^{-1}$).²⁴²

In this work, we probed the effect of NQEs on β_V for the first time by resorting to PIMD techniques. The newly developed constant-pressure SC PIMD (**Paper VIII**) can be used to accurately account for NQEs on the equilibrium volume, but also more approximate techniques (GLE quantum thermostat, PIGLET)^{221, 243} were tested and evaluated in a systematic way (**Paper VI**). Figure 2.8 displays the simulation results and associated fit for the negative thermal expansion of HKUST-1.²⁴²

Finally, it is important to note that the above described methods are not applicable on flexible MOFs as constant-pressure simulations force the system in the most dense configuration due to large pressure fluctuations.²⁰⁴ For these materials, the thermal expansion coefficient can be derived by constructing the Helmholtz free energy profile as a function of volume at different temperatures. The thermal expansion coefficient can then simply be obtained by fitting the equilibrium volume as a function of temperature (similar to QHA) as we showed in **Paper I**.^{136, 184}

2.3.3 Thermal conductivity

This property is often defined through the empirical Fourier's law for heat conduction:

$$\mathbf{J} = -\boldsymbol{\kappa} \cdot \nabla T, \quad (2.27)$$

where $\mathbf{J}$ is the local heat flux density, ∇T the local temperature gradient, and $\boldsymbol{\kappa}$ is the second-order thermal conductivity tensor. This relation is used to describe macroscopic heat transport. When a temperature gradient is present, a heat flux will push the material back to thermodynamic equilibrium. The dominant contribution to the thermal conductivity comes from the phonons for most MOFs as they are insulators.

The microscopic heat flux is not uniquely defined and predictive, parameter-free estimates of the thermal conductivity tensor are desired. A number of the existing methods are mentioned below together with their known disadvantages. A first possible approach to model the thermal conductivity in solids is based on the Boltzmann transport equation.²⁴⁴ It can be solved numerically and requires the second-order and third-order derivatives of the energy to the atomic positions.²⁴⁵ However, this method only accounts for the lowest order contributions to the anharmonicity and is known to deliver less accurate results than other techniques.²⁴⁶ The limited available data for MOFs strongly suggests very low thermal conductivities. Hence, it can be expected that the thermal transport is dominated by contributions of the lowest-frequency phonons which can be strongly anharmonic.²⁴⁷

A second class of methods relies on MD simulations.²⁴⁸ The direct method is a steady-state approach based on non-equilibrium MD. Similar to the experimental setup, a heat current is applied between two interfaces of the simulation cell. At one end of the material, energy is added, while simultaneously the same amount is extracted at the other side. The thermal conductivity in one direction can then be deduced by dividing the applied heat flux with the computed temperature gradient in between the interfaces. This method heavily suffers from finite-size effects, and has a strong non-linear response behavior due to the artificially large temperature gradients.²⁴⁹

A last approach is the use of equilibrium molecular dynamics together with the Green-Kubo formalism. Schelling *et al.*²⁴⁸ found that both MD methods agree with each other for crystalline silicon within uncertainties. It also suffers from finite-size effects, but to a lesser extent than the direct method.²⁴⁹ Furthermore, the thermal conductivity tensor can be extracted from one simulation which is a clear advantage for MOFs with anisotropic crystal directions.²⁵⁰ In future studies, a first-principles treatment of MOFs

with the Green-Kubo formalism might be doable with increased computer power and more efficient algorithms,²⁵¹ but for now this approach mainly relies on a force field PES. During this thesis, we applied the Green-Kubo formalism together with force field equilibrium molecular dynamics (**Paper X**). This method is well-established in condensed matter physics and has been applied on MOFs in the past,^{250, 252–254} but the accuracy is difficult to validate as there is almost no experimental information.

I. Green-Kubo equilibrium molecular dynamics

The Green-Kubo formalism provides a relation between a transport coefficient (thermal conductivity) and an integral over a time-correlation function (heat flux). This has been derived for various transport properties other than the thermal conductivity such as shear viscosity and electrical conductivity.²⁰⁷ It is based on the fluctuation-dissipation theorem in nonequilibrium statistical mechanics.^{255, 256} This formalism yields a method capable of obtaining a transport property from a simulation of a system in thermodynamic equilibrium.

$$\kappa_{ij} = \frac{1}{k_B V T^2} \int_0^{+\infty} \langle J_i(t) J_j(0) \rangle dt \quad (2.28)$$

The microscopic heat current in a solid with N atoms is defined as²⁵⁷

$$\mathbf{J} = \sum_{i=1}^N E_i \mathbf{v}_i + \sum_{i=1}^N \mathbf{r}_i (\mathbf{F}_i \cdot \mathbf{v}_i) + \sum_{i=1}^N \mathbf{r}_i \frac{dU_i}{dt} \quad (2.29)$$

Here E_i , U_i , $\mathbf{r}_i$, and $\mathbf{v}_i$ are the per-atom energy, per-atom potential energy, position, and velocity of atom i , respectively. $\mathbf{F}_i$ is the total force exerted on atom i . The first term is called the kinetic part and barely contributes for solids. The second and third term is referred to as the potential part. These expressions can be simplified for various force field potentials.²⁵⁷ The partitioning of the energy and potential energy per atom is not uniquely defined, but studies have indicated that the specific choice does not significantly influence the result.²⁴⁸

Data to approximate the integral are collected from simulations run in the microcanonical ensemble (NVE). To obtain the thermal conductivity at room temperature, the system has to be equilibrated first at the desired temperature before going over to the NVE ensemble. The heat current autocorrelation function (HCACF) is obtained from and averaged over a large number of independent simulations to properly account for the relevant

phase space. These simulations do not include NQEs in contrast to our data on the thermal expansion and the heat capacity.²⁵⁸

Many techniques have been proposed to obtain a good estimate of the thermal conductivity from the often capricious HCACF such as the first avalanche method and the double-exponential-fitting of HCACF.^{259, 260} However, these methods primarily work for monotonically decreasing HCACF,²⁶¹ which is not the case for MOFs (Figure 2.9). In this work, the same approach as Kaviany and co-workers applied on MOF-5 was followed.²⁵³ Here, the fluctuations in the integrated HCACF are removed with a running average.²⁶¹ Figure 2.9 displays the normalized HCACF and associated thermal conductivity for the isotropic IRMOF-16.

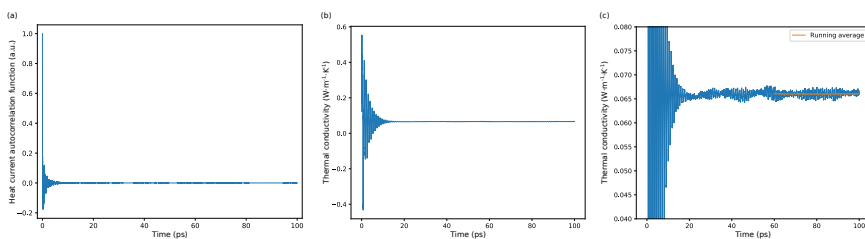


Figure 2.9: (a) Normalized heat current autocorrelation function (HCACF) of IRMOF-16. (b) Thermal conductivity of IRMOF-16 obtained by integrating the HCACF. (c) A thermal conductivity of $0.066 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ is obtained by removing the fluctuations with a running average.²⁶¹

3

Understanding Flexibility in Stimuli-Responsive Metal-Organic Frameworks

*Seek the treasure you value most dearly:
if you bow your head, let it be to a lofty mountain*
Maori whakataukī (proverb)

As stated in Section 1.2, the aim of this chapter is to provide insight in the factors contributing to the stimuli-responsive behavior of flexible MOFs. A better understanding of framework flexibility is required to evolve from an academic, peculiar phenomenon toward a reproducible and exploitable material's property for specific applications. The associated original papers are listed in Part II.

3.1 A thermodynamic protocol to identify the macroscopic conditions of breathing

An important step to establish a thermodynamic understanding of flexibility on the macroscopic level was taken in **Paper III** as a collaborative effort of various researchers within the CMM working on the flexible behavior of MOFs. The idea to characterize flexibility through the construction of

Helmholtz free energy profiles originated from a technical paper by Rogge *et al.* where an implementation of a barostat was introduced to simulate MOFs.²⁰⁴ The practical application of this scheme to qualitatively detect the conditions for breathing was probed for the first time in **Paper I**¹⁸⁴, where MIL-47(V)-type materials were systematically investigated.

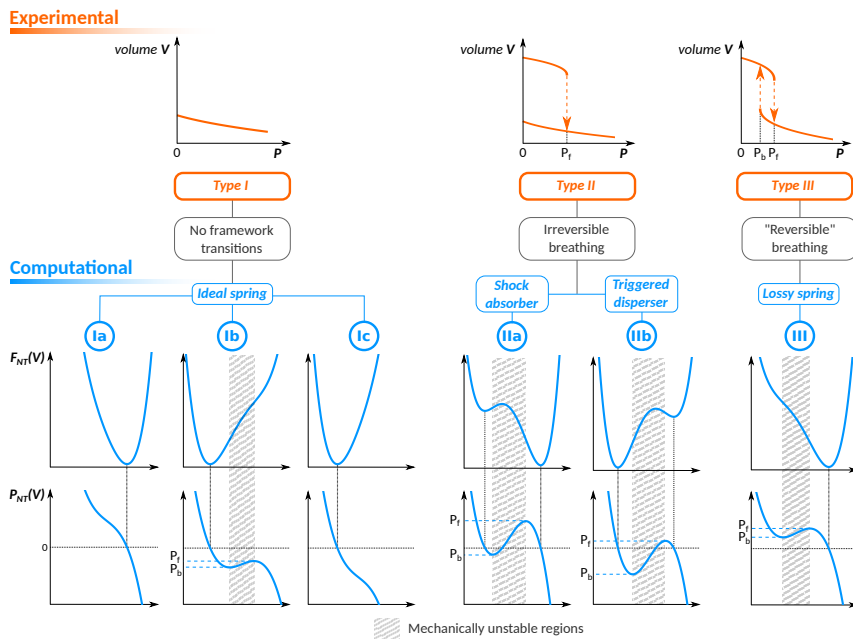


Figure 3.1: Comparison of experimental response with corresponding hypothetical Helmholtz free energy. Top panel: illustration of the possible experimental responses of a material upon exerting a positive mechanical pressure. Bottom panel: hypothetical Helmholtz free energy $F_{NT}(V)$ and mechanical pressure $P_{NT}(V)$, with N the number of particles and T the temperature, in terms of the volume. Shaded areas correspond to mechanically unstable regions. Reproduced from Ref. 47 with permission of Springer Nature, copyright 2018.

However, in **Paper III**, the potential of this elegant thermodynamic approach surfaced. Here, we proposed a protocol to identify the conditions and triggers upon which a framework will display a breathing transition based on molecular simulations. The main principle was already explained in Chapter 2 and relied on the second law of thermodynamics. As the breathing transition is associated to a large volume change, the relevant thermodynamic potential that needs to be known is the Helmholtz free energy F . Identifying the

minima of the Helmholtz free energy as a function of the volume allows to determine the various (meta)stable phases that can potentially be reached with thermodynamic stimuli. Experimentally, one is typically limited to measuring the response of a specific trigger, while the underlying Helmholtz free energy surface remains unexplored. This is illustrated in Figure 3.1, where experimental volume-versus-pressure curves are shown to yield non-unique Helmholtz free energy profiles. In other words, the same curve can result from a fundamentally different thermodynamic potential, whereas a crucial distinction can be made between the latter. This in turn makes it possible to properly understand the viable applications of a stimuli-responsive material under a given set of thermodynamic conditions.

Furthermore, the Helmholtz free energy curves enable to determine the transition stimulus required to switch between the open and contracted phase according to the assumption of collective behavior. Under this assumption, a transition becomes possible if there exists no barrier between the different states. For mechanical pressures, this can directly be derived from the pressure-volume curves, which are the derivative of the Helmholtz free energy to the volume. A local maximum (minimum) indicates the maximum (minimum) pressure that the material can withstand in the open (closed) state. Going beyond the transition pressure will force the system to transform. For other triggers X , this can be determined by generating the Helmholtz free energy profile in terms of the volume for various values of the external trigger X (Figure 3.2). In **Paper III**, our approach was justified by the study and reproduction of a wide range of experimentally known stimuli-responsive MOFs. The necessary tools to make such a theoretical study possible were already discussed in Chapter 2.

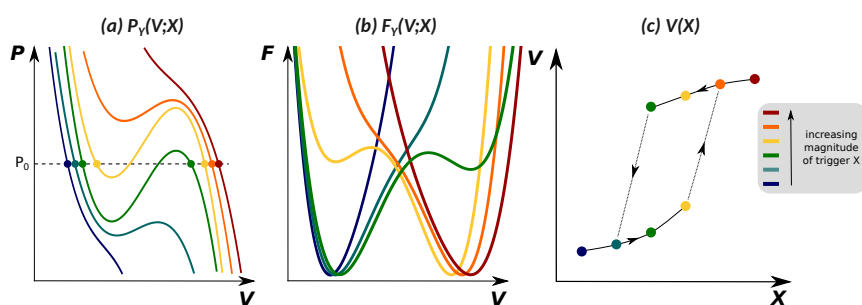


Figure 3.2: Illustration of the structural transitions induced by a general state variable X . (a) Mechanical equation of state (b) Helmholtz free energy and (c) the response $V(X)$. Reproduced from Ref. 47 with permission of Springer Nature, copyright 2018.

3.2 The importance of adequately modeling long-range dispersion in flexible MOFs

How to unravel the macroscopic conditions for breathing MOFs should be clear from the generalized approach discussed in **Paper III** and explained in the previous section. Of course, this assumes the availability of an accurate Helmholtz free energy profile as a function of the volume. This can be a daunting task for flexible MOFs, since the nanoscopic interactions and transition mechanisms governing the flexible behavior are not properly understood. For instance, Walker *et al.* showed for the prototypical MIL-53(Al) that weak dispersion forces give rise to the bistability of this framework, and hinted that entropy might be responsible for its experimentally observed temperature-induced breathing process.¹⁴¹ Both dispersion and entropy, however, belong to the most challenging phenomena to accurately capture with molecular simulation methods.

In **Paper I**, an MD study was conducted to explain the difference in experimental behavior between three types of MIL-47(V)-like materials, i.e. MIL-47(V), COMOC-2(V) and COMOC-3(V). These structures share one-dimensional chains of corner-sharing $V^{IV}O_6$ octahedra but differ in organic linkers. To this end, new first-principles derived force fields were constructed with QuickFF for the covalent and electrostatic part of the potential. In the process of validating these force fields with experimental information on the breathing behavior under pressure, we found that slight modifications of the existing MM3 van der Waals model were required to achieve a good correspondence between theory and experiment. Furthermore, we noticed that changing the parameters of the well-depth and radius of the pairwise van der Waals interactions with not more than 15 % tremendously influenced the quantitative breathing behavior of the materials under study.

Optimally, one would use MD techniques to sample the relevant phase space as was done for the MIL-47(V)-type materials. However, this simple example showed that the results for flexible MOFs are highly sensitive to the long-range part of the force field and may coincide in many cases with experiment for the wrong reasons. Hence, we took a step back in this PhD thesis and focused the attention on getting an accurate quantum mechanical description of the potential energy surface. Nevertheless, even for DFT, the problem of inadequately modeling long-range dispersion is a well-known issue as mentioned in Chapter 2.

Therefore we revisited MIL-53(Al) in **Paper V** as it was a well-studied system in literature with many reference data. This material was shown to breathe under temperature by Liu *et al.*⁶⁰ and Figure 3.3 (b) displays the volume

as a function of temperature. At low temperatures, a nonporous, dense narrow-pore (np) phase is found. After increasing the temperature, the framework opens up and a porous large-pore (lp) phase is formed. This transition can be reversed with a significant temperature hysteresis (Figure 3.3 (b)). Following our theoretical approach introduced in **Paper III**, a set of hypothetical Helmholtz free energy curves is proposed to explain these experimental findings (Figure 3.3 (c)). The strength of the dispersion interactions will heavily influence the stability of the np phase as it is mainly stabilized by $\pi - \pi$ stacking between the organic linkers. A computational method overestimating this stabilization effect will shift the Helmholtz free energy of the np phase downwards, which will increase the np-to-lp transition temperature (Figure 3.3 (d)).

To assess the validity of typical DFT methods, we investigated the Helmholtz free energy between both phases as this quantity controls the possibility of a phase transformation in terms of the temperature. The Helmholtz free energy of the np phase needs to be higher than the lp phase beyond T_4 (Figure 3.3) to reconcile with the sole existence of the lp phase above this temperature. The same is true for the temperature region below T_2 , where the np phase has to be more stable than its open counterpart. This hysteresis behavior requires a critical crossing temperature (T_{cross}) where both phases are equally stable. Experiment suggests that this temperature should roughly lie in between 130 K and 350 K.

Nevertheless, popular and commonly applied XC functionals and dispersion schemes situate T_{cross} at too high temperatures (410-1474 K) using a harmonic approximation (Section 2.2.1) as shown in **Paper V**. A critical analysis indicated that a good description of the electronic energy difference at 0 K ($\Delta E_{\text{lp-np}}^{\text{el}}$) – which is dominated by dispersion – is the essential ingredient to obtain a reliable prediction. This fact stimulated us to go beyond DFT and to apply for the first time RPA on a flexible MOF in collaboration with Prof. Kresse of the Computational Materials Physics group at the University of Vienna. This state-of-the-art technique consistently combines long-range dispersion effects with short-range interactions and results in an excellent agreement with experimental data for various systems.^{164–166} Similar to the case of molecular crystals,²⁶² we had to incorporate single-excitation (SE) effects on top of our RPA data to obtain an accurate electronic energy profile in terms of the volume at 0 K (Figure 3.4). This many-electron treatment produced a $\Delta E_{\text{lp-np}}^{\text{el}}$ of 7.7 kJ/mol with a numerical error bar around 3.5 kJ/mol and decisively showed that almost all DFT methods overestimate the dispersion stabilization of the np phase. After establishing this benchmark value for the 0 K relative stability between the lp and np phase, we returned to our DFT-based thermal corrections and showed that combining results from both

techniques yields a crossing temperature in satisfactory agreement with experiment (Figure 3.5). On a minor note, the RPA+SE profile predicts that the lp phase remains metastable at 0 K. This suggests that the hypothesis of idealized collective behavior underlying our thermodynamic protocol (**Paper III**)⁴⁷ might be requiring a slight relaxation.

Both **Paper I** and **Paper V** highlight that flexible MOFs prone to subtle long-range dispersion interactions are difficult to model without feedback from experiment. Unfortunately, with the current computational resources, RPA+SE is too demanding to be employed frequently for materials design. DFT methods should therefore be identified with similar predictable quality. A comparison between the RPA+SE energy profile and the DFT results revealed a close correspondence between the high-level benchmark data and PBE+D3(BJ)^{ATM} (Table 3.1). The latter level of theory is a computationally cheap approach to accurately model MIL-53(Al), although this might be somewhat accidentally. Extrapolating the good performance to widely different materials should hence be done with great caution.

While it was clear from the theoretical spread on the DFT simulations that the predictions are highly method-dependent and not in accordance with experiment, some interesting aspects could be noted that might stimulate the theoretical community to develop more appropriate XC functionals and dispersion methods for challenging systems like flexible MOFs. For instance, purely pairwise models for the dispersion interactions do not suffice and tend to overbind the np phase, but the inclusion of destabilizing many-body effects shifts both the phase stability and equilibrium volume toward the benchmark data in case of MIL-53(Al) (Table 3.1). In principle, additive dispersion schemes should be designed to produce results largely independent of the corresponding XC functional, which was not the case for all methodologies. Therefore, we could not definitely find an improved agreement with the RPA+SE data when moving along the rungs of Jacob's ladder given a certain dispersion scheme (from GGA to hybrid XC functionals). A possible explanation could be that MOFs are not well-represented in typical databases used for fitting the coupling between the XC functional and dispersion scheme. Overall, we showed in **Paper V** that a meticulous choice of both the XC functional and dispersion method is important to obtain a reliable prediction of phase stability in flexible MOFs.

Table 3.1: The electronic energy difference between the lp and np phase of MIL-53(Al) with different methods. ΔE_{lp-np}^{el} is the 0 K electronic energy difference at the equilibrium volumes of both phases (V_{np} and V_{lp}) relaxed with the specific method (or PBE+D3(BJ) for RPA+SE). $\Delta E_{lp-np}^{el,*}$ is the 0 K electronic energy difference at fixed structures (864 Å³ (np) and 1427 Å³ (lp)). GGA (PBE¹²¹), meta-GGA (SCAN¹²⁴) and hybrid (HSE06¹²⁷, B3LYP¹²⁸) XC functionals were included together with dispersion models ranging from pairwise (D2,¹⁵³ D3(BJ),^{145, 151} TS¹⁵⁷) to many-body schemes (D3(BJ)^{ATM},^{145, 151, 154} MBD,^{146, 147} MBD/FI²⁶³). Three XC functionals inherently including long-range dispersion were also tested, i.e. SCAN+rVV10,¹²⁵ vdW-DF2¹²³ and M06-L.¹²⁶ ^a The sample was going toward the np phase on a longer time scale than the measurement.⁶⁰ ^b The error bar on the RPA+SE result reflects the uncertainty due to numerical convergence effects. More details can be found in **Paper III**.

	V_{np} (Å ³)	V_{lp} (Å ³)	ΔE_{lp-np}^{el} (kJ/mol)	$\Delta E_{lp-np}^{el,*}$ (kJ/mol)
Experiment (77 K) ⁶⁰	864	1419 ^a	-	-
RPA+SE	860	1455	7.4	7.7±3.5 ^b
PBE	np unstable	1489	np unstable	-118.5
PBE+D2	808	1457	15.7	12.8
PBE+D3(BJ)	843	1426	26.6	26.1
PBE+D3(BJ) ^{ATM}	874	1448	5.8	6.2
HSE06+D3(BJ)	825	lp unstable	lp unstable	42.3
HSE06+D3(BJ) ^{ATM}	850	1389	22.3	22.4
B3LYP+D3(BJ)	789	lp unstable	lp unstable	58.9
B3LYP+D3(BJ) ^{ATM}	806	1405	43.8	39.0
PBE+TS	793	lp unstable	lp unstable	74.2
PBE+MBD	828	1425	25.8	24.5
PBE+MBD/FI	851	1439	16.4	16.4
SCAN	np unstable	1430	np unstable	-43.6
SCAN+rVV10	803	1384	31.2	28.3
vdW-DF2	869	1456	34.8	35.5
M06-L	829	lp unstable	lp unstable	36.6

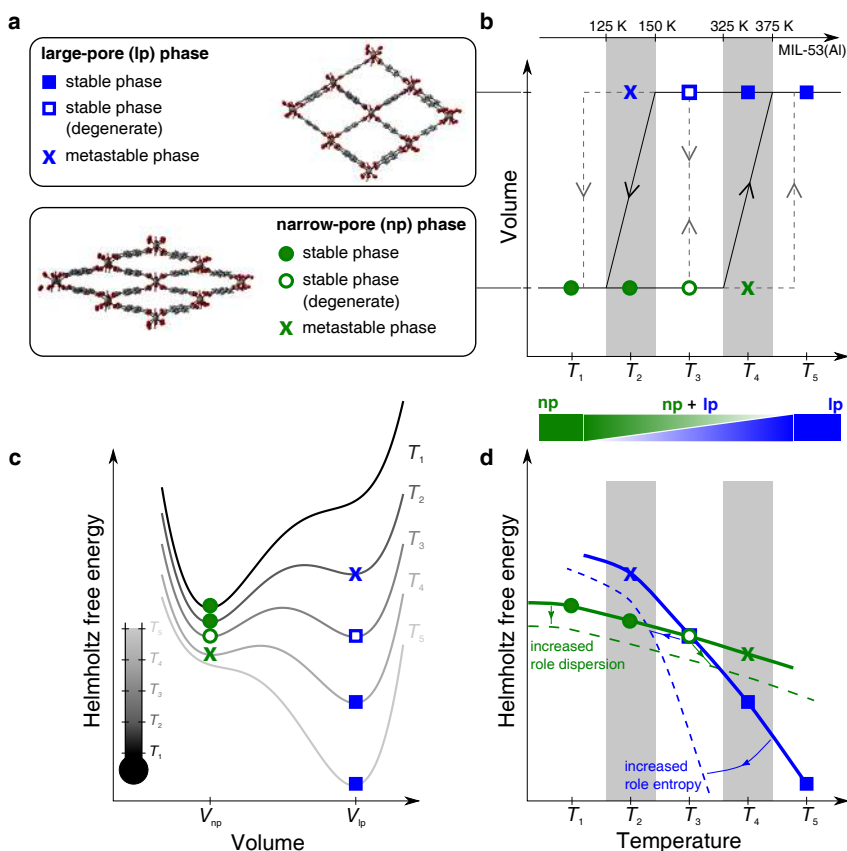


Figure 3.3: Temperature-induced breathing of a flexible MOF. The definition of the blue and green symbols is indicated in the top left panel. **a** Two (meta)stable phases of MIL-53(Al). **b** Thermo-responsive behavior of MIL-53(Al) as measured by experiment. The system switches as a function of temperature between the np and lp phase with a hysteresis loop. Different transition regimes are indicated with arrows. The gray shaded areas correspond to the experimentally measured transition regions.⁶⁰ **c** Hypothetical Helmholtz free energy curves as a function of volume at different temperatures (T_1, T_2, T_3, T_4, T_5) as an explanation for the observed experimental behavior. **d** Hypothetical evolution of the Helmholtz free energy for the np and lp phase as a function of temperature. The gray shaded areas correspond to the experimentally measured transition regions.⁶⁰ Reproduced from Ref. 133 with permission of Springer Nature, copyright 2018.

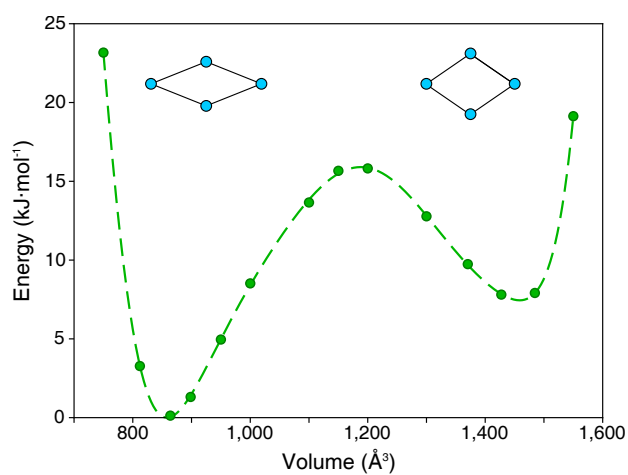


Figure 3.4: RPA+SE electronic energy profile as a function of volume for MIL-53(Al). Reproduced from Ref. 133 with permission of Springer Nature, copyright 2018.

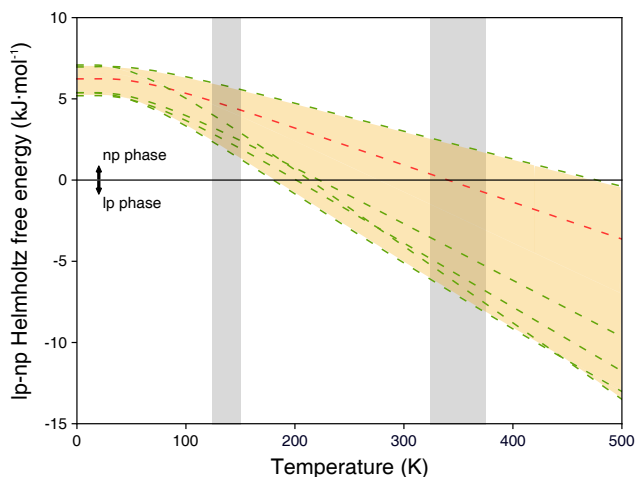


Figure 3.5: Helmholtz free energy difference between the lp and np phase of MIL-53(Al) as a function of temperature. This Helmholtz free energy difference was calculated with the harmonic approximation. An accurate electronic energy difference between the lp and np phase was obtained using RPA+SE. The displayed spread (orange shaded area) is obtained using predictions of the evolution of the Helmholtz free energy difference with various density-functional theory methods. The red curve indicates the corrections at the PBE+D3(BJ) level of theory, while the green curves represent the other levels of theory (from bottom to top starting from the right: vdW-DF2, SCAN+rVV10, PBE+D2, PBE+MBD, PBEsol+D3(BJ) and PBE+MBD/FI). The gray shaded areas correspond with the experimentally measured transition region.⁶⁰ Reproduced from Ref. 133 with permission of Springer Nature, copyright 2018.

3.3 From wine-rack-type frameworks to pillared-layered MOFs: A delicate balance between dispersion and entropy

In **Paper III**, it was discussed how fundamental insight into the macroscopic conditions at which MOFs display flexibility can be gained through knowledge of the Helmholtz free energy. Nevertheless, to pinpoint the microscopic factors controlling the shape of this thermodynamic potential, additional in-depth studies are required. For instance, some groups have shown that the flexibility of the prototypical MIL-53(Al) highly depends on the experimental synthesis procedure.^{264, 265} Theoretical investigations of flexible MOFs are not hampered by such sensitivities, but might suffer from inaccurate modeling of the long-range interactions. Below, the findings for three distinct material types are summarized based on the theoretical work performed in **Papers I-V, VII and IX**. An overview of the investigated materials can be found in Figure 1.2.

3.3.1 MIL-47(V)-type materials

MIL-47(V) was synthesized for the first time in 2002 by Férey and co-workers. The structure contains one-dimensional VO chains connected by 1,4-benzenedicarboxylate (bdc) linkers (Figure 3.6). It does not display breathing upon gas adsorption or temperature in contrast to members of the MIL-53 series, but Yot *et al.* revealed a reversible pressure-induced breathing transition with hysteresis between a np and a lp phase.⁶¹ At the Center for Ordered Materials, Organometallics and Catalysis (COMOC) under leading of Prof. Van Der Voort at Ghent University, variants were synthesized with elongated organic linkers such as 4,4'-biphenyl-dicarboxylate (bpdc) (COMOC-2) and 2,6-naphthalenedicarboxylate (ndc) (COMOC-3) with a remarkable flexibility upon specific guests.^{23, 24, 266}

To unravel and understand the intrinsic flexibility of this MIL-47(V) family of materials, we constructed in **Paper I** the Helmholtz free energy profiles in terms of the volume at different temperatures using MD simulations.¹⁸⁴ New force fields were derived from DFT cluster calculations inspired by the successful work of Vanduyfhuys *et al.* on MIL-53(Al).²⁶⁷ The force fields for these materials were built by combining a model for the metal-oxide chain with the corresponding organic linker. The general purpose QuickFF software package had to be extended for the asymmetric O-V=O chain with two distinct potential energy minima. In this way, fine-tuned system-specific force fields able to model the complex coordination environment of MIL-47, COMOC-

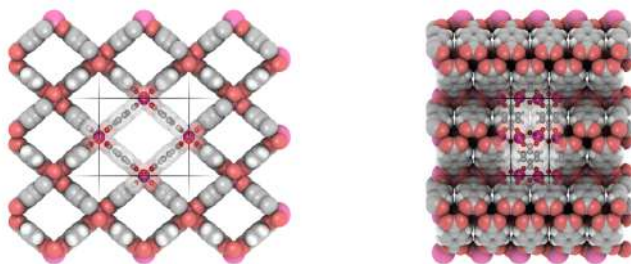


Figure 3.6: Molecular representation of the lp phase of MIL-47(V).

2 and COMOC-3 were obtained. Unfortunately, as mentioned above, we had to slightly adapt the van der Waals parameters to accurately mimic the pressure-volume experiment by Yot *et al.* on MIL-47.⁶¹ Subsequently, we transferred these parameters to the other two systems – because of their large similarity with MIL-47 – and investigated their intrinsic flexibility for the first time after validating the results with the limited available data.

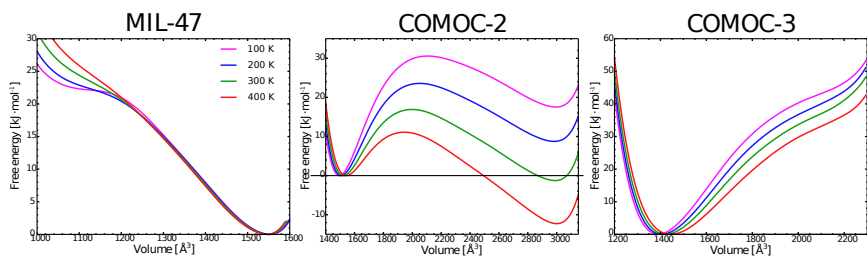


Figure 3.7: Helmholtz free energy profiles as a function of the volume and temperature for MIL-47, COMOC-2 and COMOC-3.

We found that the organic linkers have a tremendous influence on the flexibility of the framework (Figure 3.7). On the one hand, MIL-47(V) with the shortest linker only has a stable lp phase at temperatures in between 100 K and 400 K. A high mechanical pressure (≈ 120 MPa) is necessary to force the system into a dense np state, which opens up when the pressure is released below 50 MPa. On the other hand, COMOC-3 with an ndc linker is highly stabilized by host-host dispersion interactions and stays in the np phase. The bistable COMOC-2 with a bpdc linker is at low temperatures in an np configuration and favors the lp phase at higher temperatures because of the entropy difference. From the Helmholtz free energy curves, we also observed that these materials are very soft with bulk moduli on the order of 1 GPa, which enhance in strength in case of the lp phase with increasing

temperature and vice versa for the np phase. Finally, we also showed that the lp-to-np transition pressures are rather insensitive to the temperature in contrast to the reverse transition pressures which significantly increase with temperature.

3.3.2 Isorecticular MIL-53 materials

The first signs of breathing behavior in wine-rack-type frameworks like MIL-53 were discovered by monitoring the structure when varying the temperature and guest concentration.^{25, 60, 268} More recently, the use of mechanical pressure has emerged as an important characterization tool to probe the intrinsic flexibility.^{61, 269} This is illustrated by the efforts of the experimental community to systematically characterize a number of frameworks in the MIL-53 branch with the overall aim to detect relevant materials for future mechanical energy storage applications.^{28, 270–273} In **Paper II**, a joint experimental-computational study was executed to explore the potential of MIL-53(Ga)-FA.

This structure is the gallium equivalent of the commercially available aluminum fumarate A520 or MIL-53(Al)-FA.²⁷ The material consists of the same Al(OH) chain like in MIL-53(Al), but is connected through fumaric acid organic linkers. A structural lp-to-np transition was found for the gallium variant with mercury intrusion and confirmed with high-pressure powder X-ray diffraction experiments in **Paper II**. In contrast to MIL-53(Al)-FA, this pressure-induced phase transition was irreversible. These observations were corroborated by the computed DFT energy profile as a function of the volume for both materials. MIL-53(Ga)-FA possesses a stable np minimum, whereas the np phase is only mildly bound and expected to disappear at room temperature in case of aluminum. While there were some inconsistencies between theory and experiment (e.g. the predicted volume contraction), the simulations in **Paper II** did provide support to the fact that MIL-53(Ga)-FA displays an irreversible pressure-induced transition as opposed to the reversible one of MIL-53(Al)-FA.

Paper V investigated the delicate balance between long-range dispersion and entropy in MIL-53(Al). The difficulties with accurately including long-range dispersion were discussed in Section 3.2. After identifying the convenient PBE+D3(BJ)^{ATM} method for MIL-53(Al), we continued in **Paper V** with an extended series of MIL-53 materials including MIL-53(Ga),^{26, 196} MIL-53(Al)-FA,²⁷ DUT-4^{29, 274} and DUT-5.²⁹ The latter two materials contain ndc and bpdcc organic linkers similar to COMOC-3 and COMOC-2, respectively. In this study, we investigated the possibility to rationally design temperature-responsive breathing MOFs for a new generation of temperature-controlled

smart materials. The rationale behind the temperature-induced breathing transition was shown in Figure 3.3, and our most important simulation results are summarized in Figure 3.8.

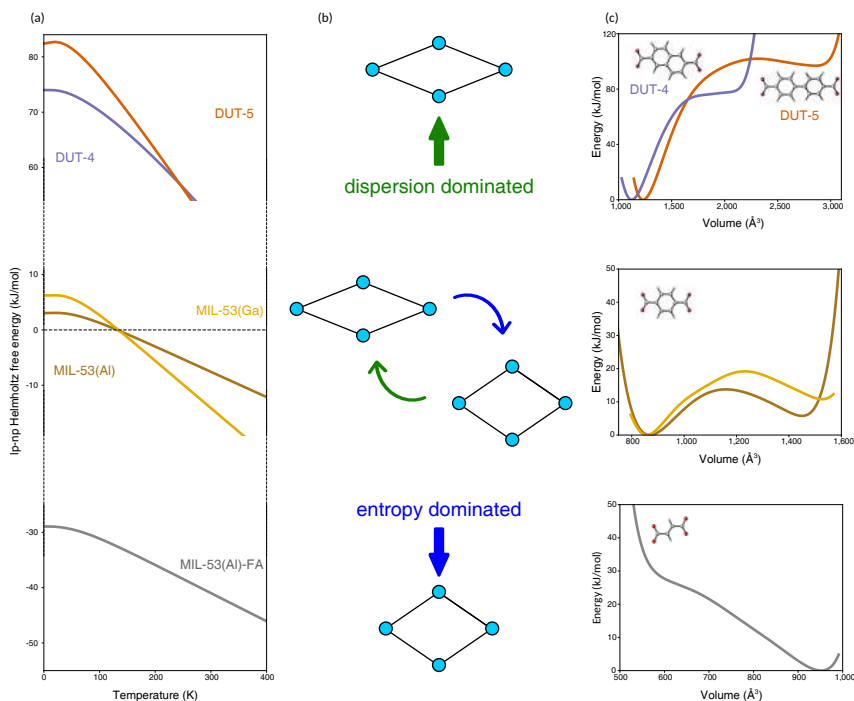


Figure 3.8: Design of temperature-dependent flexibility in isoreticular MIL-53 materials. The yellow shaded area highlights the desired temperature-responsive case. (a) Helmholtz free energy difference between the lp and np phase as a function of temperature for the series of isoreticular MIL-53 frameworks. The harmonic temperature corrections were calculated at the PBE+D3(BJ) level of theory, and were added on top of the 0 K PBE+D3(BJ)^{ATM} electronic energy difference. (b) Schematic depiction of the (meta)stable phases and the dominating contributions. (c) Electronic energy profiles as a function of the volume for different materials at the PBE+D3(BJ)^{ATM} level of theory. The corresponding organic linkers are indicated in the different panels. Reproduced from Ref. 133 with permission of Springer Nature, copyright 2018.

According to the classification introduced in Figure 3.1, we find a lossy spring (MIL-53(Al)-FA), triggered dispersers (MIL-53(Al,Ga), DUT-5) and an ideal

spring (DUT-4). The computed Helmholtz free energy difference between the lp and the np phase as a function of temperature illustrates that only MIL-53(Al) and MIL-53(Ga) switch in stability within a reasonable temperature window. The structures with elongated linkers (DUT-4 and DUT-5) possess too stable np configurations to spontaneously open up at temperatures below their decomposition temperature. MIL-53(Al)-FA assumes an lp state over the entire temperature range. A subtler effect is achieved by substituting aluminum with gallium in the metal-oxide chain. The crossing temperature did not change much due to the compensation of an increase in dispersion stabilization with an increase in entropy difference. These theoretical observations were validated to some extent by the limited available experimental literature.^{26, 29, 196, 272, 275}

The above discussion shows how the organic linker and metal ion influence the breathing behavior of MIL-53 materials by focusing on the energetics. Nevertheless, to elucidate the microscopic key features that govern this transition, vibrational spectroscopy is better suited. Tan and co-workers suggested that specific soft modes are responsible for flexibility in MOFs by investigating the low-frequency spectrum.¹⁰⁰ Insight in how these collective modes propagate on the molecular level enables to recognize possible triggers for breathing. To illustrate this we investigated the infrared and Raman spectrum of the prototypical MIL-53(Al) using computational techniques in **Paper IV** and **Paper VII** in collaboration with experimental partners at Ghent University (Prof. Vrielinck and Prof. Van Der Voort).

As a first step, it was shown that static DFT calculations using PBE+D3(BJ) are capable in reproducing the experimental mid-infrared spectrum. In this range of frequencies ($600\text{--}1800\text{ cm}^{-1}$), a unique vibrational fingerprint was found that allows to characterize the state of the material (np or lp) during routine experimental measurements. However, the difference between both phases becomes more pronounced and interesting in the far-IR range ($0\text{--}700\text{ cm}^{-1}$) as shown in Figure 3.9. A detailed discussion of the modes is presented in **Paper IV** and **Paper VII**. Nevertheless, it is important to mention here that several modes were identified as potentially relevant for the flexibility in MIL-53(Al). Especially the collective vibrations in the terahertz region (below 300 cm^{-1}), which affect the lattice as a whole, are responsible for the temperature-induced breathing transition. A large contribution to the entropy difference between the lp and the np phase arises from the frequency shift in the linker rotations. As such motions are more constrained in the np phase, they are situated at higher frequencies. Similar conclusions can be drawn for the trampoline-like motions of the organic linkers and the metal-oxide backbone motions. The former weaken the $\pi - \pi$ dispersion interactions and are able to open the pore. This case study limited to MIL-

53(Al) highlights the wealth of microscopic information that can be obtained through computational vibrational spectroscopy, and future work is under-way to perform a systematic evaluation of a large set of flexible MOFs.

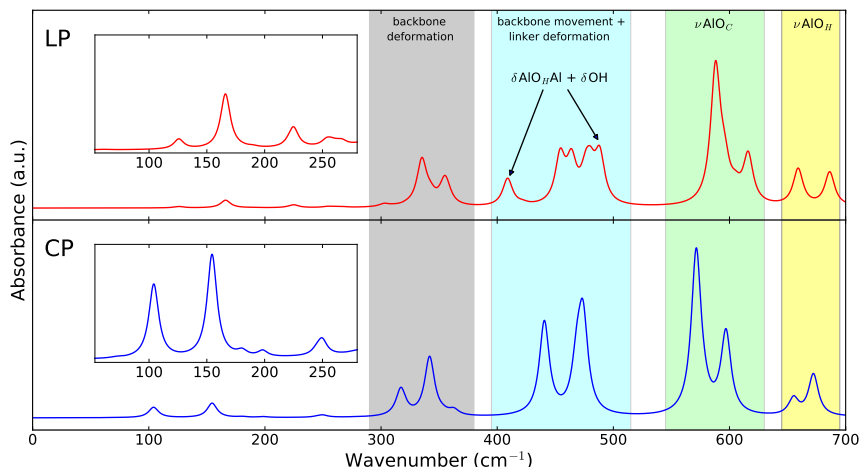


Figure 3.9: Comparison of the theoretical far-IR spectrum ($0\text{--}700\text{ cm}^{-1}$) of the np and lp phases of MIL-53(Al). Reproduced from Ref. 105 with permission of the American Chemical Society, copyright 2018.

3.3.3 DMOF-1

Up to now, only wine-rack topologies like MIL-47 and MIL-53 were discussed. In **Paper IX**, the DMOF-1 framework was investigated as a representative of the pillared-layered MOFs.^{276, 277} This family has already demonstrated to be an excellent testing platform for flexible behavior in the past.^{278–280} In DMOF-1, the two-dimensional layers are formed by paddle wheels composed of divalent metal cations, which are bridged by 1,4-benzenedicarboxylate (bdc) organic linkers (Figure 3.10). The layers are connected through 1,4-diazabicyclo[2.2.2]octane (dabco) pillar ligands via the axial sites of the paddle wheels.

Guest-induced flexibility was found when the material was synthesized with zinc as metal cation in 2004.¹⁹¹ Dybtsev *et al.* observed that the framework contracted upon adsorption of benzene and soon after other molecules were found that trigger breathing.^{191, 281, 282} Nevertheless, this material is rather weakly responsive to most guests when considering the limited volume contraction ($\approx 15\%$). In addition, temperature-induced breathing has not yet

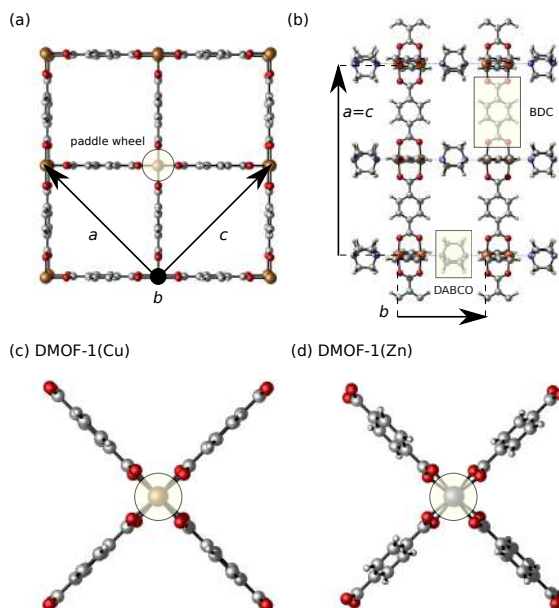


Figure 3.10: Molecular representation of the open-pore phase of DMOF-1 and its building blocks (paddle wheel, 1,4-benzenedicarboxylate (bdc) and 1,4-diazabicyclo[2.2.2]octane (dabco)). (a) Two-dimensional layer formed by paddle wheels connected through bdc organic linkers. (b) The connection of the two-dimensional layers through dabco pillar ligands. (c-d) Paddle wheel present in the equilibrium unit cell of DMOF-1(Cu) and DMOF-1(Zn), obtained at the PBE+D3(BJ) level of theory at 0 K. Reproduced from Ref. 106 with permission of the Royal Society of Chemistry, copyright 2019.

been reported for this jungle-gym-type framework.²⁸³ Through a combination of theoretical and experimental techniques, we examined the pressure-induced flexibility of DMOF-1(Zn)¹⁹¹ and DMOF-1(Cu)²⁸⁴ in **Paper IX** to explore the intrinsic flexibility of these highly tailorable frameworks. In terms of the pore opening angle, we illustrate in Figure 3.11 that pressure can be used to induce a volume contraction beyond earlier reported stimuli and modifications.

The phase transition responsible for this pressure-induced contraction was again discovered by constructing the energy profile as a function of the volume using PBE+D3(BJ)^{ATM} calculations at 0 K. These DFT $E(V)$ profiles are shown in the top left panel of Figure 3.12 for DMOF-1(Zn) and DMOF-

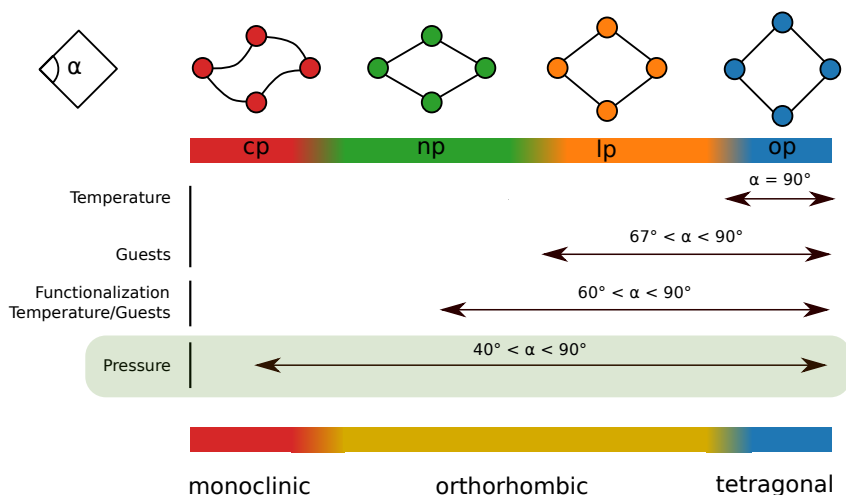


Figure 3.11: Schematic overview of the reported flexibility in DMOF-1 illustrated as a function of the pore angle α . Our definition of the different states is indicated. The crystal system of the different states is indicated at the bottom, distinguishing between tetragonal (op), orthorhombic (lp and np) and monoclinic (cp). Reproduced from Ref. 106 with permission of the Royal Society of Chemistry, copyright 2019.

1(Cu) and immediately emphasize that changing the nature of the metal allows to significantly tune the breathing behavior of DMOF-1. According to our classification in Figure 3.1, the copper variant behaves as a lossy spring. In that case, mechanical pressure can be used to reversibly switch between an open and dense configuration. The remarkable volume contraction of 40 % can be found at a pressure of about 240 MPa ($P_{\max}$ in Figure 3.12 (b)). Based on its $E(V)$ curve, DMOF-1(Zn) can be classified as a nanoshock absorber, where the material irreversibly switches to a contracted state but never returns. These predictions at 0 K were supported by force field MD simulations at experimental conditions for DMOF-1(Zn).

In order to gain molecular-level insight in this volume contraction, we monitored the behavior of some important structural parameters as a function of the volume. Not surprisingly, we found that the metal-dabco pillar axis remains nearly constant, indicating that the volume reduction entirely results from breathing in the 2D layers. At finite temperatures, both knee-cap and paddle wheel deformations are present during the breathing process.

A valuable figure of merit for mechanical energy storage applications is

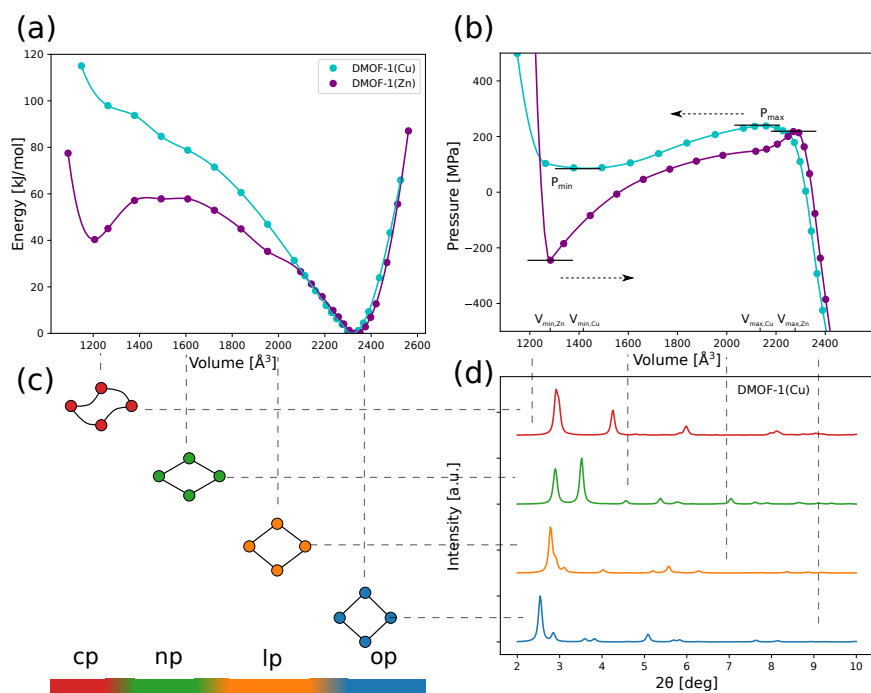


Figure 3.12: (a) DFT energy profiles $E(V)$ as a function of the volume for DMOF-1(Cu) and DMOF-1(Zn) at 0 K (PBE+D3(BJ)^{ATM}). The lines only represent a guide to the eye. (b) Pressure profiles $P(V)$ (at 0 K) as a function of the volume obtained by numerically deriving the energy profiles via $P(V) = -\frac{\partial E(V)}{\partial V}$. (c) The definition of the states (open pore (op)), large pore (lp), narrow pore (np) and closed pore (cp)) used in this work is inspired by the pore angle α as defined in Figure 3.11. (d) Simulated XRD patterns for different representative phases of DFT-optimized DMOF-1(Cu) ($\lambda = 0.4859 \text{ \AA}$). Reproduced from Ref. 106 with permission of the Royal Society of Chemistry, copyright 2019.

the relation $P_{\max}\Delta V$. It presents a theoretical upper bound for the energy stored during the pressure-induced breathing process. As both the predicted transition pressure $P_{\max}$ (more than 200 MPa) and the associated volume change ($\approx 40\%$) of DMOF-1 are among the highest reported so far for flexible MOFs, this material could thus potentially be interesting for mechanical energy storage. Motivated by these predictions, our experimental collaborators at the University of Montpellier investigated both DMOF-1 structures via mercury intrusion experiments. They confirmed the existence of a massive

volume contraction ($\Delta V \approx 30\text{-}40\%$), but could not return to the original phase after releasing the pressure. The computational transition pressures are overestimated in comparison with experiment, but this discrepancy could be related to the difficulty of getting accurate predictions between different phases without the use of computationally very heavy methodologies as RPA+SE (**Paper V**).

Unfortunately, however, the powder X-ray diffraction patterns collected after Hg-intrusion displayed amorphization. As a result, our experimental partners could not conclusively confirm the reversible or irreversible nature of the structural transition. It was suggested that the contracted phase is vulnerable and structurally collapses at pressures beyond the transition pressure (as the experiment goes up to 420 MPa). However, despite our computational efforts, this amorphization could not yet be interpreted. Therefore, we calculated the XRD patterns of our DFT-optimized structures to predict the evolution of an ideal in-situ high-pressure powder X-ray diffraction experiment (Figure 3.12 (d)). This may serve as a useful tool in future experimental characterization studies targeted on unraveling the contracted phase.

3.3.4 Design rules for flexibility

As evidenced by the different case studies performed in the context of this PhD work, breathing can only be achieved when several constraints are fulfilled. The obtained results enable to formulate some minimal design rules for tailoring intrinsic flexibility in the absence of guest molecules with a particular focus on wine-rack topologies.

The central premise was that we can identify the triggers for breathing by constructing the (Helmholtz) free energy profile in terms of the volume (**Paper III**). For both the MIL-47 and MIL-53 series of materials investigated in this work, we found that changing the organic linkers results in a large shift of the Helmholtz free energy difference between the np and the lp phase. The choice of the organic linkers has a drastic influence on the macroscopic behavior, which is strongly related to the extent of dispersion stabilization that they encounter in the dense state. When interested in temperature-controlled smart materials, it is unlikely that you can slightly adapt a working temperature-responsive breathing MOF by replacing the linker as witnessed from the results on MIL-53(Al) (**Paper V**) and COMOC-2(V) (**Paper I**). In contrast, modifying the metal could be a viable way of fine-tuning the performance.

For mechanical energy storage applications, this last strategy was pursued in collaboration with our experimental partners to modify the pressure response

of the frameworks. Our simulations for MIL-53-FA (**Paper II**) and DMOF-1 (**Paper IX**) indeed predicted that it is possible to switch between a nanoshock absorber and a lossy spring. Hence, we can theoretically tune the nature of the pressure-induced transition – irreversible or reversible – by simply substituting the metal. Experimentally, the same breathing transitions were observed, but the measured pressure-volume hysteresis loop did not always follow the predictions.

4

Thermal Properties of Metal-Organic Frameworks

*After climbing a great hill, one only finds
that there are many more hills to climb.*

Nelson Mandela (1918 – 2013)

MOFs belong to the class of the most promising porous materials envisioned to play a role in gas storage and separation.^{65, 285} These adsorbent materials can be exposed to large thermal fluctuations, because the adsorption and desorption of guests implies the release or consumption of energy. As MOFs are slowly progressing toward industrial applications, attention increasingly turns toward important thermal engineering issues such as thermal stability⁴³ and heat management^{83, 250} as both have been identified as important obstacles. While efficient heat transport in MOFs will ultimately be limited by their inherent porosity, it is nevertheless essential to understand and improve the intrinsic thermal characteristics to reduce the costs of, for instance, compensating heat exchangers.

In this PhD thesis, the nanoscale behavior of a diverse set of frameworks is investigated using molecular simulation techniques. The focus lies on the study of the heat capacity, thermal expansion and thermal conductivity of empty MOFs, together with the evaluation of the influence of guests on the thermal performance of the combined system as schematically illustrated in Figure 4.1. However, before discussing the MOFs under study (Figure 1.2),

the insights obtained about reliably modeling thermal properties with MD simulations are discussed. The associated original papers are listed in Part II.

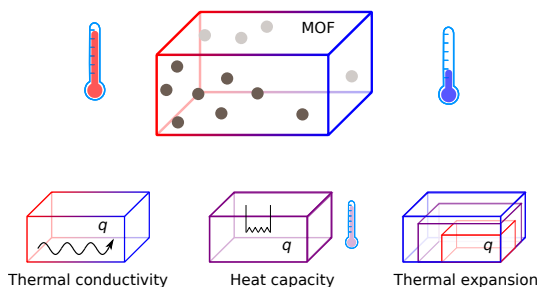


Figure 4.1: Schematic overview of the investigated thermal properties.

4.1 The importance of anharmonicities and nuclear quantum effects in modeling the structural and thermal properties of MOFs

As mentioned in Section 2.3, several methods exist to calculate thermal characteristics. Some of these methods include NQEs, while others focus on correctly sampling the anharmonic motions of the atoms. The importance of the latter has been stressed in various examples in the past. In contrast, the effect of NQEs on MOFs has been assumed negligible for a long time, although it was not yet thoroughly investigated. The importance of anharmonicities and NQEs on various structural and thermal properties was assessed in **Paper VI** and **Paper VIII**. In these papers, MOF-5 served as the model to evaluate the impact and interplay of both effects. Initially, the well-known negative thermal expansion of the empty framework²³⁹ was investigated with different MD-methodologies.¹⁸⁵ As explained in Chapter 2, standard MD treats the atoms as classical particles, but there exist a variety of techniques that capture NQEs in an approximate way at a reduced computational cost. In **Paper VI**, it is found that some of these methods are capable of reproducing the computationally more expensive PIMD results as shown in Figure 4.2.

The PES of MOF-5 was described with two different force fields in this study. The first one used harmonic bond and bend terms to model the network of chemical bonds in the framework, whereas the second force field explicitly included anharmonicity in these terms. Only upon inclusion of these an-

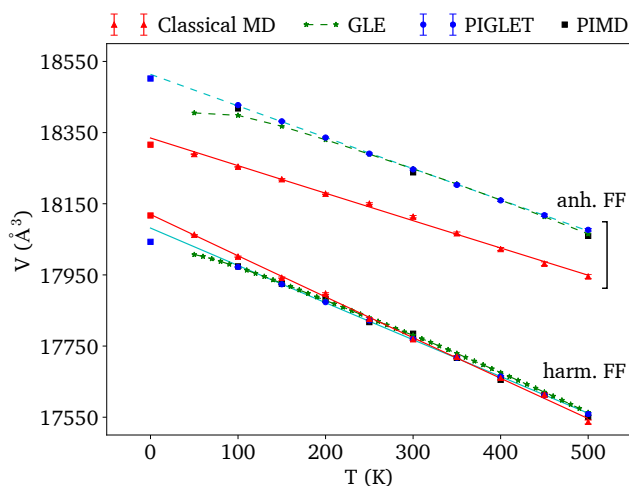


Figure 4.2: Volume of MOF-5 as a function of temperature as obtained from (PI)MD simulations using the harmonic ("harm. FF", bottom curves) and anharmonic ("anh. FF", top curves) force field of MOF-5. The data points at 0 K were obtained from geometry optimizations. Reproduced from Ref. 185 with permission of the American Institute of Physics, copyright 2019.

harmonic corrections, a thermal expansion coefficient could be retrieved in agreement with experiment.^{135, 185} The NQEs appeared to be of secondary importance as they only mildly influence this property as observed from the slope of the $V(T)$ curves. However, they do influence the equilibrium volume when the anharmonic effects are taken into account as witnessed by the vertical shift of the volume in Figure 4.2. More importantly, the results show that especially the GLE method is very promising for the thermal expansion of empty MOFs as it comes at the cost of standard MD.²⁴³ The upward shift of the volume when including NQEs was explained by the huge zero-point energy effects. Only at unrealistically high temperatures, the classical and quantum simulations will converge to each other. In **Paper VI**, it was also shown that the quantum fluctuations affect structural properties such as the interatomic radial distribution functions through broadening of the peaks.

The complexity was increased by adding methane inside the pores of the framework in **Paper VIII**. In this work, the focus lay on obtaining an accurate prediction of the heat capacity for challenging guest-loaded systems. For this particular purpose, a new PIMD scheme was developed in collaboration with Prof. Ceriotti from the EPFL, which is able to capture both anharmonicities

and NQEs simultaneously. First, we evaluated the performance of the force field and compared the different methodologies on the empty framework as experimental data is available for the heat capacity of this system.^{232, 233, 286} The left panel in Figure 4.3 learned that NQEs dominate this property in MOFs. Standard MD deviates and results in the Dulong-Petit limit over the investigated temperature range, while upon inclusion of NQEs with the newly developed Suzuki-Chin PIMD scheme (Section 2.3) a reasonable agreement with experimental measurements is found. Anharmonic effects play no role as the harmonic approximation produces the same results as PIMD.

However, when guest molecules are added to the system, they again become important. The same simulation methods are compared in Figure 4.3 (b). PIMD proves to be crucial to capture the correct temperature dependence of the heat capacity. The discrepancy between the harmonic approximation and PIMD can be understood through the mobility and low-frequency anharmonic motion of the guest molecules inside the pores. This is supported by the fact that standard MD seems to be able to qualitatively capture the low-temperature dependence of the heat capacity.

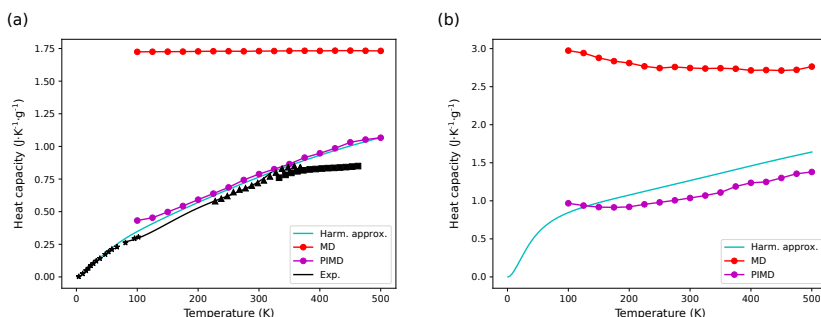


Figure 4.3: Specific heat capacity as a function of temperature as obtained from (PI)MD simulations and the harmonic approximation: (a) MOF-5 (b) MOF-5 with 100 CH₄ in the pores of the conventional unit cell. Experimental data is added for the empty MOF-5.^{232, 233, 286}

An analysis of the simulations in both **Paper VI** and **Paper VIII** lead to the formulation of empirical relations for the volume (and thus thermal expansion) and the heat capacity of methane-loaded MOF-5 based on standard MD and the harmonic approximation.¹⁸⁶ These relations illustrated that a full treatment of NQEs and anharmonicities is not always necessary to obtain reasonably accurate predictions. They could therefore serve as an efficient

Table 4.1: Structural and thermal properties of a number of MOFs. The structural properties (density ρ , accessible surface area (ASA), and void fraction) were derived from the optimal structure at 0 K using Zeo++²⁸⁷ (N₂ probe molecule with kinetic diameter 3.64 Å). The thermal properties are simulated at room temperature (300 K): thermal conductivity κ , isobaric heat capacity C_P , and volumetric thermal expansion coefficient β_V . A comparison of the simulated thermal properties with experiments is done in **Paper X**.

material	Al-soc-MOF-1	HKUST-1	MOF-505	UiO-66	MOF-5	IRMOF-10	IRMOF-16	UMCM-1	MOF-177
ρ (kg · m ⁻³)	343	851	888	1162	555	304	193	366	406
ASA (m ² · g ⁻¹)	5016	2229	2423	1246	3894	5230	6123	4584	4899
Void fraction (%)	52	28	20	9	42	62	73	56	49
κ (W · m ⁻¹ · K ⁻¹)	0.22	0.45	1.16-1.26	0.87	0.29	0.09	0.07	0.07-0.13	0.08-0.09
C_P (J · kg ⁻¹ · K ⁻¹)	1051	774	800	758	786	860	913	865	894
β_V (10 ⁻⁶ K ⁻¹)	-19	-15	-17	-9	-41	-48	-52	-47	-39

procedure to screen a larger number of systems at the cost of standard MD.

4.2 Intrinsic thermal properties of the framework

MOFs are generally considered to be poor thermal conductors with a low heat capacity. In addition, their porous, flexible nature gives rise to high and often negative thermal expansion coefficients. Except for the thermal stability – which is typically measured for every new material–,⁴³ experimental and even computational data about these properties are mainly limited to the well-known MOFs. Systematic studies evaluating more than one thermal property are even more scarce. A fundamental understanding of the structural and chemical features underpinning their intrinsic thermal properties is therefore highly sought-after and research into these fundamental relations is central to the optimal performance of adsorption-based technologies.

The intrinsic thermal properties of MOFs that were studied in this PhD thesis include the heat capacity, thermal expansion and thermal conductivity. The approaches to accurately model the first two characteristics were established in the previous section, where the effects of anharmonicities and NQEs were underlined. Like other computational studies of MOFs, the Green-Kubo method was applied to calculate the thermal conductivity.^{250, 254} In **Paper X**, these properties were evaluated for a diverse set of MOFs (Figure 1.2). They are given in Table 4.1.

To put the calculated values from Table 4.1 for the different properties immediately into perspective, a comparison is first made with more common material classes such as metals, ceramics and polymers.²⁸⁸ This is done in

the materials property chart in Figure 4.4, where a two-dimensional representation based on the specific heat capacity and thermal conductivity is shown for the MOFs under study alongside other materials. The data show that MOFs have thermal properties at the crossing of the ceramics, polymers and hybrid materials. More specifically, the MOFs with the lowest thermal conductivity are relatively unique in this set of materials. The ones with the highest value lie in the neighborhood of typical ceramics such as borosilicate glass ($\kappa \approx 1\text{--}1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $C_P \approx 800 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) and brick ($\kappa \approx 0.45\text{--}0.75 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $C_P \approx 800 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$).

In Figure 4.5, the separate thermal properties are displayed as a function of the density in a comparison with the same materials. This reveals, for instance, that MOFs provide similar heat conduction as natural materials (e.g. softwood) and specific heat capacities in the order of foams (e.g. ceramic foam) for the same density, while the thermal expansion behavior is rather exceptional. All other material representatives have positive thermal expansion coefficients, while the opposite is true for the investigated MOFs. However, the magnitude of the thermal expansion coefficient is quite similar to foams.

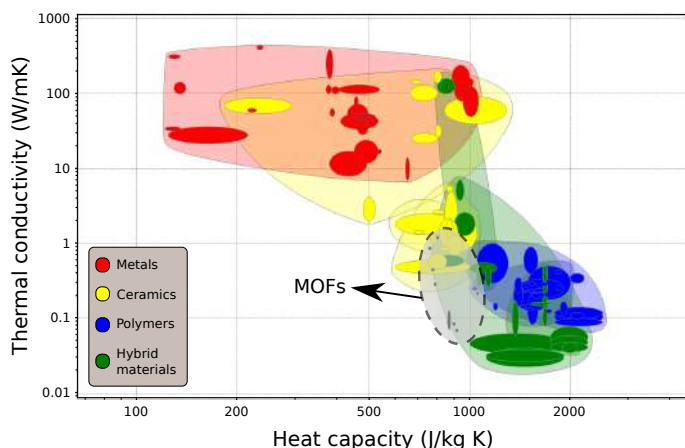


Figure 4.4: Materials property chart displaying the thermal conductivity and the specific heat capacity of MOFs alongside other material classes, namely, metals (and alloys), ceramics (glasses and (non-)technical ceramics), polymers and hybrid materials (composites, foams and natural materials). Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

Within the class of MOFs, there are also some important trends to be noted. MOFs containing the Zn_4O inorganic node have notably larger negative

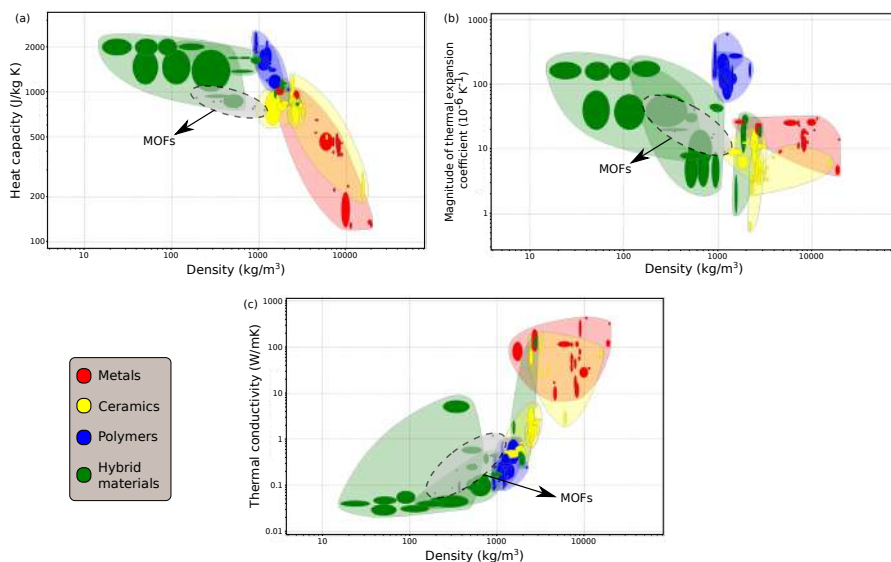


Figure 4.5: Materials property chart displaying the density and (a) the heat capacity (b) the magnitude of the thermal expansion coefficient (c) the thermal conductivity of MOFs alongside other material classes, namely, metals (and alloys), ceramics (glasses and (no)technical ceramics), polymers and hybrid materials (composites, foams and natural materials). Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

thermal expansion coefficients, while UiO-66 exhibits a smaller coefficient that might be explained by the higher connectivity of the inorganic nodes. The origin of negative thermal expansion has been investigated for several of these structures, and studies have suggested that low-energy transverse vibrational modes play an important role, and that it strongly depends on the topology of the structure.²⁸⁹ Figure 4.6, on the other hand, shows that MOFs possessing the lowest density have a larger specific heat capacity, which is also reflected in the IRMOF-series. The inverse correlation between specific heat capacity on a mass basis and the density is found in regular solids as well (Figure 4.5 (a)). The aluminum-based Al-soc-MOF-1 has the highest value per gram MOF, which is due to the lighter inorganic node as compared to zinc, copper and zirconium, and the presence of a tetratopic linker containing many light atoms. This can be understood by realizing that the specific heat capacity is a measure for the available degrees of freedom on a mass basis.

Furthermore, as the low thermal conductivity of MOFs mainly stems from

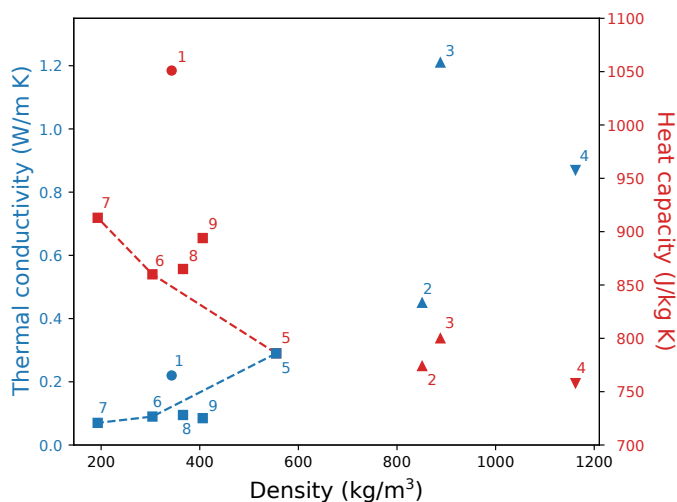


Figure 4.6: Thermal conductivity (blue) and heat capacity (red) as a function of the density at room temperature. The markers indicate the metal ion: Zr (triangle down), Zn (square), Cu (triangle up), and Al (circle). The IRMOF-series (MOF-5, IRMOF-10 and IRMOF-16) are connected by a line. 1 = Al-soc-MOF-1, 2 = HKUST-1, 3 = MOF-505, 4 = UiO-66, 5 = MOF-5, 6 = IRMOF-10, 7 = IRMOF-16, 8 = UMCM-1, 9 = MOF-177. Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

the large empty voids, it is not a surprise that the coefficient of heat conduction decreases with increasing linker length. Indeed, it goes down in Figure 4.6 from MOF-5 (bdc-linker) toward IRMOF-16 (tpdc-linker) in line with the toy model predictions of Wilmer and co-workers.²⁵⁰ The suggested correlation between the size of the pores and the thermal conductivity appears to be relatively independent of the underlying chemical structure. MOFs with a density below $500 \text{ kg} \cdot \text{m}^{-3}$ have ultralow thermal conductivities. Unfortunately, these are the most porous frameworks which can store the largest amount of gas at high pressure (see textural properties in Table 4.1). Moreover, MOF-5, HKUST-1 and UiO-66 have a similar linker length in between the inorganic nodes, but their performance seems to be solely dominated by the density. MOF-505 with copper-paddle wheels in the popular NbO-topology has a significantly higher value than the other frameworks and could be an interesting topology with improved thermal characteristics to start from.

Overall, the systematic evaluation of this diverse set of MOFs in **Paper X**

supports the current ideas about the thermal performance of MOFs. On the basis of these examples it is clear that a careful trade-off between the intrinsic thermal characteristics and adsorption properties will have to be made. Finally, it should also be noted that all properties were evaluated on infinite perfect single crystals, while in reality MOFs are loose powders that will have to be shaped using compaction methods. To succeed in system integration of MOF powders together with an acceptable thermal performance, engineering approaches beyond improving the intrinsic MOF thermal properties such as heat exchangers or MOF composites will have to be developed.

4.3 Thermal performance of frameworks containing adsorbates

4.3.1 Thermal properties of guest-loaded MOFs

In practical applications, the pores will often be filled with adsorbates. Nevertheless, the thermal properties of complex guest-loaded MOFs have barely been examined.^{186, 252, 254, 290} In this PhD thesis, the heat capacity and the thermal expansion behavior were evaluated with and without the presence of adsorbates in the pores. Some of these results were taken up in **Paper VIII** and **Paper X**, and they are repeated below. The impact on the thermal conductivity remains an open question.^{252, 254, 290}

As mentioned above in Section 4.1, methane-loaded MOF-5 was used to illustrate the advantages of the new Suzuki-Chin PIMD approach in **Paper VIII**. These simulations additionally revealed that the heat capacity of the guest-loaded system strongly depends on the temperature and the number of guests in the pores. At low loadings, the heat capacity monotonically increases with temperature like in the case of the empty framework. However, the curve exhibits a minimum at high loadings around 200 K as can be seen in Figure 4.7. The large heat capacity at low temperatures was suggested to originate from the tail of the first-order structural phase transition of methane in MOF-5 at 60 K.²⁹¹ This phenomenon was investigated in **Paper VIII** by analyzing the structural properties of methane inside the framework and by decomposing the contributions of the force-field energy to the heat capacity in host, host-guest and guest-guest interactions. The latter analysis revealed that the contribution of the host-guest interactions sharply decreases with temperature when a sufficient number of guest molecules is included in the framework.

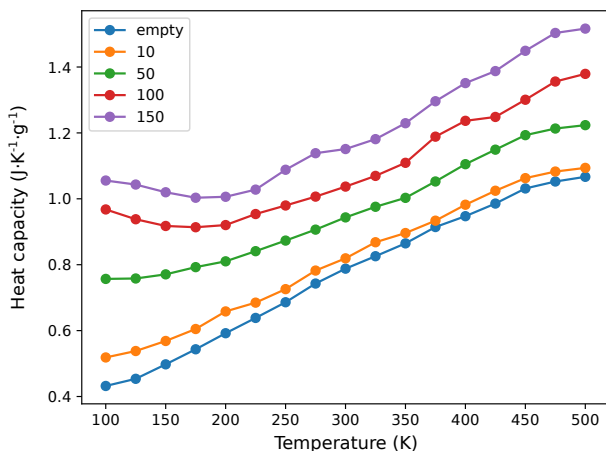


Figure 4.7: Isobaric heat capacity of methane-loaded MOF-5 as a function of temperature. The results from **Paper VIII** are shown for the empty MOF-5, and the framework with 10, 50, 100 or 150 methane molecules in its conventional unit cell.

Given these intriguing results, the set of materials and adsorbates was expanded and simulations were performed to investigate the possibility of tuning the heat capacity of a system by varying the guest loading. Figure 4.8 shows how it is influenced by the adsorbate type and the loading for the frameworks investigated in **Paper X** (Figure 1.2). The guest loading was varied from 25% to 100% of the loading at 300 K and 100 bar (obtained with GCMC).²⁹² For all frameworks and guests, it is found that the heat capacity expressed per kilogram MOF almost linearly scales with the number of guests. The slope, however, depends on the framework and type of guest, and the figure suggests that the impact of CO₂ and C₆H₆ is much larger than the alkanes. This can be understood by the fact that the investigated frameworks have more affinity for CO₂ and C₆H₆, and that these guest molecules are present in a higher concentration. Note also that the guest-loaded frameworks largely follow the same ranking in magnitude of the heat capacity as the empty frameworks (Table 4.1).

The thermal expansion behavior is a second thermal property that was evaluated in the presence of guests. Controlling the expansion behavior as a function of temperature with guests in MOFs was already suggested earlier.²⁴⁰ In **Paper VIII**, we showed that it is possible to go from a negative to a positive thermal expansion coefficient for MOF-5 when methane is in

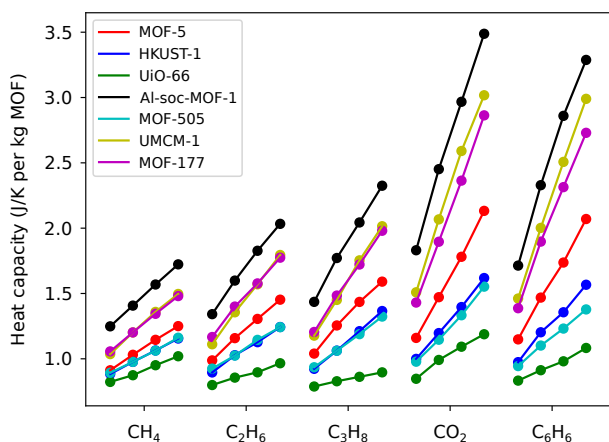


Figure 4.8: Isobaric heat capacity of a diverse set of MOFs at various loadings of methane, ethane, propane, carbon dioxide and benzene at room temperature and 1 bar. Data are shown for 25 %, 50 %, 75 % and 100 % of the loading at 300 K and 100 bar found with GCMC simulations.

the pores. The same is true for the other MOFs and guests investigated in this work. At a sufficiently high loading (100 bar gas pressure at 300 K), all frameworks display regular positive thermal expansion. Furthermore, it is also important to note that the adsorption of guest molecules can alter the equilibrium volume of the system as well. Due to the responsive nature of MOFs to guest adsorption, this should together with thermal expansion mismatch be considered in practical applications. In Figure 4.9, we show for HKUST-1 that the introduction of a large number of CO_2 molecules induces a similar volume change as observed in the empty framework in the range from 250 K to 350 K. Methane on the other hand only mildly affects the volume in this example.

4.3.2 Thermodynamic cycle

As a final application of the SC PIMD scheme for the study of thermal properties, we examined the generated heat when gas molecules adsorb in the pores. To this end, a hypothetical thermodynamic cycle was proposed which allows to predict the temperature rise within a MOF due to guest adsorption. This quantity depends on the intrinsic thermal properties of the

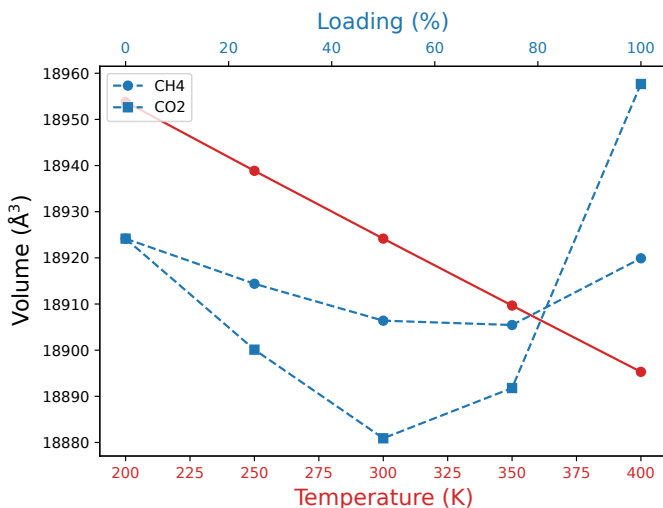


Figure 4.9: Volume of HKUST-1 as a function of temperature and as a function of loading (CH₄ and CO₂).

adsorbent, but also on the guest-host and guest-guest interactions of the adsorbates.

The thermodynamic cycle starts from an empty MOF at temperature T and ends at a guest-loaded final state at a higher temperature $T + \Delta T$. During the actual filling process a complex dynamical combination of mass and thermal transport takes place at the molecular level, which was nicely divided in different phenomena by Babaei *et al.*²⁹³ In **Paper X**, a detailed thermodynamic analysis of our hypothetical cycle is presented. Figure 4.10 displays the different steps and thermodynamic states of the cycle. The initial state (the empty MOF adsorbent) adsorbs n guest molecules (**1**), a step which evolves under isothermal and isobaric conditions and is subdivided into

- **1a:** the introduction of n non-interacting molecules in the MOF, i.e. neither guest-guest, nor guest-host interactions are already present
- **1b:** the physisorption of n particles (including all physical interactions)

After step **1a**, the thermodynamic system S is thermally isolated and does not allow for mass and heat transfer with the gas reservoir. The internal energy U can still change due to the exchange of $P\Delta V$ work. The heat Q required during step **2** to increase the temperature with ΔT can be found by integrating the isobaric heat capacity of the guest-loaded MOF from T to $T + \Delta T$.

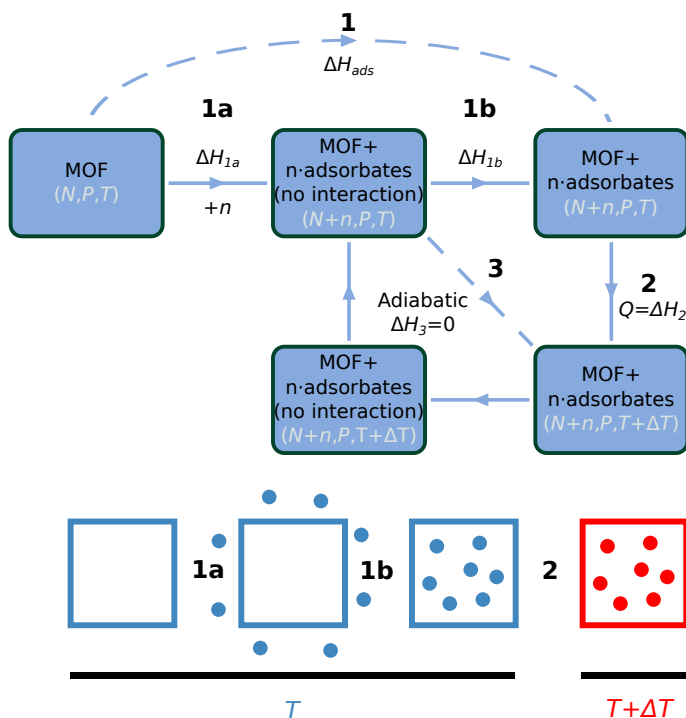


Figure 4.10: Definition of our hypothetical thermodynamic cycle. After step **1**, n guest molecules are adsorbed in the MOF (N atoms) under isothermal (T) and isobaric (P) conditions. This step is subdivided into two parts. First (**1a**), n non-interacting particles are introduced in the MOF. Subsequently, these guests are physisorbed in **1b**. During step **2**, the released heat of adsorption is used to heat up the thermodynamic system to a temperature $T + \Delta T$. We assume that **1b+2=3** proceeds adiabatically. Molecular simulations are performed to obtain the relevant quantities. Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

We consider an adiabatic process **3** ($= \mathbf{1b+2}$), which enables us to calculate ΔT . Based on the first law of thermodynamics, we can write following integral equation for the unknown ΔT :

$$-\Delta H_{1b} = \Delta H_2 = Q = \int_T^{T+\Delta T} C_P(\mathcal{T}; n) d\mathcal{T}. \quad (4.1)$$

This equation emphasizes the importance of the heat capacity of the adsor-

bent including adsorbates $C_P(\mathcal{T}; n)$.¹⁸⁶ In other words, the heat of adsorption released due to the stabilizing guest-host and guest-guest interactions is subsequently used to heat up the thermodynamic system and to increase the temperature during step 2. We assume adiabatic walls as this process happens very rapidly, with fast temperature rises.²⁹⁴ This assumption is supported by a molecular simulation study by Babaei *et al.*²⁹³ They showed that the heat generated due to adsorption is conducted easier than the diffusion of the guest molecules making the temperature spatially uniform at any time. The heat can, however, not easily be transferred to the pure gas region in contact with the MOF interface due to a high thermal resistance at this interface. They concluded that the interface presents a bottleneck making the heat transfer to the surroundings a slow process. The assumption of an adiabatic process presents an ideal limiting case, which will result in an upper bound for a temperature rise at the material's level. The other extreme case is the isothermal process, where the heat is immediately dissipated through its surroundings. In practice, heat exchangers in contact with the adsorbent bed are used to steer the process toward the latter as this results in a more efficient (dis)charging process.

The most important results are displayed in Figure 4.11. This graph indicates the increasing temperature as a function of loading for the same set of MOFs (Figure 1.2) in combination with CH_4 and CO_2 . We find a temperature rise ΔT ranging from 100 K to 250 K depending on the framework and the adsorbate at a high-pressure loading of hundred bar. Figure 4.11 shows that CH_4 has less influence on the material's temperature than CO_2 , but it should be noted that more CO_2 molecules are adsorbed than CH_4 at the same gas pressure. The copper paddle wheel MOFs HKUST-1 and MOF-505 have the highest increase for methane, while the Zn-MOFs (MOF-5, UCMCM-1 and MOF-177) respond the most on CO_2 . UiO-66 has the lowest increase in temperature for both adsorbates. These trends are already visible at lower loadings (25 % of the high-pressure loading), and ΔT in general keeps increasing with loading. Although this temperature increase is an idealized upper bound, its magnitude is indicative for the huge temperature fluctuations that are associated to gas adsorption. For some MOFs, it is even on the same order of their decomposition temperature (e.g. 550 K for HKUST-1²³²) in the case of 100 bar CO_2 adsorption.

Figure 4.12 displays the correlation between the heat of adsorption ($-\Delta H_{1b}$) (on a mass basis) and the temperature increase ΔT of the thermodynamic system containing adsorbent and adsorbates. It comes as no surprise that the temperature rise increases with an increasing heat of adsorption. Furthermore, as methane has weaker guest-guest and guest-host interactions than CO_2 , the released heat is lower and so is ΔT , as observed above.

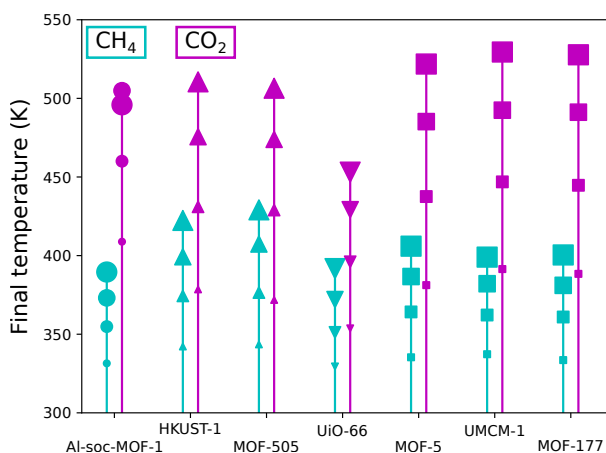


Figure 4.11: Temperature rise of MOFs when adsorbing CH_4 (cyan) and CO_2 (magenta) at 300 K. The size of the symbols increases with the loading, and represents 25 %, 50 %, 75 % and 100 % of the loading at 300 K and 100 bar. The markers indicate the metal ion: Zr (triangle down), Zn (square), Cu (triangle up), and Al (circle). The numerical results of these data are presented in SI Table V. Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

To understand how much heat the framework atoms can absorb, we focus here on the heat capacity of the empty framework. The grey shaded area covers the specific heat Q^{MOF} that the MOFs under study can intrinsically absorb (based on empty framework simulations) according to following relation:

$$Q^{\text{MOF}}(\Delta T) = \int_{300}^{300+\Delta T} C_P^{\text{MOF}}(\mathcal{T}) d\mathcal{T}, \quad (4.2)$$

with Q^{MOF} on the horizontal axis and ΔT on the vertical axis of Figure 4.12. This is a good approximation as the presence of guests doesn't significantly modify the contribution of the MOF to the heat capacity.¹⁸⁶ Hence, the horizontal distance between the grey area and the simulated results illustrates how much heat of adsorption is captured by the adsorbates in the pores. For most loadings of CO_2 , this is significantly more than the heat absorbed by the framework itself. The mixture of guests inside the pores thus dominates the total heat capacity and thus controls the temperature rise. The narrow

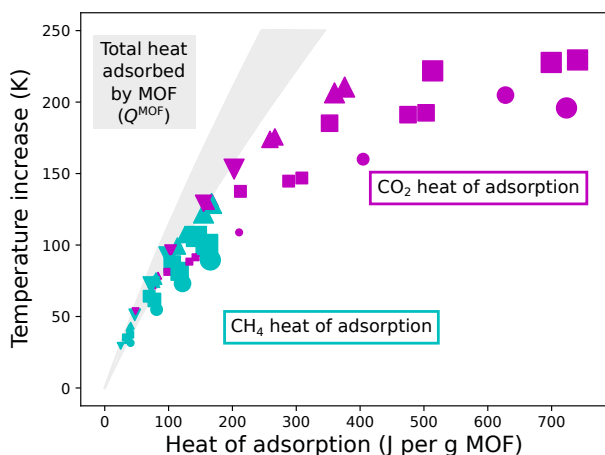


Figure 4.12: Temperature increase (starting from 300 K) after adsorbing CH_4 and CO_2 as a function of the heat of adsorption. The size of the symbols increases with the loading, and represents 25 %, 50 %, 75 % and 100 % of the loading at 300 K and 100 bar. The markers indicate the metal ion: Zr (triangle down), Zn (square), Cu (triangle up), and Al (circle). The gray shaded area indicates the total heat that can be adsorbed by the MOF. Reproduced from Ref. 187 with permission of the American Chemical Society, copyright 2019.

range of observed heat capacities for MOFs does not offer much potential in limiting temperature spikes by optimizing within the space of known MOFs. Interesting is also the apparent plateau in ΔT for the heat of adsorption in a wide range between 500 and almost 800 J per gram MOF. This suggests that the additional heat of adsorption beyond 500 J/g MOF can be stored rather efficiently by the inter- and intramolecular interactions of the adsorbates.

Nevertheless, it is clear that for weaker interacting molecules such as methane most heat can be adsorbed by the framework. This can be understood by the fact that the grey shaded area is close to the simulated methane-loaded data. However, in this region, the narrow spread on the performance of the diverse set of MOFs again suggests that selecting a MOF with a higher heat capacity within the currently known range will only have a minor impact on the temperature peaks. This will probably also be the case when the adsorbent is coupled with a heat exchanger.

Overall, the analysis thus indicates that replacing a MOF by another MOF

with similar adsorption properties but with a higher heat capacity in the studied range will not significantly modify the performance. Rather, new frameworks should be constructed to extend the width of the grey area toward the right, such that the materials are capable of absorbing more heat. As we showed that MOFs are relatively clustered in the materials property chart for thermal properties, conceptually new structures should be devised.

5

Conclusions and Perspectives

*Don't adventures ever have an end? I suppose not.
Someone else always has to carry on the story.*

The Fellowship of the Ring, J.R.R. Tolkien (1892 – 1973)

The development of advanced functional materials for nanotechnology is a hot topic in science. A particularly popular class of materials are metal-organic frameworks (MOFs). These porous, hybrid inorganic-organic crystalline frameworks possess excellent chemical and physical properties, and may therefore contribute to solutions for present-day world problems such as the reduction of the greenhouse effect and the use of sustainable energy. The first MOFs were originally synthesized in the late nineties, and nowadays the transition from academia into industry is taking place as companies offering MOF solutions are entering the market. In this PhD thesis, the nanoscale behavior of some prototypical materials (Figure 1.2) was investigated using a variety of molecular simulation techniques. Through various case studies (Figure 1.5), a fundamental understanding of two major topics – flexibility and thermal properties – was acquired that enables theoretical guidance toward improved materials and predictive computational design of MOFs.

First, a thermodynamic protocol was established as the result of a collaborative effort of researchers within the Center for Molecular Modeling to characterize and classify flexibility upon different thermodynamic stimuli in **Paper III**. This approach offered the necessary insight required to unravel and predict macroscopic breathing, and was subsequently applied on flexible

MOFs ranging from wine-rack-type frameworks to pillared-layered MOFs. Here, the focus lay on the intrinsic flexibility of the structures in absence of guest molecules. **Paper I** considered and explained the measured breathing transitions in the MIL-47-type family via force field molecular dynamics. It was shown that the relative stability of the open large-pore (lp) and closed narrow-pore (np) states of the framework drastically depends on the organic linkers. While MIL-47 is expected to breathe only under a large mechanical pressure, the inherent bistable COMOC-2 could also display temperature hysteresis. COMOC-3 remains in a stable, nonporous narrow-pore state upon these stimuli. The effect of the metal ion on the breathing behavior was investigated for MIL-53-FA in a joint experimental-theoretical collaboration in **Paper II**. The gallium variant was shown to have a more stable np phase than its aluminum counterpart as witnessed from the DFT energy profiles in terms of the volume, which predict an irreversible pressure-induced breathing transition for MIL-53(Ga)-FA. Experimentally, the structure was classified as a nanoshock absorber, which could be used in mechanical energy storage applications.

The influence of the organic linker and the metal ion was examined more closely and systematically in **Paper V** by probing an isorecticular MIL-53 series. Again, DFT (Helmholtz free) energy profiles were constructed as a function of the volume and temperature and simple design rules for thermo-responsive MOFs were proposed. In line with our initial case studies, we revealed that the organic linker has a huge impact on the breathing behavior in wine-rack-type frameworks. Only for the prototypical MIL-53 structure, temperature-induced flexibility was detected in a reasonable temperature window, which could slightly be changed by substituting the metal ion. In this work, we emphasized the two factors influencing the lp-np relative stability that ultimately drives the phase transition: long-range dispersion stabilizing the dense np phase and vibrational entropy favoring the lp phase. This delicate balance explains why mostly the organic linkers determine the predicted flexibility. Complementary to the simulated macroscopic breathing curves, we used computational vibrational spectroscopy to further unravel the breathing behavior at the molecular level. In **Papers IV** and **VII**, we were able to pinpoint specific vibrational modes that could trigger the phase transition in MIL-53(Al).

A last case study in **Paper IX** involved the intrinsic flexibility of DMOF-1, a representative of the pillared-layered MOFs. This successful class of breathing materials has demonstrated earlier intriguing flexibility upon temperature and guest loading after linker functionalization. Nevertheless, we discovered through our thermodynamic protocol a massive volume contraction in the nonfunctionalized parent material with copper and zinc at the

metal nodes. This phase transition is only reachable by exerting a large mechanical pressure and the reversibility was predicted to depend on the type of metal. The excellent characteristics for mechanical energy storage, i.e. a large transition pressure and volume change, inspired our experimental collaborators to measure its promise for these applications. Both DMOF-1(Zn) and DMOF-1(Cu) behaved experimentally as a nanoshock absorber. A high energy of $80 \text{ J} \cdot \text{g}^{-1}$ was associated to the pressure-induced transition of DMOF-1(Cu), which outperforms many other flexible MOFs to date.

However, although many of the qualitative and quantitative predictions are corroborated by experiments, one should not remain blind for the measured deviations. In **Papers II** and **IX**, our experimental collaborators of the DAMP group at the University of Montpellier detected the signature of a pressure-induced phase transition in agreement with the simulations, but in both cases discrepancies were found ranging from the extent of the volume contraction to the nature of the transition (i.e. reversible or irreversible). Experiments on flexible MOFs are very challenging as they are currently almost impossible to synthesize in large pure single crystals. The effect of crystal size and shape was already excellently highlighted by the practice of crystal downsizing to modify the flexibility. In addition, the presence of a few remaining solvent or guest molecules is known to significantly modify the expected behavior. Hence, it comes as no surprise that flexibility can strongly depend on the used synthesis protocol. Perhaps, there are simply other effects present in the sample which are not well understood. Close collaborations between theoreticians and experimentalists may resolve these discrepancies in the (near?) future.

Molecular modeling should in principle be able to overcome these puzzling experimental sensitivities, when applied adequately. It is the responsibility of the modeler to verify and discuss the validity of the applied computer models. In **Paper V**, a major step forward was taken in identifying the critical aspects of accurately modeling the potential energy surface, which forms the basis of properly describing a system. By applying the high-level RPA method on MIL-53(Al), we were able to discuss for the first time the deficiencies of common electronic structure methods applied on flexible MOFs. We showed that special attention should be given to the accurate description of long-range interactions and the necessity of including many-body effects. This will hopefully stimulate the community developing exchange-correlation functionals and dispersion methods to investigate flexible MOFs more closely. In anticipation of potential improvements, it should be required to assess the sensitivity of qualitative predictions on flexible MOFs with standard DFT methods by applying a number of them.

Of course, this level of accuracy is difficult to maintain when going toward

molecular dynamics simulations at realistic conditions. Accuracy has to be balanced with computational efficiency, and in such a case the quantum mechanical potential energy surface has to be replaced by a force field expression. These models typically do not accurately account for the important van der Waals interactions, but are fitted to quantum mechanical input data. While the predictive quality of this approach may disappear, much remains to be learned from such simulations if validated carefully and tested to experiment as in **Paper I**. For instance, in **Paper IX**, force field molecular dynamics was used to elucidate the motion during the phase transition at the nanoscale. In the long run, force field fitting approaches such as QuickFF will probably become redundant, and should be replaced by machine learning potentials that promise a quantum mechanical accuracy.

Lastly, a multiscale modeling approach is necessary for further progress in the flexible MOF field to tackle relevant questions such as how the phase transition kinetically proceeds or how it is influenced by interfacial effects. All results in this work were obtained by modeling MOFs as an infinite crystal through periodic boundary conditions applied on a unit cell containing a limited number of atoms. Simulations at more realistic representations of the experimental structure (including interfaces, micrometer-sized clusters of atoms, a polycrystalline structure, ...) will become an unavoidable prerequisite and the first hurdles are currently being taken by, for example, the development of coarse-grained or even continuum models. Although these models may completely lose their quantitative value, a qualitative understanding of the flexible behavior would greatly aid the community.

A second major topic involves the thermal properties of MOFs. Although a good understanding of these characteristics seems imperative for adsorption-based applications, not much information is available on these materials. Even molecular simulation studies are lacking in literature.

In collaboration with Prof. Ceriotti from the COSMO group (EPFL), we developed and established an accurate and efficient simulation protocol for the characterization of structural and thermal properties such as the heat capacity and the thermal expansion coefficient in **Paper VIII**. This was based on the fourth-order Suzuki-Chin path integral formalism, which allows to correctly model anharmonic and nuclear quantum effects. Using MOF-5 as the model system, we highlighted the failure of standard molecular dynamics for the description of the heat capacity. Given that the particles are described classically and that nuclear quantum effects are not taken into account, this did not come as a surprise. However, when methane molecules were added in the pores, also anharmonic effects started to play a role, which could only be captured with Suzuki-Chin PIMD. Additionally, in **Paper VI**, the interplay of both anharmonic and nuclear quantum effects was examined for the negative

thermal expansion of MOF-5. Here it was shown that mainly the former dominates the behavior, but that large zero-point effects could be expected on the equilibrium structure.

Until now, nuclear quantum effects in molecular dynamics simulations were largely neglected in the MOF community. This assumption is acceptable at sufficiently high temperatures and for heavy atoms subjected to moderate interatomic interactions. As MOFs contain many light atoms, this approximation should nevertheless be checked when studying new and different properties. In both **Paper VI** and **Paper VIII**, empirical relations and/or approximate methods were put forward that allow to include nuclear quantum effects at the cost of standard molecular dynamics. Even better would be to utilize the Suzuki-Chin PIMD scheme to benchmark the investigated property and to systematically evaluate the importance of neglecting the quantum nature. This method and many other advanced algorithms are present in the universal force engine i-PI. Since most popular simulation codes have been coupled to this program, the barrier to include nuclear quantum effects has significantly been lowered in recent years.

In **Paper X**, we applied the insights obtained about modeling thermal expansion and the heat capacity. We investigated both properties together with the thermal conductivity of a diverse set of MOFs. In this way, the first systematic molecular simulations study of thermal properties was realized, giving a broader view on the thermal performance of MOFs and their associated limitations. Additionally, a materials property chart was presented, where the thermal properties of MOFs are visualized alongside other material classes such as metals, polymers and ceramics. It showed that MOFs have thermal properties at the crossing of the ceramics, polymers and hybrid materials. Another goal was to obtain insight into how the overall thermal properties are affected by the nanoscale design. Our systematic evaluation supported the current ideas that a trade-off between porosity and desired intrinsic thermal characteristics will be required. It can therefore be expected that for a good application performance, MOF composites will have to be produced (for instance with expanded natural graphite) in combination with external heat management technologies.

The presence of guest molecules can drastically alter the thermal properties and result in temperature fluctuations. We used the knowledge of the intrinsic thermal properties to estimate to what extent the temperature of the material would rise when adsorbing CH_4 and CO_2 . To this end, a hypothetical thermodynamic cycle was proposed in **Paper X** that relies on macroscopic quantities found through simulations at the molecular level. Our thermodynamic considerations revealed significant temperature increases at the material's level. This quantity itself is a relevant material's

parameter balancing both thermal and adsorption properties in MOFs. In this way, it was clear that the adsorption of CO_2 has much more impact on the temperature than the weaker interacting CH_4 . Furthermore, by visualizing the correlation between the increase in temperature and the heat of adsorption, we were able to assess the relevance of the heat capacity of the framework and note its limited impact. Our simulations suggest that selecting a MOF with a higher heat capacity would only be a viable strategy to limit temperature spikes if new and improved MOFs are synthesized.

The overall aim of this PhD thesis was to achieve a better understanding of the flexibility and thermal properties of MOFs. For both topics, important steps toward reliably simulating these complex materials were taken. Using the methodology developed and outlined in this PhD thesis, computational researchers are provided with improved tools to target predictive design, which is vital to explore these materials for high-tech industrial applications. Moreover, the wide range of studied materials and the various case studies contributed to the rising insight into the nanoscopic interactions that govern the behavior of these fascinating materials.

Part II

Published Papers



**A Selection of Publications in
International Peer-Reviewed
Journals**

Paper I

**Exploring the flexibility of MIL-47(V)-type materials
using force field molecular dynamics simulations**

J. Wieme, L. Vanduyfhuys, S.M.J. Rogge,
M. Waroquier, and V. Van Speybroeck

The Journal of Physical Chemistry C, **2016**, 120, 14934–14947

J. Wieme performed the research and wrote the manuscript.

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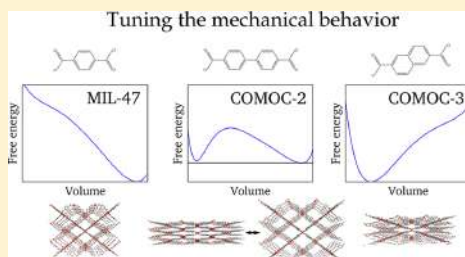
Exploring the Flexibility of MIL-47(V)-Type Materials Using Force Field Molecular Dynamics Simulations

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S Supporting Information

ABSTRACT: The flexibility of three MIL-47(V)-type materials (MIL-47, COMOC-2, and COMOC-3) has been explored by constructing the pressure versus volume and free energy versus volume profiles at various temperatures ranging from 100 to 400 K. This is done with first-principles-based force fields using the recently proposed QuickFF parametrization protocol. Specific terms were added for the materials at hand to describe the asymmetry of the one-dimensional vanadium-oxide chain and to account for the flexibility of the organic linkers. The force fields are used in a series of molecular dynamics simulations at fixed volumes but varying unit cell shapes. The three materials show a distinct pressure–volume behavior, which underlines the ability to tune the mechanical properties by varying the linkers toward different applications such as nanopropellers, dampers, and shock absorbers.



1. INTRODUCTION

Metal–organic frameworks (MOFs) are a class of nanoporous, crystalline materials consisting of inorganic moieties connected through organic linkers.^{1–3} Their diversity in chemical and physical properties, combined with the possibility to rationally design and synthesize them, makes MOFs an attractive field of research with many potential applications.^{4–7} An intriguing subclass of MOFs are those that display a large structural flexibility induced by various stimuli (temperature, pressure, guests, etc.), the so-called flexible or stimuli-responsive MOFs.^{7–13}

Because an increasing number of MOFs are synthesized for the first time each year,¹⁴ and an even larger number of them have also been hypothesized,¹⁵ the true challenge consists of identifying materials for specific applications. In this respect, molecular simulations can play a very important role^{16–19} in characterizing materials, understanding certain phenomena, and guiding the development of diverse applications. Although accurate first-principles calculations on MOFs are becoming more and more feasible,^{18,20} in many cases one is interested in time and length scales only accessible with molecular mechanics, i.e., force fields, and not with computationally more expensive electronic structure methods such as density functional theory (DFT). Nonetheless, the disadvantage of using force fields is that they need to be derived and parametrized properly, which is a nontrivial task that is typically accomplished using experimental and/or theoretical input. If the target is the study of stimuli-responsive MOFs, one has to construct a flexible force field, allowing the framework atoms to move, to describe the envisaged structural transformation. To date, several procedures for the construction of

flexible force fields for MOFs have been proposed in the literature.^{21–24} However, as recently pointed out by Coudert and Fuchs in a comprehensive review,¹⁹ there is a need for the systematic development of accurate force fields for stimuli-responsive MOFs. Despite various successful force field studies of stimuli-responsive MOFs (see e.g. refs 25–33), an easy way to obtain these force fields did not exist until recently. A variety of studies is available where generic force fields such as UFF³⁴ (or UFF4MOF²²), CVFF,³⁵ and GAFF³⁶ are used, which are slightly modified for the given purpose. They all succeed in reproducing qualitatively well the expected behavior, or at least give insight in the mechanism, but some features that are inherent to the material require more specific nongeneric force fields. A procedure, hereafter called QuickFF, to generate these force fields was only recently proposed by some of the presenting authors.²⁴ In this work, we apply and extend QuickFF and show that it is possible to study the flexibility of guest-free MIL-47-type materials.

The metal–organic framework MIL-47(V^{IV}) (MIL, materials of Institut Lavoisier) was synthesized for the first time in 2002 by Barthelet et al.³⁷ of the Férey group and was originally considered to be rigid under mild working conditions. The structure exhibits a framework pattern similar to that of the MIL-53 series, consisting of one-dimensional (1D) diamond-shaped straight channels with a free diameter of about 8 Å and forming infinite chains of corner-sharing V^{IV}O₆ octahedra connected by 1,4-benzenedicarboxylate (BDC) linkers. The

Received: May 2, 2016

Revised: June 12, 2016

Published: June 13, 2016



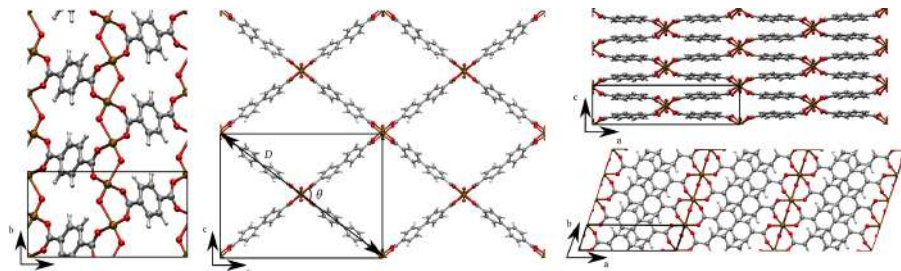


Figure 1. From left to right: MIL-47, COMOC-2, and COMOC-3. The unit cell is indicated, and the interdiagonal distance, D , and the pore opening angle, θ , are defined.

most striking difference with the MIL-53 series is the oxidation number of the metal. While in MIL-53 all metals have oxidation number +III, the vanadium metal in MIL-47 has an oxidation number +IV. Direct results are the appearance of an O–V=O vanadium-oxide chain, without hydrogens on the bridging oxygens, and asymmetric V–O bond distances. Another difference with the MIL-53 framework is the displaced vanadium chains visible in single-crystal X-ray diffraction.^{37,38}

While MIL-47(V^{IV}) receives the most attention in the literature, other vanadium MOFs have been synthesized and were summarized in a recent review by Van Der Voort et al.³⁹ In this work, two variants of MIL-47(V^{IV}), COMOC-2(V^{IV})⁴⁰ and COMOC-3(V^{IV}),⁴¹ will also be studied (COMOC, Center for Ordered Materials, Organometallics and Catalysis, Ghent University). These MOFs are the vanadium equivalent of the DUT-5 and DUT-4⁴² topologies (DUT, Dresden University of Technology), which were constructed by Senkovska et al.⁴² with aluminum-oxide chains. Both frameworks have asymmetric vanadium-oxide chains connected with 4,4'-biphenyl-dicarboxylate (BPDC) linkers for COMOC-2 and 2,6-naphthalenedicarboxylate (NDC) linkers for COMOC-3 (see Figure 1). In a synthesis protocol, typically the inorganic moieties are formed in situ, while the organic linkers are preformed, and recent advances in synthesis have made it possible to focus on linker design.⁴³ By replacing the linker in MIL-47 with other ditopic carboxylate linkers, a different flexibility behavior can be obtained, which is also observed in our simulations. On the one hand, COMOC-2 is considered to be a bistable MOF because it displays breathing toward certain guest molecules^{40,44,45} in contrast to DUT-5, its rigid Al analogue.⁴² This peculiar trend is the opposite of the adsorption behavior of MIL-47 as compared to MIL-53(Al), i.e., its flexible Al analogue. It was also observed that the presence of V^{III} compared to a pure COMOC-2(V^{IV}) increases the rigidity, again in contrast to MIL-47.⁴⁶ Moreover, the COMOC-2(V^{IV}) sample is a mixture of a large-pore (lp) and narrow-pore (np) phase,⁴⁰ which could indicate that both phases are minima of the free energy surface, similar to the intrinsic bistability of MIL-53(Al) at certain temperatures.^{47,48} This was confirmed with periodic DFT calculations by Liu et al.,⁴⁰ and the authors even obtained a third hypothetical, overstretched np phase. On the other hand, guest-free COMOC-3 has a good chemical and thermal stability and is considered to be nonporous, as observed by N₂ sorption measurements.⁴¹ It remains in the np state upon removal of water molecules.⁴¹

In general there is only a limited number of studies available on mechanical properties of MOFs.^{49–52} However, the first-principles full elastic tensor has been calculated and discussed for MIL-47^{20,50,53} and its NH₂ substituted variant,⁵⁴ as well as the influence of the spin configuration on the bulk modulus.⁵⁵ Related to these mechanical properties are some high-end applications in the field of mechanical energy storage. MOFs that undergo structural transitions under pressure are especially interesting.^{29,56–61} One typically distinguishes three different classes of MOFs depending on the amount of dissipated mechanical energy in the compression–decompression cycle: a nanospring (no dissipation, i.e., no hysteresis), a damper (partial dissipation, i.e., reversible transformation with hysteresis), and a shock absorber (total dissipation, i.e., irreversible transformation). In this context, the adjective “reversible” means that the system (i.e., MOF) can be reversed to its initial condition. In the context of thermodynamics, a process exhibiting hysteresis is always irreversible, which in this case is due to the fact that the environment cannot return to its initial condition. Only recently, Yot et al.²⁹ proved with mercury porosimetry measurements that MIL-47 is in fact a stimuli-responsive MOF, displaying a structural transformation under a large mechanical pressure. This so-called pressure-induced breathing is associated with a volume reduction of approximately 38% going from a lp state to a np state. Very similar experimental results were obtained by Rodriguez et al.⁶¹ with a silicon oil pressure medium. The transition is reversible with hysteresis, making MIL-47 a candidate for damper applications, although more recently A520 or MIL-53(Al)-FA was identified to be a better choice because of a higher amount of energy absorbed per unit of mass.⁶⁰

Different thermodynamic studies have been devoted to the construction of free energy profiles and phase diagrams in terms of guest–host interactions for the MIL series.^{62–69} However, free energy profiles of the guest-free frameworks have only seldomly been studied^{67,69,70} and are completely absent for MIL-47 or MIL-47-type materials. In this work, we also aim to fill this gap, using a recently proposed procedure by Rogge et al.,⁷⁰ which was applied to both rigid and flexible MOFs. This method consists of extracting the averaged pressure at each volume by performing independent molecular dynamics (MD) simulations at different volume points on a grid in a new ensemble, the $(N, V, \sigma_z = 0, T)$ ensemble. The free energy profile as a function of the volume can then be obtained via thermodynamic integration.⁷¹

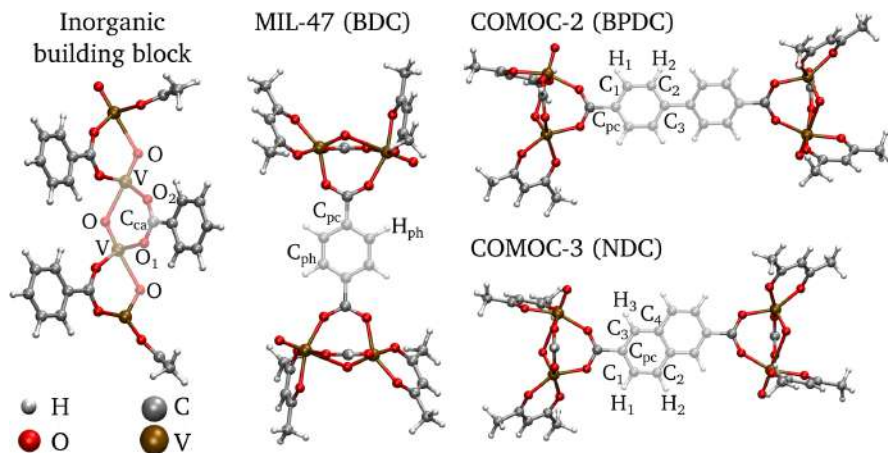


Figure 2. Overview of the model systems. The inorganic building block is used for the three MIL-47-type materials to describe the vanadium–oxide chain. The BDC, BPDC, and NDC building blocks are used in MIL-47, COMOC-2, and COMOC-3, respectively. The transparent region corresponds to the core region, and the unique atom types are indicated.

2. METHODOLOGY

2.1. Force Field Development. The workflow to generate force fields with QuickFF may be briefly summarized as

1. Perform electronic structure calculations on model systems representative for the building blocks of the MOF.
2. Use the optimized geometry, Hessian, and, optionally, atomic charges as input for QuickFF.
3. Transfer the derived force field parameters of the building blocks to the periodic cell.
4. Optionally add a van der Waals model a posteriori.

More elaborate details about the parametrization protocol can be found in ref 24.

2.1.1. Model Systems. In this work, DFT calculations are performed on several model systems representing the different parts of MIL-47, COMOC-2, and COMOC-3 to generate the required first-principles input data. A single inorganic cluster model is proposed to model the vanadium–oxide chain in all three MOFs, while for each organic linker (BDC, BPDC, and NDC) a separate cluster is built. The model systems in this work are inspired by the ones for the MIL-53(Al) force field by Vanduythuys et al.⁷² The strong similarities between MIL-53 and MIL-47 suggest analogous cluster models for the inorganic part and organic linker, but the presence of asymmetric V–O bonds along the vanadium–oxide chain demands some crucial interventions in the description of the V–O bond. This asymmetric pattern is forced by terminating only one side of the vanadium–oxide chain with an oxygen atom (see Figure 2). In this way, an alternating short and long bond is obtained, identical to the periodic structure. The other oxygens of the octahedral coordination environment of the outermost vanadium atoms are capped with an acetylacetone molecule instead of hydrogens. The final cluster models have a neutral charge and are shown in Figure 2. They are optimized with a maximum spin of 2 (four vanadium atoms with one unpaired d-

electron), as this yields the most reliable single-determinant description.¹⁸

2.1.2. Force Field Energy Expression. The force fields (FFs) are composed of two contributions: the covalent and the noncovalent interactions. The covalent force field terms (cov) describe the chemical bonds, while the noncovalent interactions (noncov) are the long-range interactions, and they are by definition separated into an electrostatic part (El) and a part mimicking the van der Waals interactions (vdW). The multidimensional potential energy surface is then approximated with the following expression:

$$V^{\text{FF}} = \underbrace{V_{\text{bond}} + V_{\text{bend}} + V_{\text{oopd}} + V_{\text{torsion}}}_{V_{\text{cov}}^{\text{FF}}} + \underbrace{V_{\text{El}} + V_{\text{vdW}}}_{V_{\text{noncov}}^{\text{FF}}} \quad (2.1)$$

The covalent interactions include harmonic bonds (bond), harmonic bends (bend), harmonic out-of-plane distances (oopd), and cosine dihedrals (torsion). All unknown parameters related to these expressions are estimated with QuickFF. The electrostatic interactions are modeled with a Coulombic potential between Gaussian charge distributions, and all interactions are included; that is, there are no exclusion rules. The atomic charges are derived from the DFT electron density of each model system via the MBIS procedure, a new iterative variant of the Hirshfeld atom-in-molecules (AIM) scheme.⁷³ The radii of the Gaussian charge distributions are determined with the method proposed by Chen and Martínez.⁷⁴

The MM3-Buckingham potential⁷⁵ is used to describe the van der Waals interactions.

$$V(r) = \epsilon_{ij} \left[1.84 \times 10^5 \exp \left(-12 \frac{r}{\sigma_{ij}} \right) - 2.25 \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (2.2)$$

The two parameters σ_{ij} and ϵ_{ij} are the equilibrium distance and the energy parameter of the potential, respectively, and are

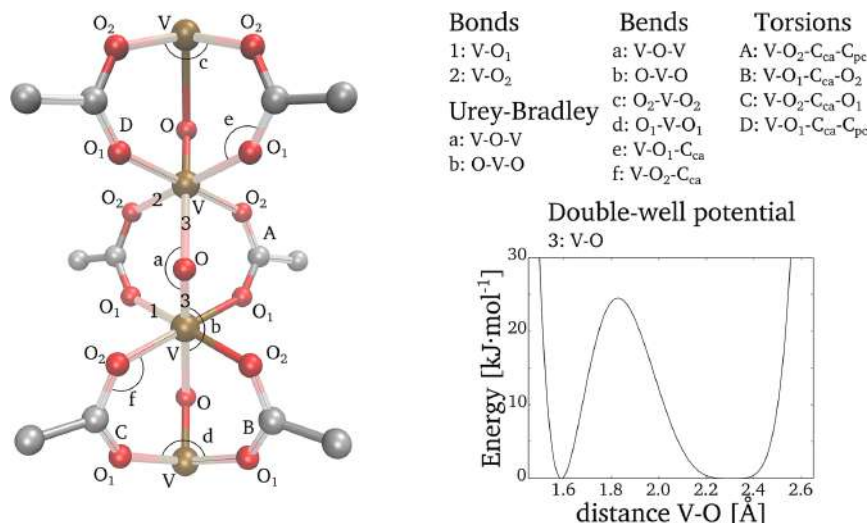


Figure 3. Overview of all covalent force field terms describing the inorganic chain. The double-well potential is shown on the right.

determined with empirical mixing rules for the interaction between atom i and atom j :

$$\sigma_{ij} = s_{\sigma} \cdot (\sigma_i + \sigma_j) \text{ and } \epsilon_{ij} = s_{\epsilon} \cdot (\sqrt{\epsilon_i \epsilon_j}) \quad (2.3)$$

The interactions between the 1–2 and 1–3 bonded pairs are excluded following the MM3 rules, together with the 1–4 interactions as they were found to be too repulsive in the inorganic part of the MOFs under study, causing discrepancies in the reproduction of the correct unit cell shape. A possible reason is that the MM3 parameters have been fitted in environments that are not as dense as in the inorganic bricks encountered in MOFs. To compensate for this deficiency, slight modifications of the exclusion rule and the parameter values (section 4.2) are justified. Therefore, we define two uniform scaling parameters s_{σ} and s_{ϵ} to slightly modify the values from the literature. The atomic ϵ_i and σ_i parameters are taken from refs 75 and 76. This part is added to the force field after the QuickFF procedure has been applied, as it is assumed that these contributions are not present in the DFT calculations on the building blocks. This is indeed the case here, as an exchange–correlation functional has been employed that includes only Pauli repulsion but no long-range dispersion interactions (vide infra).

The force field atom types used in the structure are indicated on the core region of the model systems (see Figure 2). The difference between the force fields for MIL-47, COMOC-2, and COMOC-3 are thus the parameters related to the organic linker. Hence, the force field parameters extracted from the inorganic model system remain unaffected, comparable to synthesizing a MOF by combining the same inorganic salt with different carboxylic acids. Two different, alternating atom types (O₁ and O₂) are assigned to the oxygens in the organic linkers, and both have different force field parameters. This is found to be necessary to accurately model the asymmetry arising because of the strong and weak bonds along the vanadium-oxide chain.

The force field parameters of the atoms inside the core region are transferred following the approach in ref 72. An overview of all force field parameters is provided in the [Supporting Information](#).

2.1.3. Extending QuickFF with MOF-Specific Force Field Terms. Some unique molecular environments in MOFs require more specific analytical expressions to adequately model all structural features. The MIL-47-type materials are typical examples where this is necessary because of the presence of the vanadium-oxide chain. The standard QuickFF protocol has been designed to give a first reasonable force field, but it can easily be modified with specific terms as illustrated hereafter.

The asymmetric 1D vanadium-oxide chain in MIL-47 cannot be described with a harmonic potential term, which has only one minimum, because the V–O bond clearly has two distinct minima (see also Figure 3). To reproduce this pattern with a force field, the V–O bond term is represented by a double-well potential with minima corresponding with the two equilibrium distances. Both a short (strong) and a long (weak) V–O bond are included in the core region of the inorganic model system (see Figure 2), and both bonds are approximated separately with a harmonic term in the QuickFF fitting procedure. This results in the corresponding force constants and rest values, which are used as input data to construct the double-well potential, satisfying the following conditions:

1. The potential energy has local minima both at the short (r_1) and long (r_2) bond distances.
2. The second-order derivative of the potential energy with respect to the bond distance in r_1 and r_2 corresponds with the determined force constants.

It is found via QuickFF that the weak bond has a zero force constant. The lowest-order polynomial approximation satisfying these conditions is given by

Table 1. Comparison of Some Key Parameters for MIL-47(V) Obtained in This Work^a and by Bogaerts et al.³⁸ with Periodic DFT Calculations in the Ferromagnetic (FM) and Antiferromagnetic (AFM) Spin Configuration^b

	force field - periodic		DFT - cluster	DFT - periodic ³⁸	
	excl. vdW	incl. vdW	B3LYP(FM)	PBE+D3(FM)	PBE+D3(AFM)
bond lengths [Å]					
V–V	3.524	3.481	3.531	3.435	3.441
V=O	1.594	1.592	1.588	1.655	1.652
V–O	2.313	2.305	2.311	2.090	2.106
V–O _i	1.988/2.038	1.983/2.028	1.977/2.033	1.992/2.001	1.981/1.985
O _i –C _{ca}	1.256/1.274	1.255/1.273	1.257/1.274	1.277/1.278	1.278/1.280
C _{ca} –C _{pc}	1.489	1.504	1.493	1.489	1.487
C _{pc} –C _{ph}	1.399	1.403	1.399	1.404	1.404
C _{ph} –C _{ph}	1.387	1.386	1.388	1.390	1.389
C _{ph} –H _{ph}	1.082	1.081	1.082	1.089	1.089
bond angles [deg]					
V–V–V	168.0	165.1	166.4	166.6	167.2
V–O=V	127.9	125.6	128.8	132.7	132.3
O–V=O	178.2	175.8	176.8	172.4	173.3
V–O _i –C _{ca}	131.2/140.1	130.8/141.5	130.3/141.7	130.5/137.7	130.7/138.3
O _i –V–O _i	87.4/91.9	91.9/95.5	87.7/91.3	88.9/92.2	89.1/91.2
O _i –C _{ca} –O ₂	125.6	124.0	125.3	125.6	125.3

^aThe MM3 van der Waals parameters are rescaled [see section 4.2 ($s_e = 0.92$, $s_o = 1.14$)]. ^bThe structures of Bogaerts et al. are taken from the Cambridge Structural Database⁹⁹ (CCDC numbers 1402265 and 1402266).

$$V_{\text{bond}}(r) = \frac{K}{2} \frac{(r - r_1)^2 (r - r_2)^4}{(r_1 - r_2)^4} \tag{2.4}$$

with K the curvature of the strong bond. Together with the double-well potential, two Urey–Bradley terms were added for the O–V=O and V–O=V bonds along the asymmetric chain only to avoid overfitting. These terms can be interpreted as constraints such that the structure has an alternating short–long pattern of V–O bonds. A Urey–Bradley term is a term accounting for angle bending and is modeled via a harmonic bond between 1–3 neighbors:

$$V_{\text{Urey–Bradley}}(r) = \frac{K}{2} (r - r_0)^2 \tag{2.5}$$

The Urey–Bradley force constants, K , and rest values, r_0 , can be derived with QuickFF by adding V–V and O–O bonds in the initial topology. In Figure 3, an overview of all covalent force field terms describing the inorganic chain is given.

A second case where the basic covalent terms are not sufficient is in the construction of an accurate force field for COMOC-2. A simple cosine term cannot correctly describe the dihedral motion of the C₂–C₃–C₃–C₂ pattern of the BPDC linker. It is not possible to obtain energy minima at $\pm\phi_0$ and $\pm(\pi - \phi_0)$ with a cosine with period $\frac{2\pi}{m}$ ($m \in \mathbb{N}$) for a general ϕ_0 . The potential term used for the C₂–C₃–C₃–C₂ pattern is

$$V_{\text{C}_2\text{--C}_3\text{--C}_3\text{--C}_2}(\phi) = \frac{K_\phi}{2} [\cos(2\phi) - \cos(2\phi_0)]^2 \tag{2.6}$$

with ϕ_0 taken from the DFT optimized geometry, which here is 38.225°. The advantage of QuickFF is that such terms can easily be added in the force constant refinement step of the fitting procedure.²⁴

2.2. Characterization via ($N,V,\sigma_a=0,T$) MD Simulations. The volume, V , is chosen as the collective variable to study the structural flexibility of the MIL-47-type materials. Obtaining the free energy, F , as a function of the volume enables us to clearly quantify the relative stability of the np and lp states at a certain

temperature T , because both phases have a well-separated volume. The $F(V)$ curve can be obtained via thermodynamic integration according to the scheme recently proposed by Rogge et al.⁷⁰ There, the ($N,V,\sigma_a=0,T$) ensemble was introduced, in which the cell shape and instantaneous isotropic pressure can fluctuate freely, while the volume is kept fixed and the anisotropic contribution σ_a to the stress tensor is controlled by a barostat during the MD simulation. The ensemble-averaged isotropic pressure $\langle P \rangle$ is extracted from such a simulation, making it possible to construct the $P(V)$ profile by repeating the simulations at different volumes. These data are then fitted with a polynomial.⁷⁰ A volume grid spacing of 5 Å³ is considered, and the initial structures for each volume are obtained by selecting different snapshots from a ($N,P,\sigma_a=0,T$) MD simulation. Furthermore, from the $P(V)$ curve, the bulk modulus of the equilibrium structure can be determined with the following relation:

$$B = -V \frac{dP}{dV} \Big|_{P=0} \tag{2.7}$$

Moreover, some features from the fitted curve can be compared directly to the available experimental and theoretical data for MIL-47. This will be used as a validation of the first-principles derived force field. It is also possible to study the influence of temperature on the relative phase stability and on mechanical properties, such as the bulk modulus, by generating these profiles at various temperatures.

3. COMPUTATIONAL DETAILS

The model systems for the building blocks of MIL-47, COMOC-2, and COMOC-3 are constructed with Zeobuilder.⁷⁷ VMD⁷⁸ was used to visualize the structures. The DFT calculations on these systems are performed with Gaussian⁷⁹ using the B3LYP exchange–correlation functional^{80–83} and the 6-311G(d,p) basis set.^{84–87} The model systems have a neutral charge and spin 2 (one d-electron on four vanadium atoms). The covalent force field parameters are generated with QuickFF,²⁴ and the atomic charges are derived according to

the MBIS partitioning scheme as implemented in Horton.⁷³ All force field calculations are carried out with Yaff⁸⁸ using a supercell consisting of two unit cells along the lattice direction b (see Figure 1). The long-range interactions are computed as follows: an Ewald summation with a real-space cutoff of 15 Å, an α of 0.213 Å⁻¹, and a reciprocal space cutoff k_{max} of 0.320 Å⁻¹ for the electrostatic interactions and a smooth cutoff at 15 Å for the van der Waals interactions. Normal mode analysis is performed with TAMkin.⁸⁹ A Verlet time step of 0.5 fs is used in all $(N,P,\sigma_s=0,T)$ and $(N,V,\sigma_s=0,T)$ MD simulations. The temperature is controlled with a Nosé–Hoover chain thermostat^{90–92} containing three beads with a relaxation time of 0.1 ps, while the pressure is controlled with a Martyna–Tuckerman–Tobias–Klein barostat^{93,94} using a relaxation time of 1 ps. These choices were found to be suitable for the isostructural MIL-53(Al) by Rogge et al.⁷⁰ A 100 ps equilibration time was taken into account, followed by a 500 ps production run for the $(N,V,\sigma_s=0,T)$ MD simulations.

4. FORCE FIELD VALIDATION

4.1. Geometry Optimization of MIL-47. To validate the force fields, we mainly concentrate on MIL-47, because this is the most studied structure and sufficient reference data are available for comparison. Some important structural features at 0 K, obtained with geometry optimizations of the periodic structure using the force field, are tabulated in Table 1 and compared with the cluster models and published periodic DFT calculations.³⁸ Bogaerts et al.³⁸ presented an efficient methodology to directly compare theoretically predicted geometries for crystalline materials to experimental X-ray diffractograms. MIL-47 was chosen as a case study, and is in this context highly relevant in this discussion. Periodic DFT calculations (PBE +D3^{95–97}) on MIL-47 reveal that the most stable structure corresponds with a displaced chain structure and an antiferromagnetic spin configuration (AFM). Its counterpart with a ferromagnetic spin configuration (FM) is almost 30 kJ·mol⁻¹ per unit cell higher in energy, but the resulting diffraction pattern agrees best with the experimental pattern.³⁸ A preliminary version of the MIL-47 force field has already been used in the work of Bogaerts et al., but no structural force field terms were considered to account for the displacement of the atoms in the vanadium chain. The diffractograms produced by this force field do not show the peaks arising from the shifted chains, as could be expected, and show large similarities with those obtained from first-principles without displaced vanadium chains. The force field constructed in this work contains additional terms to better describe this displacement of the vanadium atoms. Notice that the DFT cluster calculations used for the parametrization of the force field parameters systematically used parallel spins for the V atoms and thus best resemble the ferromagnetic spin configuration.

A first-principles parametrized force field should at least reproduce the DFT-optimized model systems from which it is derived. The force field optimized structure without van der Waals contributions should be compared with the DFT cluster models employed in the fitting of the force field parameters to assess the performance of the covalent force field parameters generated with QuickFF. As shown in Table 1, a good agreement is observed, indicating that the QuickFF parameters are indeed satisfactory to describe the covalent interactions.

The same conclusion can be drawn from Table 1 by comparing the periodic DFT calculations³⁸ (with inclusion of dispersion corrections) with our periodic force field result,

including van der Waals interactions. The main discrepancy is the overestimation of the V–V bond distance and the increased asymmetry along the vanadium chain (strong bond is shorter and weak bond is longer than expected). This is a consequence of the DFT inorganic cluster model, which also displays this asymmetry, and can to a large extent be ascribed to the usage of a finite model system. However, the long and short V–O distances of the cluster model are still within the experimental range of typical vanadium–oxygen bonds (V=O, 1.55–1.75 Å; V–O, 2.1–2.6 Å).⁹⁸ Other differences with the periodic DFT result are the O₁–V–O₁ and O₂–V–O₂ bend angles, which define the pore opening angle θ (see Figure 1). However, as will be shown in section 4.3, the potential energy surface is very flat along these coordinates. Globally, we can conclude that the cluster model captures the most important features of the periodic framework, and the force field optimized structure follows this trend. Additionally a comparison may be made with the experimental structure. For that reason, MD simulations in the $(N,P,\sigma_s=0,T)$ ensemble were carried out at 300 K and 1 bar (see Table S2).

4.2. Pressure-Induced Breathing of MIL-47. Overall, one can conclude from the previous section that the force field is able to correctly model the microscopic MIL-47 structure. One of the main objectives of the force field is to accurately predict the flexibility features of the material, i.e., the macroscopic pressure-induced breathing. To that end, simulations are performed in the $(N,V,\sigma_s=0,T)$ ensemble at 300 K following the scheme outlined in Methodology. The transition pressures from the lp to the np states and vice versa are important properties describing this behavior. The lp-to-np transition pressure is defined as the maximum pressure that can be applied to the material before it transforms to the np phase and is given by the local maximum of the $P(V)$ curve between the lp and np volume. Similarly, the np-to-lp transition pressure is the minimum pressure to which the applied pressure can be lowered before the np structure opens to the lp state. It is given by the local minimum pressure between the np and lp volume (see Figure 4). In Table 2, the transition pressures observed in this work are compared to pressure ranges reported in the literature. The experimentally observed broad range of transition pressures was ascribed by Yot et al.²⁹ to the presence of crystallites with a wide distribution of sizes, each with a different critical stress to initiate the structural transformation. Various possible magnetic configurations of MIL-47 lead to the DFT range of transition pressures⁵⁵ in Table 2. They were obtained by constructing energy–volume profiles through periodic DFT calculations at different spin configurations.

Initial simulations revealed that the original MM3 values of the atomic van der Waals parameters should be slightly modified to obtain transition pressures similar to the experimental values. Two uniform scaling parameters are used: (1) $s_e = 0.92$, the uniform scaling factor for the ϵ_i ; (2) $s_o = 1.14$, the uniform scaling of the σ_i . The same scaling factors will be consistently applied to the other MIL-47-type materials. Pressure–volume profiles of MIL-47 at different scaling parameters are provided in the Supporting Information to illustrate the sensitivity (Figure S4). A similar rescaling was found to be necessary for the MIL-53(Al) force field by Vanduyfhuys et al.⁷² to reproduce the first-principles relative stability of the np and lp phases. With our values, the lp-to-np transition pressure is 125 MPa at 300 K, while the np-to-lp transition pressure amounts to 56 MPa at 300 K, coinciding with the results by Yot et al.²⁹ The simulated volume decrease

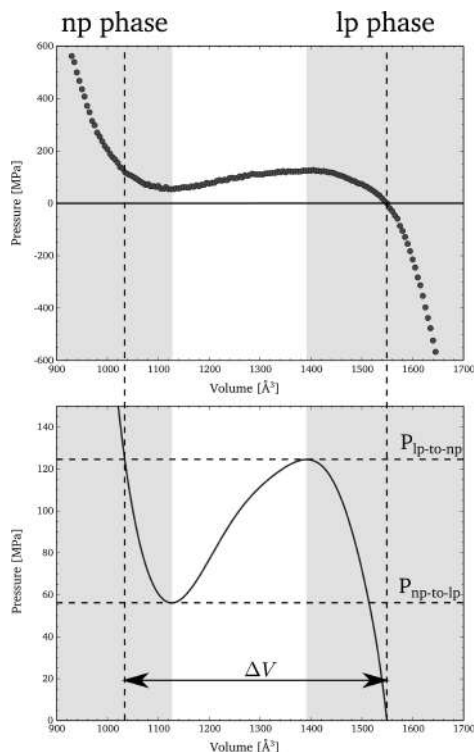


Figure 4. Resulting $P(V)$ curve of MIL-47 from the $(N,P,\sigma_s=0,T)$ MD simulations at 300 K. The simulated pressure at each volume is indicated in the top pane. The polynomial fit is shown in a smaller pressure range in the bottom pane. The lp-to-np and np-to-lp transition pressures are indicated together with the $\Delta V/V_{lp}$ volume contraction in the bottom figure. The np volume is defined here as the volume at the lp-to-np transition pressure in the np region.

Table 2. Overview of Transition Pressures for MIL-47

method	$P_{np-to-lp}$ [MPa]	$P_{lp-to-np}$ [MPa]
exp (300 K) (ref 29)	55–75	85–125
exp (298 K) (ref 61)	58–95	86–134
DFT (ref 55)	–	82–124
FF MD (300 K) (ref 29)	66	137
FF MD (300 K) (this work)	56	125

Table 3. Comparison of Lattice Parameters for MIL-47(V)

phase	method	a [Å]	b [Å]	c [Å]	α [deg]	β [deg]	γ [deg]	θ [deg]	D [Å]	V [Å ³]
lp	exp ^{37a}	16.143	6.818	13.939	90.0	90.0	90.0	81.6	21.3	1534
lp	DFT (FM) ³⁸	16.334	6.822	13.895	90.0	90.0	90.0	80.8	21.4	1548
lp	DFT (AFM) ³⁸	16.188	6.839	13.992	90.0	90.0	90.0	81.7	21.4	1549
lp	FF (this work)	16.947	6.904	13.300	90.0	90.0	90.0	76.2	21.5	1556
lp	FF (this work) ^b	16.309	6.915	14.082	90.0	90.0	90.0	81.6 ^b	21.5	1588

^aThe experimental structure at room temperature by Barthelet et al.³⁷ is also given. ^bGeometry optimization with fixed pore opening angle θ at 81.6°.

$\Delta V/V_{lp}$ of 33%, as indicated in Figure 4, is in agreement with the experimentally reported 38%. Another experimental finding was the continuously decreasing volume of the np phase, instead of collapsing under higher pressure, which can be seen in the upper panel of Figure 4. Via X-ray diffraction, Yot et al. found a np volume of 947 Å³ when applying a pressure of 178.1 MPa. Using the $(N,P,\sigma_s=0,T)$ ensemble, our force field predicts 1019(35) Å³ at the same pressure and temperature. From the results presented in this section, it can be concluded that the force field is able to correctly mimic the pressure-induced flexibility of MIL-47.

4.3. Lattice Parameters of MIL-47, COMOC-2, and COMOC-3. A final test for the force field is the prediction of the lattice parameters. This is done for MIL-47, COMOC-2, and COMOC-3, for which experimental data are available. The definitions of the pore opening angle θ and the interdiagonal distance D , together with the a , b and c directions of the unit cell, are illustrated in Figure 1.

4.3.1. MIL-47. The lattice parameters predicted via periodic force field calculations (geometry optimization at 0 K) are compared with the experimental (at room temperature) and DFT values (at 0 K) in Table 3. The most important difference is the underestimation of the pore opening angle θ . The lattice parameter a is overestimated, while c is underestimated, and this is directly correlated to θ . The overestimation of b can be ascribed to the finite model system. However, the position of the minimum at 0 K is very sensitive to the precise parametrization of both the covalent and the van der Waals contributions, as the potential energy surface is very flat along the pore opening angle. In Figure 5, the outcome of a constrained potential energy scan at 0 K in the neighborhood of the lp minimum is shown, indicating energy differences of less than 2 kJ·mol^{−1} per unit cell between the pore opening angle of the force field equilibrium on the one hand and the experimental or DFT structures on the other hand. The lattice parameters corresponding with this structure are also indicated in Table 3. Given such flat potential energy surface, it is very difficult to exactly match experimental data with theoretical methods. In general, optimizations of flexible structures with theoretical methods pose a huge challenge, as was recently shown by some of the presenting authors.⁵⁰

The symmetry breaking due to the displacement of the vanadium atoms perpendicular to the chain axis results in a lower energy (Figure S1). The structure without displacement, however, is also a stable minimum according to periodic DFT calculations.³⁸ Both geometries are minima on the force field potential energy surface as confirmed by means of a normal-mode analysis. The displaced chain is approximately 20 kJ·mol^{−1} per unit cell more stable, and all our simulations are performed in this configuration. Recall that without addition of

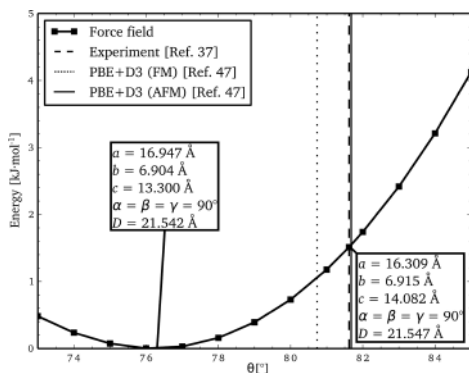


Figure 5. Scan of the pore opening angle in the lp phase of MIL-47 at 0 K. The values obtained by Barthelet et al.³⁷ and Bogaerts et al.³⁸ are indicated. The unit cell parameters at the minima and under the constraint of the experimental pore-opening angle are also given.

the Urey–Bradley terms, the second minimum with displaced chains was not found.³⁸

Note that for MIL-47 only a stable lp phase is reported at ambient conditions. With theoretical calculations both from DFT and from force field simulations it is possible to find a local minimum at the np phase on the potential energy surface at 0 K. Structural parameters are taken up in the [Supporting Information](#) but not explicitly compared here because of the lack of experimental data.

4.3.2. COMOC-2. Highly accurate structural information on the empty COMOC-2 at low temperatures is not available. However, for COMOC-2, two structures, a lp and a np phase, were reported experimentally.^{40,44,45} Their geometric characteristics are given in [Table 4](#). The np phase was found to be of monoclinic symmetry, whereas the lp corresponds to an orthorhombic unit cell. The results at 233 K were extracted by Liu et al.⁴⁰ from synchrotron XRD patterns under a certain CO₂ pressure, which hinders a direct comparison with our empty framework. They also reported a pure lp phase at 293 K. However, this structure was poorly reproducible because of the extreme synthesis procedure and with a small amount of remaining free linkers inside the pores, such that also here one should be careful with interpreting the results. Furthermore, the theoretical results reported in [ref 40](#) stem from periodic DFT calculations on COMOC-2 at the PBE+D2 level^{95,100} using only a single *k*-point approach. It was recently shown by

Vanpoucke et al.²⁰ that for flexible materials more *k*-points should be used; thus, the values from [ref 40](#) should be regarded with caution. The computational lattice parameters obtained by Liu et al. are also given in [Table 4](#). It should be mentioned that Liu et al. did not report the case of displaced vanadium chains, similar to MIL-47, while this effect was taken into account in our simulations.

Our estimate for the lp phase reproduces the experimental and theoretical structures quite well. Similar features are observed as for the MIL-47 material with an underestimation of the pore opening angle. In contrast, the experimentally observed np volume is substantially larger than the DFT and force field predictions. The force field result is in agreement with the DFT-predicted orthorhombic shape of the np phase, which could indicate that the presence of guest molecules lies at the origin of the experimentally observed transformation to the monoclinic structure.

Liu et al. also determined the energy difference between the lp and np states at 0 K and found a value of approximately 20 kJ·mol^{−1} per unit cell at the PBE+D2 level, which agrees relatively well with the 26 kJ·mol^{−1} per unit cell resulting from our force field simulations. The theoretically hypothesized so-called overstretched np phase with a pore opening angle of 147.5° is also detected with our force field. However, this phase is more than 100 kJ·mol^{−1} per unit cell less stable than the regular np state, which could explain why it has not been observed experimentally. Henceforth, we will thus discard the existence of this additional phase configuration.

4.3.3. COMOC-3. COMOC-3 is a nonporous metal–organic framework; that is, it remains in a np state (see [Figure 1](#)). Structural information is available only on COMOC-3(as) or V(OH) (NDC)·H₂O,⁴¹ which is tabulated in [Table 5](#). A periodic force field geometry optimization correctly leads to a np phase with an opening angle of 37° and a γ angle of 104°.

Summarizing, we may conclude that our force fields succeed in reproducing the essential characteristics of MIL-47-type materials. Geometrically, some bond distances and lattice parameters are overestimated or underestimated, which can mostly be ascribed to the finite cluster models used for the construction of the ab initio input data. However, the required asymmetry of the O–V=O chain is included, which allows the generation of subtle differences such as the structure with the displaced vanadium chains. The pressure-induced breathing for the MIL-47 is reproduced, which forms a solid basis to characterize the flexibility of the other materials, COMOC-2 and COMOC-3, under study.

Table 4. Comparison of Lattice Parameters for COMOC-2(V)

phase	method	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	α [deg]	β [deg]	γ [deg]	θ [deg]	<i>D</i> [Å]	<i>V</i> [Å ³]
lp	exp (293 K) ^{a40}	21.443	6.957	20.570	90	90	90	87.6	29.7	3069
	exp (233 K) ^{b40}	23.087	6.776	18.897	90	90	90	78.6	29.8	2956
	DFT ⁴⁰	21.642	6.927	20.498	90.0	90.0	90.0	86.9	29.8	3073
	FF (this work)	24.038	6.858	18.219	90.0	90.0	90.0	74.3	30.2	3003
	exp (233 K) ^{b40}	27.94	6.651	10.735	90	97.1	90	42.0	29.9	1979
np	DFT ⁴⁰	28.111	6.991	6.809	90.0	90.0	90.0	27.2	28.9	1338
	FF (this work)	28.552	6.840	7.592	90.0	90.0	90.0	29.8	29.5	1483

^aData of the experimental lp phase at 293 K was obtained from Rietveld structure refinement based on COMOC-2(V^{IV}), but with a small amount of remaining free linkers. ^bThe experimental lp phase at 233 K corresponds to a structure under 15 bar of CO₂, while the experimental np phase at 233 K corresponds to a structure under 7.5 bar of CO₂.

Table 5. Comparison of Lattice Parameters for COMOC-3(V)

method	a [Å]	b [Å]	c [Å]	α [deg]	β [deg]	γ [deg]	θ [deg]	D [Å]	V [Å ³]
exp (293 K) ^{a††}	24.985	6.880	7.508	90.0	90.0	107.7	33.5	26.1	1212
FF (this work)	24.838	6.875	8.296	90.0	90.0	103.6	36.9	26.2	1377

^{a††}The experimental structure is the COMOC-3(as) or V(OH) (NDC)-H₂O because there is no structural information available of COMOC-3(V).

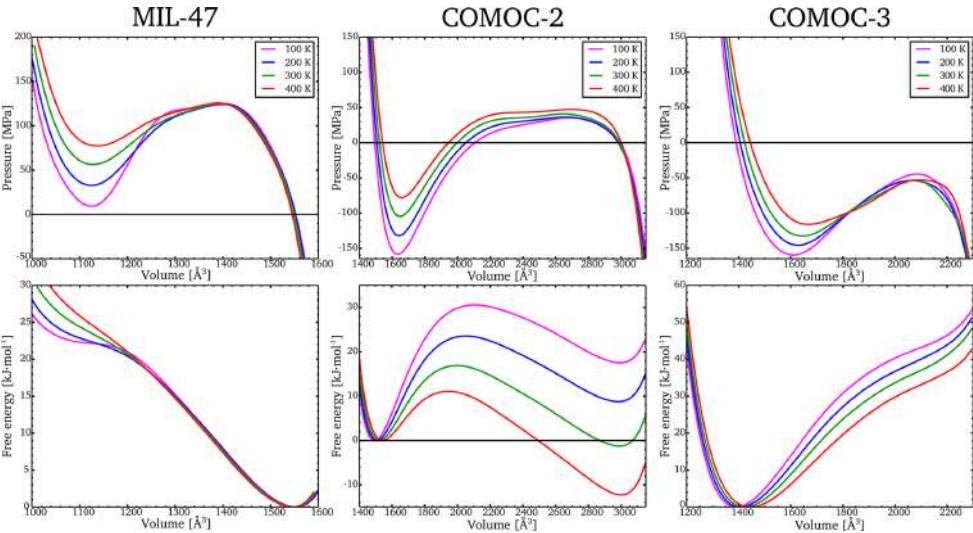


Figure 6. Fit of the $(N,V,\sigma_z=0,T)$ MD data for MIL-47, COMOC-2, and COMOC-3 at temperatures ranging from 100 to 400 K.

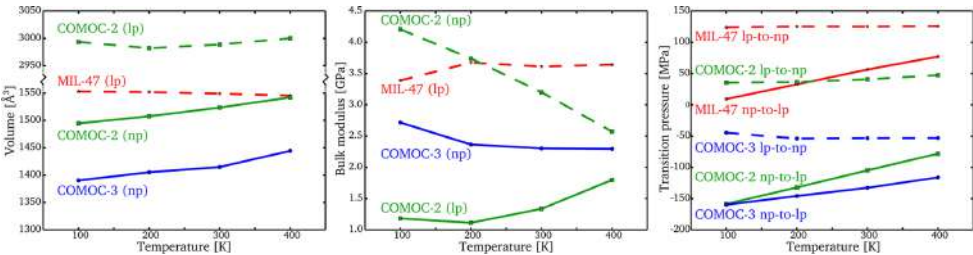


Figure 7. Influence of temperature on the volume, bulk moduli, and transition pressures of MIL-47-type materials.

5. STRUCTURAL FLEXIBILITY IN MIL-47-TYPE MATERIALS

Simulations in the $(N,V,\sigma_z=0,T)$ ensemble were carried out with the force fields validated in the previous section. In this section we discuss the pressure versus volume and free energy versus volume profiles constructed for all three materials (see Figure 6). The simulations are carried out at various temperatures to investigate the influence of the temperature on derived characteristics such as the transition pressure and the bulk modulus. To the best of our knowledge such temperature behavior of the mechanical properties has not been studied before. These results are summarized in Figure 7.

The influence of the temperature on the $P(V)$ and $F(V)$ profiles is displayed in Figure 6. It is immediately clear that the

temperature strongly affects the np–lp transition pressure, which varies in MIL-47 almost linearly between 9 and 77 MPa in the temperature range of 100–400 K, while the reverse transition pressure does not seem to change substantially. This indicates that the hysteresis in the $P(V)$ curve decreases with increasing temperature. Analogously, it can be observed for the $F(V)$ curves that the free energy at low volumes increases with respect to the lp minimum with increasing temperatures. There is no np minimum at finite temperatures because no stable zero-pressure state is found at low volumes. Also, the negative thermal expansion (NTE) of the lp phase of MIL-47 can be seen in Figure 7. Indeed, the equilibrium volume, i.e., at zero external pressure, shifts toward smaller volumes with increasing temperature, in agreement with the experimental findings by

Nanthamathee.¹⁰¹ An experimental volumetric thermal expansion coefficient, β_V , of $-1.2 \times 10^{-5} \text{ K}^{-1}$ was found by fitting the experimental $V(T)$ data in the temperature range of 12–290 K¹⁰¹ to

$$\beta_V = \left(\frac{\partial \ln(V)}{\partial T} \right)_p \quad (5.1)$$

Applying this procedure on our results reveals a simulated value of $-1.6 \times 10^{-5} \text{ K}^{-1}$ for MIL-47 in the temperature range of 100–400 K, which is in good agreement with the experimental result.

The shape of the $P(V)$ curve of COMOC-2 is shown in the middle pane of Figure 6, but the most crucial difference with MIL-47 is the range of the transition pressures. The lp-to-np transition pressure varies between 35–48 MPa depending on the temperature. The np-to-lp transition pressure even displays a larger range from –159 MPa to –78 MPa. A negative pressure should be interpreted as an isotropic pulling effect on the material. The transition pressures corresponding with the structural transformations have not been directly measured via experiment. However, Couck et al.^{44,45} applied a thermodynamic model (OFAST, developed by Couderc et al.^{62,63}) to analyze their experimental data, consisting of adsorption and desorption isotherms of light hydrocarbons (C1, C2, and C3). This thermodynamic analysis enables the extraction of free energy differences between the empty host in the lp and the empty host in the np form ($\Delta F = F_{lp} - F_{np}$). Values of about 40 $\text{kJ} \cdot \text{mol}^{-1}$ are found for temperatures around 300 K. It is an indication that the np phase is much more stable than the lp phase at room temperature, which is not in full agreement with our simulations. Moreover, Liu et al.⁴⁰ describe their COMOC-2(V^{IV}) sample as containing a mixture of np and lp phases (powder X-ray diffraction at room temperature), which seems unlikely if the free energy difference between both phases is as large as 40 $\text{kJ} \cdot \text{mol}^{-1}$. Our results, displayed in Figure 6, indeed reveal a lp and np phase with a small free energy difference around 300 K. It should also be noted that the isotherm fitting methodology, as applied by Couck et al., leads to phases of the material which are not strictly corresponding with the lp and np phases defined in this work and should rather be viewed as intermediate states at possibly different volumes.⁶⁹

Liu et al.⁴⁰ determined the energy difference between both phases as previously mentioned by means of periodic DFT calculations at the PBE+D2 level. A free energy scan as a function of the pore opening angle was also performed, thereby detecting three minima (np, lp, and overstretched np phases). They carried out frequency calculations enabling the computation of free energies. The modeled free energy profiles indicated that only at 650 K or higher does the lp phase become the most stable phase. This method, however, relies on the harmonic approximation, which is probably not the best choice for an intrinsic anharmonic material such as a flexible MOF. Our MD simulations, which include anharmonic effects, show that the lp phase already becomes the most stable structure around room temperature.

The free energy profile of COMOC-2 gives clear evidence for two stable minima of the empty frame, which are very close in free energy ($\sim 1 \text{ kJ} \cdot \text{mol}^{-1}$ per unit cell in favor of the lp) at room temperature. Over the whole temperature range, the free energy difference ($\Delta F = F_{lp} - F_{np}$) varies from 18 to $-12 \text{ kJ} \cdot \text{mol}^{-1}$ per unit cell. This is the result of a complex balance between the amount of dispersive stabilization energy (favoring

the np phase at low temperature) and the vibrational entropy (favoring the lp phase at high temperature).⁴⁸ However, COMOC-2 displays no reversible temperature hysteresis behavior in this temperature range, which was observed for MIL-53(Al),⁴⁷ because over the whole temperature range both phases remain minima of the free energy surface. The free energy profile also reveals a significant volume reduction of about 50% between the lp and np structures, which is exceptionally high. This volume reduction combined with a relatively high lp-to-np transition pressure indicates that COMOC-2 could potentially be an attractive shock absorber.⁵⁷ This is a consequence of a mechanically rigid lp phase due to the chemical nature of the vanadium chain and an increase of stabilizing dispersion interactions due to the extended BPDC linkers compared to the shorter BDC of MIL-47. The np phase displays positive thermal expansion (PTE) over the whole temperature range, while the lp phase has a more complex behavior (see Figure 7).

The third material under study is COMOC-3, for which a very stable np phase is found in agreement with experiment⁴¹ (see the right pane of Figure 6). In fact, the opposite behavior of MIL-47 is observed as both transition pressures are negative; hence, only a stable np state is obtained. Therefore, it is experimentally not possible to provoke structural transformations with a (positive) mechanical pressure as stimulus. This behavior can be understood by the predominance of stabilizing stacking interactions between two adjacent NDC linkers. The np-to-lp transition pressure is again temperature-dependent, but not as extremely as for COMOC-2 (see Figure 7), and the structure displays PTE similar to the np form of COMOC-2.

A final property that can be derived from these profiles is the bulk modulus and its dependence on the temperature (see Figure 7), which has been studied for only a very limited number of MOFs.^{53,102–104} Our simulations predict a MIL-47 bulk modulus of 3.6 GPa at 300 K, which remains constant between 200–400 K. This order of magnitude is consistent with the fact that MIL-47 is considered to be more rigid than the similar framework materials MIL-53(Al) and MIL-53(Cr), which have reported experimental bulk moduli of $\sim 0.35 \text{ GPa}$ ⁵⁷ and $\sim 2 \text{ GPa}$ ¹⁰⁵ at room temperature. The np phase of COMOC-2 and COMOC-3 show bulk moduli which decrease with temperature, indicating a temperature-induced softening effect. This effect is the most pronounced for COMOC-2, where a decrease of the bulk modulus of almost 40% over a range of 300 K is found. Although the volume slightly expands, the bulk modulus of COMOC-2 in the lp form increases in the temperature range 200–400 K. However, it still remains the material with the lowest resistance against mechanical deformation, probably due to the fact it has the longest linker.¹⁰²

6. CONCLUSIONS

We showed that the QuickFF²⁴ parametrization protocol is able to generate force fields for stimuli-responsive MOFs. Herein we presented a systematic set of first-principles-derived force fields for the MIL-47-type materials, which are able to describe all structural features, characteristic to this family of MOFs, with inclusion of the breathing behavior under pressure. For these materials, some specific terms were added to correctly describe the asymmetry of the vanadium-oxide chains. Their performance has been validated on existing experimental and theoretical data available for the MIL-47-type materials.

Subsequently, these force fields were used to study the structural flexibility of the empty framework. The three MIL-47-type materials all display a different behavior, which can be understood in terms of increasing stabilizing dispersion interactions from MIL-47 to COMOC-3. While MIL-47 only has a stable lp phase, which requires a high pressure to undergo a structural transformation, COMOC-3 resides in a very stable np phase. COMOC-2 is an intrinsic bistable MOF with lp and np minima, which are very sensitive to the temperature. The structural flexibility in empty MIL-47-type materials is thus determined by the host–host interactions, which is not so often encountered in other MOFs, as recently emphasized by Férey.¹³ As the flexibility strongly differs between the different MIL-47-type materials, our results underline the diversity of properties accessible by selecting the appropriate building blocks. To conclude, before one can assess the use of these stimuli-responsive MOFs in applications, a thorough understanding of the breathing behavior is required. The approach followed here opens up new perspectives to screen a larger set of materials and to select frameworks which behave rather as nanosprings, shock absorbers, or dampers.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b04422.

Force field parameters for the three materials, extra figures to distinguish the different MIL-47 structures, some key parameters and the lattice parameters of MIL-47 using molecular dynamics simulations at the experimental conditions compared with published experimental data, and sensitivity of the pressure versus volume and free energy versus volume profiles on the van der Waals parameters (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Fund for Scientific Research Flanders (FWO), the Research Board of Ghent University (BOF), and BELSPO in the frame of IAP/7/05. Funding was also received from the European Research Council under the European Community's Seventh Framework Programme [FP7 (2007–2013) ERC Grant Agreement 240483], and from the European Union's Horizon 2020 research and innovation programme [consolidator ERC Grant Agreement 647755 – DYNPOR (2015–2020)]. Computational resources (Stevin Supercomputer Infrastructure) and services were provided by Ghent University. We also thank S. Vandebande and T. Verstraelen for their help in generating the force fields and K. Lejaeghere for the insightful discussions on MIL-47.

■ REFERENCES

- (1) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705–714.
- (2) Kitagawa, S.; Kitaura, R.; Noro, S. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
- (3) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37*, 191–214.
- (4) Czaja, A. U.; Trukhan, N.; Müller, U. Industrial Applications of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1284–1293.
- (5) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673–674.
- (6) Zhou, H.-C.; Kitagawa, S. Metal-Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, S415–S418.
- (7) Chang, Z.; Yang, D.-H.; Xu, J.; Hu, T.-L.; Bu, X.-H. Flexible Metal-Organic Frameworks: Recent Advances and Potential Applications. *Adv. Mater.* **2015**, *27*, S432–S441.
- (8) Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nat. Chem.* **2009**, *1*, 695–704.
- (9) Férey, G.; Serre, C. Large Breathing Effects in Three-Dimensional Porous Hybrid Matter: Facts, Analyses, Rules and Consequences. *Chem. Soc. Rev.* **2009**, *38*, 1380–1399.
- (10) Nagarkar, S. S.; Desai, A. V.; Ghosh, S. K. Stimulus-Responsive Metal-Organic Frameworks. *Chem. - Asian J.* **2014**, *9*, 2358–2376.
- (11) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible Metal-Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062–6096.
- (12) Coudert, F.-X. Responsive Metal-Organic Frameworks and Framework Materials: Under Pressure, Taking the Heat, in the Spotlight, with Friends. *Chem. Mater.* **2015**, *27*, 1905–1916.
- (13) Férey, G. Structural Flexibility in Crystallized Matter: From History to Applications. *Dalton Trans.* **2016**, *45*, 4073–4089.
- (14) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.
- (15) Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q. Large-Scale Screening of Hypothetical Metal-Organic Frameworks. *Nat. Chem.* **2012**, *4*, 83–89.
- (16) Yang, Q.; Liu, D.; Zhong, C.; Li, J.-R. Development of Computational Methodologies for Metal-Organic Frameworks and Their Application in Gas Separations. *Chem. Rev.* **2013**, *113*, 8261–8323.
- (17) Colón, Y. J.; Snurr, R. Q. High-Throughput Computational Screening of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, S735–S749.
- (18) Odoh, S. O.; Cramer, C. J.; Truhlar, D. G.; Gagliardi, L. Quantum-Chemical Characterization of the Properties and Reactivities of Metal-Organic Frameworks. *Chem. Rev.* **2015**, *115*, 6051–6111.
- (19) Coudert, F.-X.; Fuchs, A. H. Computational Characterization and Prediction of Metal-Organic Framework Properties. *Coord. Chem. Rev.* **2016**, *307*, 211–236.
- (20) Vanpoucke, D. E. P.; Lejaeghere, K.; Van Speybroeck, V.; Waroquier, M.; Ghysels, A. Mechanical Properties from Periodic Plane Wave Quantum Mechanical Codes: the Challenge of the Flexible Nanoporous MIL-47(V) Framework. *J. Phys. Chem. C* **2015**, *119*, 23752–23766.
- (21) Burekew, S.; Amirjalayer, S.; Tafipolsky, M.; Spickermann, C.; Roy, T. K.; Schmid, R. MOF-FF - A Flexible First-Principles Derived Force Field for Metal-Organic Frameworks. *Phys. Status Solidi B* **2013**, *250*, 1128–1141.
- (22) Addicoat, M. A.; Vankova, N.; Akter, I. F.; Heine, T. Extension of the Universal Force Field to Metal-Organic Frameworks. *J. Chem. Theory Comput.* **2014**, *10*, 880–891.
- (23) Bristow, J. K.; Tiana, D.; Walsh, A. Transferable Force Field for Metal-Organic Frameworks from First-Principles: BTW-FF. *J. Chem. Theory Comput.* **2014**, *10*, 4644–4652.
- (24) Vanduyfhuys, L.; Vandebande, S.; Verstraelen, T.; Schmid, R.; Waroquier, M.; Van Speybroeck, V. QuickFF: A Program for a Quick and Easy Derivation of Force Fields for Metal-Organic Frameworks from Ab Initio Input. *J. Comput. Chem.* **2015**, *36*, 1015–1027.
- (25) Salles, F.; Ghoufi, A.; Maurin, G.; Bell, R. G.; Mellot-Draznieks, C.; Férey, G. Molecular Dynamics Simulations of Breathing MOFs: Structural Transformations of MIL-53(Cr) Upon Thermal Activation of CO₂ Adsorption. *Angew. Chem., Int. Ed.* **2008**, *47*, 8487–8491.

- (26) Coombes, D. S.; Corà, F.; Mellot-Draznieks, C.; Bell, R. G. Sorption-Induced Breathing in the Flexible Metal-Organic Framework CrMIL-53: Force-Field Simulations and Electronic Structure Analysis. *J. Phys. Chem. C* **2009**, *113*, 544–552.
- (27) Grosch, J. S.; Paesani, F. Molecular-Level Characterization of the Breathing Behavior of the Jungle-Gym-Type DMOF-1 Metal-Organic Framework. *J. Am. Chem. Soc.* **2012**, *134*, 4207–4215.
- (28) Hu, Z.; Zhang, L.; Jiang, J. Development of a Force Field for Zeolitic Imidazolate Framework-8 with Structural Flexibility. *J. Chem. Phys.* **2012**, *136*, 244703.
- (29) Yot, P.; Ma, Q.; Haines, J.; Yang, Q.; Ghoufi, A.; Devic, T.; Serre, C.; Dmitriev, G.; Férey, G.; Zhong, G. L.; et al. Large breathing of the MOF MIL-47(V^{IV}) Under Mechanical Pressure: A Joint Experimental-Modelling Exploration. *Chem. Sci.* **2012**, *3*, 1100–1104.
- (30) Zheng, B.; Sant, M.; Demontis, P.; Suffritti, G. B. Force Field for Molecular Dynamics Computations in Flexible ZIF-8 Framework. *J. Phys. Chem. C* **2012**, *116*, 933–938.
- (31) Ortiz, A. U.; Boutin, A.; Fuchs, A. H.; Coudert, F.-X. Investigating the Pressure-Induced Amorphization of Zeolitic Imidazolate Framework ZIF-8: Mechanical Instability Due to Shear Mode Softening. *J. Phys. Chem. Lett.* **2013**, *4*, 1861–1865.
- (32) Zhang, L.; Hu, Z.; Jiang, J. Sorption-Induced Structural Transition of Zeolitic Imidazolate Framework-8: A Hybrid Molecular Simulation Study. *J. Am. Chem. Soc.* **2013**, *135*, 3722–3728.
- (33) Wu, X.; Huang, J.; Cai, W.; Jaroniec, M. Force Field for ZIF-8 Flexible Frameworks: Atomistic Simulation of Adsorption, Diffusion of Pure Gases as CH₄, H₂, CO₂ and N₂. *RSC Adv.* **2014**, *4*, 16503–16511.
- (34) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
- (35) Dauber-Osguthorpe, P.; Roberts, V. A.; Osguthorpe, D. J.; Wolff, J.; Genest, M.; Hagler, A. T. Structure and Energetics of Ligand Binding to Proteins: Escherichia Coli Dihydrofolate Reductase-Trimethoprim, a Drug-Receptor System. *Proteins: Struct., Funct., Genet.* **1988**, *4*, 31–47.
- (36) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- (37) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. A Breathing Hybrid Organic-Inorganic Solid with Very Large Pores and High Magnetic Characteristics. *Angew. Chem., Int. Ed.* **2002**, *41*, 281–284.
- (38) Bogaerts, T.; Vanduyfhuys, L.; Vanpoucke, D. E. P.; Wieme, J.; Waroquier, M.; Van Der Voort, P.; Van Speybroeck, V. Fine-Tuning the Theoretically Predicted Structure of MIL-47(V) with the Aid of Powder X-Ray Diffraction. *CrystEngComm* **2015**, *17*, 8612–8622.
- (39) Van Der Voort, P.; Leus, K.; Liu, Y.-Y.; Vandichel, M.; Van Speybroeck, V.; Waroquier, M.; Biswas, S. Vanadium Metal-Organic Frameworks: Structures and Applications. *New J. Chem.* **2014**, *38*, 1853–1867.
- (40) Liu, Y.-Y.; Couck, S.; Vandichel, M.; Grzywa, M.; Leus, K.; Biswas, S.; Volkmer, D.; Gascon, J.; Kapteijn, F.; Denayer, J. F. M.; et al. New V-IV-Based Metal-Organic Framework Having Framework Flexibility and High CO₂ Adsorption Capacity. *Inorg. Chem.* **2013**, *52*, 113–120.
- (41) Liu, Y.-Y.; Leus, K.; Grzywa, M.; Weinberger, D.; Strubbe, K.; Vrielandck, H.; Van Deun, R.; Volkmer, D.; Van Speybroeck, V.; Van Der Voort, P. Synthesis, Structural Characterization, and Catalytic Performance of a Vanadium-Based Metal-Organic Framework (COMOC-3). *Eur. J. Inorg. Chem.* **2012**, *2012*, 2819–2827.
- (42) Senkovska, I.; Hoffmann, F.; Fröba, M.; Getzschmann, J.; Böhlmann, W.; Kaskel, S. New Highly Porous Aluminium Based Metal-Organic Frameworks: Al(OH) (NDC) (NDC = 2,6-Naphthalene Dicarboxylate) and Al(OH) (BPDC) (BPDC = 4,4'-Biphenyl Dicarboxylate). *Microporous Mesoporous Mater.* **2009**, *122*, 93–98.
- (43) Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T., III; et al. Tuning the Structure and Function of Metal-Organic Frameworks via Linker Design. *Chem. Soc. Rev.* **2014**, *43*, 5561–5593.
- (44) Couck, S.; Van Assche, T. R. C.; Liu, Y.-Y.; Baron, G. V.; Van Der Voort, P.; Denayer, J. F. M. Adsorption and Separation of Small Hydrocarbons on the Flexible, Vanadium-Containing MOF, COMOC-2. *Langmuir* **2015**, *31*, 5063–5070.
- (45) Couck, S.; Van Assche, T. R. C.; Liu, Y.-Y.; Baron, G. V.; Van Der Voort, P.; Denayer, J. F. M. Correction to "Adsorption and Separation of Small Hydrocarbons on the Flexible, Vanadium-Containing MOF, COMOC-2. *Langmuir* **2015**, *31*, 13467–13467.
- (46) Leclerc, H.; Devic, T.; Devautour-Vinot, S.; Bazin, P.; Audebrand, N.; Férey, G.; Daturi, M.; Vimont, A.; Clet, G. Influence of the Oxidation State of the Metal Center on the Flexibility and Adsorption Properties of a Porous Metal Organic Framework: MIL-47(V). *J. Phys. Chem. C* **2011**, *115*, 19828–19840.
- (47) Liu, Y.; Her, J.-H.; Dailly, A.; Ramirez-Cuesta, A. J.; Neumann, D. A.; Brown, C. M. Reversible Structural Transition in MIL-53 with Large Temperature Hysteresis. *J. Am. Chem. Soc.* **2008**, *130*, 11813–11818.
- (48) Walker, A. M.; Civalieri, B.; Slater, B.; Mellot-Draznieks, C.; Corà, F.; Zicovich-Wilson, C. M.; Román-Pérez, G.; Soler, J. M.; Gale, J. D. Flexibility in a Metal-Organic Framework Controlled by Weak Dispersion Forces: the Bistability of MIL-53(Al). *Angew. Chem., Int. Ed.* **2010**, *49*, 7501–7503.
- (49) Tan, J. C.; Cheetham, A. K. Mechanical Properties of Hybrid Inorganic-Organic Framework Materials: Establishing Fundamental Structure-Property Relationships. *Chem. Soc. Rev.* **2011**, *40*, 1059–1080.
- (50) Ortiz, A. U.; Boutin, A.; Fuchs, A. H.; Coudert, F.-X. Anisotropic Elastic Properties of Flexible Metal-Organic Frameworks: How Soft Are Soft Porous Crystals? *Phys. Rev. Lett.* **2012**, *109*, 195502.
- (51) Li, W.; Henke, S.; Cheetham, A. K. Research Update: Mechanical Properties of Metal-Organic Frameworks - Influence of Structure and Chemical Bonding. *APL Mater.* **2014**, *2*, 123902.
- (52) Yang, K.; Zhou, G.; Xu, Q. The Elasticity of MOFs Under Mechanical Pressure. *RSC Adv.* **2016**, *6*, 37506–37514.
- (53) Ortiz, A. U.; Boutin, A.; Fuchs, A. H.; Coudert, F.-X. Metal-Organic Frameworks with Wine-Rack Motif: What Determines Their Flexibility and Elastic Properties? *J. Chem. Phys.* **2013**, *138*, 174703.
- (54) Heinen, J.; Dubbeldam, D. Understanding and Solving Disorder in the Substitution Pattern of Amino Functionalized MIL-47(V). *Dalton Trans.* **2016**, *45*, 4309–4315.
- (55) Vanpoucke, D. E. P.; Jaeken, J. W.; De Baerdemacker, S.; Lejaeghere, K.; Van Speybroeck, V. Quasi-1D Physics in Metal-Organic Frameworks: MIL-47(V) from First Principles. *Beilstein J. Nanotechnol.* **2014**, *5*, 1738–1748.
- (56) Beurroies, I.; Boulhout, M.; Llewellyn, P. L.; Kuchta, B.; Férey, G.; Serre, C.; Denoyel, R. Using Pressure to Probe the Structural Transition of Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2010**, *49*, 7526–7529.
- (57) Yot, P. G.; Boudene, Z.; Macia, J.; Granier, D.; Vanduyfhuys, L.; Verstraelen, T.; Van Speybroeck, V.; Devic, T.; Serre, C.; Férey, G.; et al. Metal-Organic Frameworks as Potential Shock Absorbers: The Case of the Highly Flexible MIL-53(Al). *Chem. Commun.* **2014**, *50*, 9462–9464.
- (58) Rodriguez, J.; Beurroies, I.; Loiseau, T.; Denoyel, R.; Llewellyn, P. L. The Direct Heat Measurement of Mechanical Energy Storage Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2015**, *54*, 4626–4630.
- (59) McKellar, S. C.; Moggach, S. A. Structural Studies of Metal-Organic Frameworks Under High Pressure. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2015**, *71*, 587–607.
- (60) Yot, P. G.; Vanduyfhuys, L.; Alvarez, E.; Rodriguez, J.; Itié, J.-P.; Fabry, P.; Guillou, N.; Devic, T.; Beurroies, I.; Llewellyn, P. L.; et al. Mechanical Energy Storage Performance of an Aluminum Fumarate Metal-Organic Framework. *Chem. Sci.* **2016**, *7*, 446–450.
- (61) Rodriguez, J.; Beurroies, I.; Coulet, M.-V.; Fabry, P.; Devic, T.; Serre, C.; Denoyel, R.; Llewellyn, P. L. Thermodynamics of the Structural Transition in Metal-Organic Frameworks. *Dalton Trans.* **2016**, *45*, 4274–4282.

- (62) Coudert, F.-X.; Jeffroy, M.; Fuchs, A. H.; Boutin, A.; Mellot-Drazniéks, C. Thermodynamics of Guest-Induced Structural Transitions in Hybrid Organic-Inorganic Frameworks. *J. Am. Chem. Soc.* **2008**, *130*, 14294–14302.
- (63) Coudert, F.-X. The Osmotic Framework Adsorbed Solution Theory: Predicting Mixture Coadsorption in Flexible Nanoporous Materials. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10904–10913.
- (64) Coudert, F.-X.; Boutin, A.; Fuchs, A. H. A Thermodynamic Description of the Adsorption-Induced Structural Transitions in Flexible MIL-53 Metal-Organic Framework. *Mol. Phys.* **2014**, *112*, 1257–1261.
- (65) Neimark, A. V.; Coudert, F.-X.; Boutin, A.; Fuchs, A. H. Stress-Based Model for the Breathing of Metal-Organic Frameworks. *J. Phys. Chem. Lett.* **2010**, *1*, 445–449.
- (66) Bousquet, D.; Coudert, F.-X.; Boutin, A. Free Energy Landscapes for the Thermodynamic Understanding of Adsorption-Induced Deformations and Structural Transitions in Porous Materials. *J. Chem. Phys.* **2012**, *137*, 044118.
- (67) Bousquet, D.; Coudert, F.-X.; Fossati, A. G. J.; Neimark, A. V.; Fuchs, A. H.; Boutin, A. Adsorption Induced Transitions in Soft Porous Crystals: An Osmotic Potential Approach to Multistability and Intermediate Structures. *J. Chem. Phys.* **2013**, *138*, 174706.
- (68) Ghysels, A.; Vanduyfhuys, L.; Vandichel, M.; Waroquier, M.; Van Speybroeck, V.; Smit, B. On the Thermodynamics of Framework Breathing: A Free Energy Model for Gas Adsorption in MIL-53. *J. Phys. Chem. C* **2013**, *117*, 11540–11554.
- (69) Vanduyfhuys, L.; Ghysels, A.; Rogge, S. M. J.; Demuyne, R.; Van Speybroeck, V. Semi-Analytical Mean-Field Model for Predicting Breathing in Metal-Organic Frameworks. *Mol. Simul.* **2015**, *41*, 1311–1328.
- (70) Rogge, S. M. J.; Vanduyfhuys, L.; Ghysels, A.; Waroquier, M.; Verstraelen, T.; Maurin, G.; Van Speybroeck, V. A Comparison of Barostats for the Mechanical Characterization of Metal-Organic Frameworks. *J. Chem. Theory Comput.* **2015**, *11*, 5583–5597.
- (71) Kirkwood, J. G. Statistical Mechanics of Fluid Mixtures. *J. Chem. Phys.* **1935**, *3*, 300–313.
- (72) Vanduyfhuys, L.; Verstraelen, T.; Vandichel, M.; Waroquier, M.; Van Speybroeck, V. Ab Initio Parametrized Force Field for the Flexible Metal-Organic Framework MIL-53(Al). *J. Chem. Theory Comput.* **2012**, *8*, 3217–3231.
- (73) Verstraelen, T.; Boguslawski, K.; Tecmer, P.; Heidar-Zadeh, F.; Chan, M.; Kim, T. D.; Zhao, T.; Vandenbrande, S.; Yang, D.; González-Espinoza, C. E.; et al. Horton 2.0.0, 2015. <http://theochem.github.com/horton/> (accessed June 9, 2016).
- (74) Chen, J.; Martinez, T. J. QTPIE: Charge Transfer with Polarization Current Equalization. A Fluctuating Charge Model with Correct Asymptotics. *Chem. Phys. Lett.* **2007**, *438*, 315–320.
- (75) Lii, J. H.; Allinger, N. L. Molecular Mechanics. The MM3 Force Field for Hydrocarbons. 3. The van der Waals Potentials and Crystal Data for Aliphatic and Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1989**, *111*, 8576–8582.
- (76) Allinger, N. L.; Zhou, X.; Bergsma, J. Molecular Mechanics Parameters. *J. Mol. Struct.: THEOCHEM* **1994**, *312*, 69–83.
- (77) Verstraelen, T.; Van Speybroeck, V.; Waroquier, M. ZEOBUILDER: A GUI Toolkit for the Construction of Complex Molecular Structures on the Nanoscale with Building Blocks. *J. Chem. Inf. Model.* **2008**, *48*, 1530–1541.
- (78) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.
- (79) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian09*, revision E.01; Gaussian Inc.: Wallingford CT, 2009.
- (80) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A: At, Mol, Opt. Phys.* **1988**, *38*, 3098–3100.
- (81) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (82) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.
- (83) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (84) Wachters, A. J. H. Gaussian Basis Sets for Molecular Wavefunctions Containing Third-Row Atoms. *J. Chem. Phys.* **1970**, *52*, 1033–1036.
- (85) Hay, P. J. Gaussian Basis Sets for Molecular Calculations. The Representation of 3d Orbitals in Transition-Metal Atoms. *J. Chem. Phys.* **1977**, *66*, 4377–4384.
- (86) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 20. Basis Set for Correlated wave-Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (87) Raghavachari, K.; Trucks, G. W. Highly Correlated Systems. Excitation Energies of First Row Transition Metals Sc-Cu. *J. Chem. Phys.* **1989**, *91*, 1062–1065.
- (88) Verstraelen, T.; Vanduyfhuys, L.; Vandenbrande, S.; Rogge, S. M. J. Yaff, yet another force field. <http://molmod.ugent.be/software/> (accessed June 9, 2016).
- (89) Ghysels, A.; Verstraelen, T.; Hemelsoet, K.; Waroquier, M.; Van Speybroeck, V. TAMkin: A Versatile Package for Vibrational Analysis and Chemical Kinetics. *J. Chem. Inf. Model.* **2010**, *50*, 1736–1750.
- (90) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A: At, Mol, Opt. Phys.* **1985**, *31*, 1695–1697.
- (91) Nosé, S. An Extension of the Canonical Ensemble Molecular Dynamics Method. *Mol. Phys.* **1986**, *57*, 187–191.
- (92) Martyna, G. J.; Klein, M. L.; Tuckerman, M. E. Nosé-Hoover chains: The Canonical Ensemble via Continuous Dynamics. *J. Chem. Phys.* **1992**, *97*, 2635–2643.
- (93) Martyna, G. J.; Tobias, D. J.; Klein, M. L. Constant Pressure Molecular Dynamics Algorithms. *J. Chem. Phys.* **1994**, *101*, 4177–4189.
- (94) Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. Explicit Reversible Integrators for Extended Systems Dynamics. *Mol. Phys.* **1996**, *87*, 1117–1157.
- (95) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (96) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (97) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (98) Weeks, C.; Song, Y.; Suzuki, M.; Chernova, N. A.; Zavalij, P. Y.; Whittingham, M. S. The One Dimensional Chain Structures of Vanadyl Glycolate and Vanadyl Acetate. *J. Mater. Chem.* **2003**, *13*, 1420–1423.
- (99) Allen, F. H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380–388.
- (100) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (101) Nanthamathie, C. *Thermoresponsive Behaviour of Metal Organic Frameworks*. Ph.D. Thesis, University of Manchester, Manchester, U.K., 2013.
- (102) Han, S. S.; Goddard, W. A., III Metal-Organic Frameworks Provide Large Negative Thermal Expansion Behavior. *J. Phys. Chem. C* **2007**, *111*, 15185–15191.
- (103) Greathouse, J. A.; Allendorf, M. D. Force Field Validation for Molecular Dynamics Simulations of IRMOF-1 and Other Isostructural Zinc Carboxylate Coordination Polymers. *J. Phys. Chem. C* **2008**, *112*, 5795–5802.
- (104) Tafipolsky, M.; Schmid, R. Systematic First Principles Parameterization of Force Fields for Metal-Organic Frameworks

Using a Genetic Algorithm Approach. *J. Phys. Chem. B* **2009**, *113*, 1341–1315.

(105) Neimark, A. V.; Coudert, F.-X.; Triguero, C.; Boutin, A.; Fuchs, A. H.; Beurroies, I.; Denoyel, R. Structural Transitions in MIL-53(Cr): View from the Outside and Inside. *Langmuir* **2011**, *27*, 4734–4741.

Paper II

**Mechanical properties of a gallium fumarate
metal-organic framework: a joint
experimental-modelling exploration**

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Journal of Materials Chemistry A, **2017**, 5, 11047–11054

J. Wieme performed the simulations and had a large contribution in the interpretation as well as the preparation of the manuscript.

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Cite this: *J. Mater. Chem. A*, 2017, 5,
11047

Mechanical properties of a gallium fumarate metal–organic framework: a joint experimental–modelling exploration†

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A gallium analogue of the commercially available Al-fumarate MOF A520 – recently identified as isotopic to MIL-53(Al)-BDC – has been synthesized for the first time and further characterized in its hydrated and dehydrated forms. The structural response under applied mechanical pressure of this MIL-53(Ga)-FA solid was investigated using advanced experimental techniques coupled with computational tools. Hg porosimetry and high-pressure X-ray powder diffraction (XRPD) experiments evidenced that the pristine dehydrated large pore form undergoes an irreversible structure contraction upon an applied pressure of 85 MPa with an associated volume change of ~14% which makes this material promising for mechanical energy storage applications, in particular as a shock absorber. The breathing behavior was further rationalized by performing a series of periodic Density Functional Theory (DFT) calculations with the construction of an energy profile as a function of volume for both MIL-53(Ga)-FA and its aluminium analogue. As such we unravelled the microscopic origin of the difference in pressure-induced behavior for the aluminium and gallium fumarate based materials.

Received 20th February 2017
Accepted 14th May 2017

DOI: 10.1039/c7ta01559c

rsc.li/materials-a

1. Introduction

Metal–Organic Frameworks (MOFs) are a versatile class of porous crystalline hybrid materials consisting of metal ions bridged by organic ligands.^{1,2} This family of porous solids is especially of interest due to the wide spectrum of materials that can be prepared. Almost all the elements of the periodic table and a large variety of organic linkers have been used in one structure or another, leading to materials with a huge variety of physical properties. MOFs have hitherto been envisaged for a large number of applications such as gas storage and gas/liquid separation,^{3–11} adsorption-based heat-pump,¹²

biomedicine,^{13,14} catalysis,^{15–18} photoluminescence,^{19,20} magnetism,^{21,22} proton conductivity^{23,24} etc. However, the thermo-mechanical properties of MOFs and their potential related-applications have been less explored so far.^{25–39} One of the early reports in literature by Chapman *et al.* focused on the study of the effect of the size and penetrability of guest molecules on the compressibility of CuBTC or HKUST-1.²⁶ Later, the pressure-induced structure behaviour of ZIFs was investigated.^{27–29} More recently, MIL-53(Al) and its amino-functionalized form were explored under applied pressure by Serra-Crespo *et al.*, and this study revealed a negative linear compressibility in these solids.³⁰ Other studies focused on the pressure-induced amorphization of a series of MOFs in a wide range of applied pressures, from 6.5 GPa for ZIF-4 (ref. 33) to 3.5 MPa for MOF-5,³¹ and 1.8 GPa for UiO-66.^{32,40,41} Most of these experiments have been performed by *in situ* high-pressure X-ray or neutron powder diffraction based on the use of diamond anvil cells and a non-penetrating inert fluid to ensure hydrostatic compression of the solids. With regard to potential applications, several members of the highly flexible MIL-53 series have been shown to possess structural features that render them attractive for use in energy absorption/storage related-applications such as dampers and shock absorbers.^{34–38} In this context, some of us recently reported the optimized synthesis and structural characterization of the commercially available aluminium fumarate A520.⁴² We showed that this solid exhibits a structure strongly related to the

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MIL-53 topology and thus was labelled as MIL-53(Al)-FA. This material undergoes a reversible structural contraction which can be controlled by the application of an external pressure, resulting in unprecedented values for work and heat energies, thereby showing great promises for mechanical storage applications.³⁷ MIL-53(Al)-FA was also found to exhibit interesting heat transfer reallocation properties that could have potential interests for thermally-driven adsorption chillers or heat-pumps.⁴³ In this latter application, one point of attention is the material's mechanical stability under the influence of capillary forces during successive adsorption/desorption cycles, which needs to be ensured.⁴³

In light of the diverse range of technologically relevant properties exhibited by this aluminium-fumarate MOF, we decided to expand our investigations into the series of MIL-53-fumarate with various metal cations. Previous studies on the related highly flexible MIL-53-BDC (Al, Cr, Fe, Ga, Sc, BDC = 1,4-benzene dicarboxylate) frameworks have demonstrated that the metal center plays a very crucial role in tuning the magnitude of the flexibility of this family of materials, not only upon adsorption, but also under thermal and mechanical stimuli, leading to strong differences in terms of energy storage as well as reversible or irreversible structural switching behaviours.^{34–36,44–50} Herein we report our results on the gallium fumarate, denoted MIL-53(Ga)-FA, whose characterizations are strongly in favour of an isoreticular character between this solid and the MIL-53(Al)-FA MOF. Hg-porosimetry and *in situ* high-pressure synchrotron X-ray diffraction were combined with advanced periodic Density Functional Theory (DFT) calculations to study the structural changes of this flexible solid under applied moderate pressures up to 2 GPa. This joint experimental-computational approach allowed the determination of the transition pressure and the magnitude of the volume change related to the structural switching of MIL-53(Ga)-FA towards a more contracted phase. Finally, the reversibility of the structural transition was explored for potential applications of this solid to the field of mechanical energy storage. As anticipated by similar studies performed on the MIL-53-BDC frameworks, the nature of the metal center impacts the pressure-induced behaviour of the fumarate-based materials and the origin has been revealed by the DFT calculations.

2. Material and methods

2.1. Synthesis and characterisations

MIL-53(Ga)-FA was prepared from a reaction mixture of composition Ga(III) nitrate ($\text{Ga}^{\text{III}}(\text{NO}_3)_3(\text{H}_2\text{O})_x$):fumaric acid: water : NaOH = 1 : 0.5 : 275 : 1, which was heated at 403 K in a Teflon-lined autoclave for 10 hours with a ramped heating rate of 7 K min^{−1}. The solid was recovered by filtration and washed with water and ethanol. In the infra-red (IR) spectrum of MIL-53(Ga)-FAas (as for as-synthesized), a band at about 1710 cm^{−1}, characteristic of the $\nu(\text{C}=\text{O})$ mode of the carboxyl groups of residual traces of the free fumaric acid was observed (Fig. S1, ESI†). This band subsequently disappears with successive washings, indicating the full departure of the entrapped or recrystallized fumaric acid. The thermogravimetric analysis

(Fig. S2†) shows two different weight losses at 360 and 460 K corresponding to the loss of water and linker respectively. This is consistent with the proposed formula, $\text{Ga}(\text{OH})(\text{fum})$ (fum for fumarate), the difference possibly arising from an excess of metal oxide or linker defects (experimental: 54% vs. theoretical: 47%), similar to that observed previously in the synthesis of the aluminium fumarate solid.³⁷ MIL-53(Ga)-FA reveals at first sight a I-type N₂ adsorption isotherm characteristic for microporous solids (Fig. S3†). The corresponding BET area is 750(20) m² g^{−1} slightly lower than the value previously reported for the Al-fumarate phase, partially due to the higher crystal density of this solid.⁴² The X-ray powder diffraction pattern of MIL-53(Ga)-FA is very close to the one of MIL-53(Al)-FA, associated with a slight shift of the main diffraction Bragg peaks to low angle in agreement with a larger ionic radius of Ga³⁺ compared to Al³⁺ (Fig. 1). Further experimental details are provided in the ESI.†

2.2. Mercury intrusion

Mercury intrusion experiments were carried out to characterize the pressure-induced structural response of the dehydrated

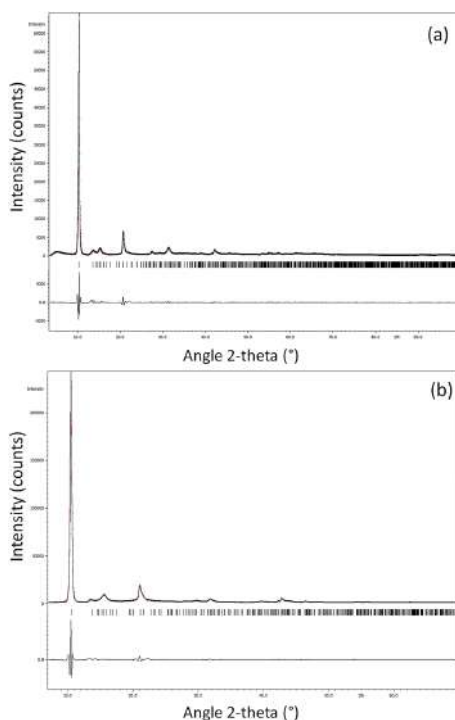


Fig. 1 (a) Structure-independent refinement of the unit cell parameters for the hydrated phase of MIL-53(Ga)-FA, space group $P2_1/c$. $a = 7.159(1)$ Å, $b = 12.283(1)$ Å, $c = 14.461(2)$ Å, $\beta = 122.87(1)^\circ$, $V = 1068.0(2)$ Å³. GoF = 5.37, $R_p = 9.22$, $wR_p = 13.79$. (b) Structure-independent refinement of the unit cell parameters for the hydrated phase of MIL-53(Al)-FA (see Table 1).

solid with a Micromeritics Autopore 9240 porosimeter. Prior to intrusion, the sample was first activated at 383 K under secondary vacuum for 8 hours. Two intrusion–extrusion (compression–decompression) cycles were applied to the samples in the pressure range 10^{-4} to 420 MPa (see ESI†).

2.3. X-ray powder diffraction

The hydrated and dehydrated forms of MIL-53(Ga)-FA were studied using a laboratory PANalytical X'PERT II powder diffractometer using a monochromatic $\text{Cu-K}\alpha_1$ source ($\lambda = 1.5406 \text{ \AA}$) with an operating voltage of 40 kV and a beam current of 40 mA. For the dehydrated phase, the sample was heated under secondary vacuum at 383 K for 8 hours and subsequently sealed in a glass capillary of diameter 0.5 mm. The patterns were collected for $2\theta = 5\text{--}100^\circ$. Full profile analysis (Le Bail intensity fitting together with refinement of lattice parameters) of individual X-ray powder diffraction (XRPD) patterns was performed using Jana 2006 software.⁵¹

2.4. High pressure X-ray powder diffraction

Angle-dispersive high-pressure XRPD data were collected at PSICHE beam line of the Synchrotron Soleil (Saint-Aubin, France) using a monochromatic beam ($50 \times 50 \mu\text{m}^2$) with a wavelength of $\lambda = 0.37380 \text{ \AA}$. The pressure was generated with a membrane diamond anvil cell (MDAC) using silicon oil AP100 (Aldrich) as the pressure-transmitting medium. The kinetic diameter of this silicon oil largely exceeds the window size of the MOF that ensures that this fluid does not enter the pores. The applied pressure was determined from the shift of the ruby R1 fluorescence line. XRPD measurements were also performed in-house (filtered $\text{Cu-K}\alpha_1$, $\lambda = 1.5406 \text{ \AA}$) on the MOF powder samples that were pressed under a 13 mm IR-die at 6 tons corresponding to a mechanical pressure of 440 MPa. This experiment was performed in order to improve the resolution of the XRPD patterns of the contracted phase. Full profile analysis of this pressure-induced phase was performed with the same Jana 2006 software⁵¹ that was used for indexing the hydrated and dehydrated phases.

2.5. Molecular simulations

2.5.1. DFT structure optimization of MIL-53-FA frameworks. The crystal structure of the dehydrated MIL-53(Ga)-FA was constructed starting from the framework model of the Al form we previously proposed.⁴² This initial structure was further optimized at the DFT level with the Vienna *Ab initio* Simulation Package (VASP).^{52–56} The PBE functional⁵⁷ was used and the van der Waals interactions were taken into account *via* semi-empirical dispersion corrections (DFT-D3 with Becke–Johnson damping).^{58,59} A plane wave energy cut-off of 500 eV is employed together with a Gaussian smearing scheme with a smearing scheme with a corresponding factor of 0.05 eV. The electronic (ionic) energy convergence is set to 10^{-8} eV (10^{-7} eV). A $6 \times 2 \times 2$ *k*-point mesh is used with 6 *k*-points along the direction of the metal-oxide chain. These settings were found to be accurate for the analogue MIL-47(V^{IV}) material by Vanpoucke *et al.*⁶⁰ The MIL-53(Al)-FA was treated similarly in this work. The structures

were optimized by constructing a local energy *versus* volume profile. As such the computational recipe of Vanpoucke *et al.*⁶⁰ was followed for the optimization of these structures with the construction of an equation-of-state (EOS) avoiding strong Pulay effects in flexible materials.⁶⁰ The cell shape and atomic positions at each volume were fully relaxed. Finally, the profiles were fitted with a Vinet EOS^{60,61} (see ESI†). The hessian of the large pore minimum for both materials was calculated with two displacements of 0.01 $\text{\AA}$ for every Cartesian degree of freedom. Afterward, the elastic constant tensor was calculated with the extended hessian approach.⁶⁰ The crystal structure of the hydrated MIL-53(Ga)-FA constructed starting from the framework model of the Al analogue, some of us previously proposed,⁴² was further geometry optimized using the same computational strategy while fixing the cell parameters to that derived experimentally.

2.5.2. DFT energy profile as a function of volume. The *ab initio* energy profile as a function of volume at 0 K was computed for both empty aluminium and gallium fumarate based materials by means of a set of constrained geometry optimizations, in which the unit cell volume was kept fixed but the cell shape as well as the atomic positions are fully relaxed. Starting from the large pore phase, the volume was decreased until a metastable contracted phase was obtained. Subsequently, the structures around the metastable structure were optimized with a denser *k*-point mesh ($6 \times 2 \times 6$) and the Vinet EOS was used to obtain the minimum (see ESI†). The hessian was then calculated together with the elastic constant tensor.

3. Results and discussion

The hydrated form of MIL-53(Ga)-FA was considered initially, and its experimental XRPD pattern (see Fig. 1) was indexed in a monoclinic space group $P2_1/c$, with a unit cell volume of $\sim 1068.0(2) \text{ \AA}^3$, slightly larger than the unit cell of the Al analogue ($990 \text{ \AA}^3$) (see Table 1). A plausible structural model of this hydrated structure was built using DFT calculations at fixed experimental unit cell parameters. This proposed structural model (Fig. S11†) is similar to the Al-analogue with however a more pronounced tilting of the organic linker which suggests a higher degree of flexibility of the Ga phase. Extensive hydrogen bonding interactions are observed between the water oxygens (Ow) and the μ_2 -hydroxyl groups of the framework, and

Table 1 Experimental unit cell parameters of the hydrated, dehydrated and contracted phases of MIL-53(Al)-FA^{37,42} as well as those of the hydrated and dehydrated phases of MIL-53(Ga)-FA

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
MIL-53(Al)-FA					
Hydrated ⁴²	6.842(3)	12.088(3)	14.207(1)	122.55(7)	990.0(1)
Dehydrated ³⁷	7.022(3)	12.154(3)	14.745(5)	127.62(2)	998.0(1)
Contracted ³⁷	6.630	15.120	8.907	123.027	750.0
MIL-53(Ga)-FA					
Hydrated	7.159(1)	12.283(1)	14.461(2)	122.87(1)	1068.0(2)
Dehydrated	6.979(1)	12.458(4)	14.967(4)	128.48(2)	1018.8(6)

between the water protons and carboxylate oxygens (Fig. S12†). The Ow-H(μ_2 -OH) distances are about 1.6 Å, indicating that the adsorbed water forms strong hydrogen bond with the MOF framework. Additionally, the water molecules form a 3D-hydrogen bond network with Ow-Hw distances ranging from 1.75 to 1.87 Å.

Referring to our previous report on the mechanical behaviour of MIL-53(Al)-FA, the water molecules in the pores resist to the external pressure, and hence the solid does not undergo any structural change under applied pressure.³⁷ Since the hydrated MIL-53(Ga)-FA appears as isostructural to MIL-53(Al)-FA (Fig. 1(a) and (b)), mercury porosimetry and high-pressure XRPD experiments were not performed on the hydrated solid.

The dehydrated phase of MIL-53(Ga)-FA was then investigated. A structure-less refinement was successfully carried out for this structural form leading to a proposed unit cell with monoclinic symmetry (S.G. $P2_1/c$) and a volume of 1018.8 Å³ (Fig. 2) slightly higher than the Al analogue (volume of 998.0 Å³). Based on the indexed cell parameters, a structural model was constructed and optimized with DFT by only relaxing the atomic positions. The resulting structural model of the dehydrated MIL-53(Ga)-FA is very close to that obtained earlier for the pristine dehydrated MIL-53(Al)-FA (Fig. 2).³⁷ The dihedral angles for M–Oc–Cc–Cg₂ are similar, *i.e.* 176° and 170.1° for the Al and the Ga phases respectively (see Fig. S8†). The calculated powder pattern generated from the structural model was found to be in fair agreement with the experimental XRPD pattern (see Fig. S13†).

The Hg porosimetry experiments on the dehydrated solid further indicated an increase in intruded volume until 20 MPa, which corresponds to compaction of the sample and intrusion of mercury between the particles (Fig. 3).

A subsequent sharp increase in the intruded volume of Hg was observed above 85 MPa. Referring to our previous work on flexible microporous MOFs,^{36,37,39} this can be ascribed to

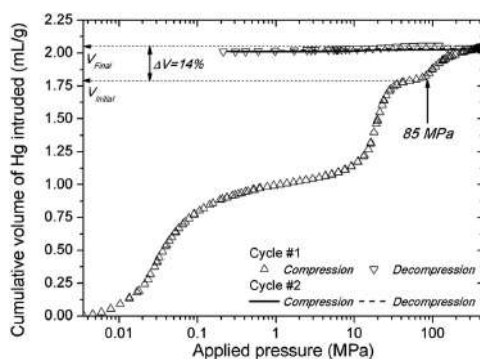


Fig. 3 Cumulative volume of intruded mercury in two intrusion–extrusion cycles as a function of the applied pressure obtained for the activated MIL-53(Ga)-FA solid (V_{initial} and V_{final} are the volumes of mercury intruded before and after the contraction of the solid respectively).

a structural transition (contraction) as Hg cannot penetrate into the micropores in the explored range of pressure. Similar pressure-induced behaviour has been observed for other flexible MOFs such as MIL-53(Cr)-BDC,³⁴ MIL-53(Al)-BDC³⁶ and MIL-47(V)-BDC.³⁹ The lower pressure of transition from the pristine to the contracted form with respect to the value evidenced for the isostructural Al-phase ($P_{\text{trans}} = 110$ MPa) indicates a higher compressibility of the MIL-53(Ga)-FA.

The increase in the volume of intruded Hg measures 0.26 mL g^{−1}. Starting with a unit cell volume of 1018.8 Å³ for the dehydrated MIL-53(Ga)-FA structure, the volume of the contracted structure can be estimated to be ~875 Å³ which remains higher than the volume for the Al contracted phase (750 Å³). In contrast to MIL-53(Al)-FA, the structural transition is irreversible, which is noteworthy. Hence, the solid remains in its contracted pore form even after the pressure is released. Among the MIL-53-BDC frameworks, a similar behaviour has been observed previously in the case of MIL-53(Al)-BDC,³⁶ wherein an irreversible structural transition occurred at a lower pressure of 13–18 MPa. However, under similar conditions, the MIL-53(Cr)-BDC³⁴ analogue exhibits a reversible transition from the large pore form to a contracted pore form at a pressure of 55 MPa. High-pressure XRPD experiments were further performed on the dehydrated MIL-53(Ga)-FA in order to confirm the structural contraction of the structures expected from Hg porosimetry. These measurements reported in Fig. 4 show that as the applied pressure increases, additional Bragg peaks appear which can be assigned to a new phase resulting from the pressure-induced contraction of the structure.

One can notice that a small amount of the contracted phase is still present at the initial stage of the experiment, arising due to a low transition pressure for the structural contraction, coupled with experimental limitations of the high-pressure cell. The low-angle peaks in the patterns recorded up to a pressure of 0.25 GPa correspond to $d = 8.46$ Å ($2\theta = 2.51^\circ$) and $d = 7.82$ Å ($2\theta = 2.74^\circ$) which can be assigned to the pristine and the

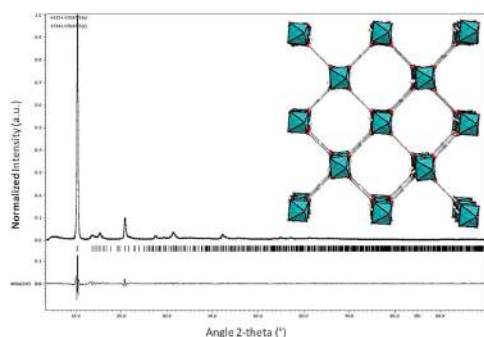


Fig. 2 Structure-independent refinement of the unit cell parameters for the pristine phase of the dehydrated MIL-53(Ga)-FA, space group $P2_1/c$. $a = 6.979(1)$ Å, $b = 12.458(4)$ Å, $c = 14.967(5)$ Å, $\beta = 128.48(2)^\circ$, $V = 1018.8(6)$ Å³. GoF = 3.09, $R_p = 7.9$, $wR_p = 11.21$. Inset: polyhedral representation of the dehydrated MIL-53(Ga)-FA. Ga octahedra: cyan, O: red and C in gray.

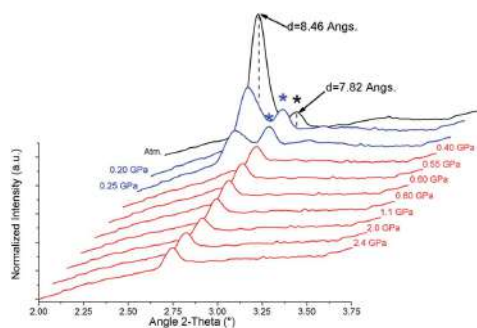


Fig. 4 X-ray powder diffraction patterns of MIL-53(Ga)-FA as a function of the applied pressure ($\lambda = 0.37380$ Å). The values of the applied pressure are in GPa (* indicates the diffraction peaks assigned to the contracted pore form). The low-angle peaks at $2\theta = 2.51^\circ$ ($d = 8.46$ Å) and $2\theta = 2.74^\circ$ ($d = 7.82$ Å) correspond to the initial and contracted pore forms respectively.

contracted phases, respectively. Above 0.55 GPa, the experimental XRPD patterns correspond on the whole to this new phase, with the first peak at $2\theta = 2.74^\circ$ (Fig. 4).

Since Hg porosimetry revealed that the pressure-induced contraction of MIL-53(Ga)-FA is an irreversible process, a way to confirm this was to collect a XRPD pattern on the Ga-fumarate sample pressed in an IR-die (refer to experimental methods). The pattern shows peaks corresponding to the presence of both the initial and the contracted pore forms (Fig. 5), the low-angle peaks at $2\theta = 10.46^\circ$ ($d = 8.46$ Å) and $2\theta = 11.32^\circ$ ($d = 7.82$ Å) corresponding to the same distances found in Fig. 4. This clearly confirms the irreversibility of the structural transition. The poor experimental resolution of the high pressure XRPD patterns precluded an indexing of the contracted pore phase.

Periodic DFT calculations were performed to further unravel the underlying features that are responsible for the different pressure-induced behaviour between the aluminium and gallium fumarate systems. The resulting energy profile as

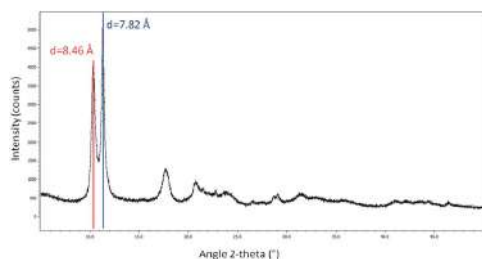


Fig. 5 X-ray powder diffraction pattern ($\lambda = 1.5406$ Å) of dehydrated MIL-53-Ga-FA pressed under a 13 mm IR-die up to a pressure of 440 MPa. The low-angle peaks at $2\theta = 10.46^\circ$ ($d = 8.46$ Å) and $2\theta = 11.32^\circ$ ($d = 7.81$ Å) correspond to the initial dehydrated form and contracted pore form respectively.

a function of volume $E(V)$ is shown for both solids in Fig. 6. The lattice parameters of the minima on the potential energy surface are summarized in Table 2.

The energy profile for both materials clearly illustrates the significant flexible behaviour of both materials. First, we focus our attention to Al-fumarate, for which the energy profile features a stable global minimum at a unit cell volume of 947 Å^3 (corresponding to the large pore or dehydrated phase, see Table 2) as well as a second metastable minimum at a smaller unit cell volume (corresponding to a contracted phase). The latter phase is barely bound as it is separated from the large pore phase by a very small barrier of less than 1 kJ mol^{-1} per unit cell. At finite temperature difference this minimum is expected to disappear due to entropic effects.⁶² To motivate this statement, we computed that, within the normal mode approximation (NMA), the free energy of the contracted phase increases from 15 kJ mol^{-1} per unit cell at 0 K to 24.8 kJ mol^{-1} per unit cell at 300 K with respect to the large pore phase. As this increase of almost 10 kJ mol^{-1} is much larger than the barrier of 1 kJ mol^{-1} per unit cell, we expect the barrier to disappear at 300 K. More details on this NMA analysis can be found in the ESI.†

The Ga-fumarate profile is fundamentally different from the Al-variant, as now two well-defined stable structures are observed, one at a high volume of 1000 Å^3 (corresponding to a large pore or dehydrated phase) and one at a lower volume of 564 Å^3 (corresponding to a (fully) contracted pore phase). The large pore form of Ga is associated with a unit cell volume (1000 Å^3) higher than the value simulated for the Al-analogue (947 Å^3). This prediction is in good agreement with the experimental sequence reported in Table 1. Furthermore, the large pore phase of Ga is 7 kJ mol^{-1} per unit cell more stable than the

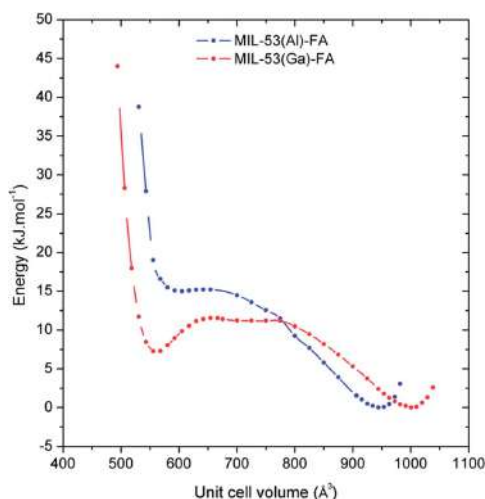


Fig. 6 *Ab initio* energy profile as a function of the unit cell volume for Al- and Ga-fumarate at 0 K computed using constrained geometry optimizations in which only the unit cell volume is kept fixed.

Table 2 Computed unit cell parameters of the large pore or dehydrated and the contracted pore forms of MIL-53(Al)-FA and MIL-53(Ga)-FA

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
MIL-53(Al)-FA							
Dehydrated	6.688	13.437	13.760	90.0	130.0	90.0	947.0
Contracted	6.721	15.052	10.493	90.0	145.3	90.0	605.0
MIL-53(Ga)-FA							
Dehydrated	6.781	13.543	14.091	90.3	129.4	89.9	1000.4
Contracted	6.815	15.605	9.475	97.0	145.7	84.5	563.7

contracted pore phase. Some care should be taken when considering absolute energy values, as they may vary upon using a different dispersion scheme,⁶² although qualitatively the difference between the two materials bearing either aluminium or gallium is very clear. Due to the more strongly bound nature of the contracted phase with a higher barrier of almost 5 kJ mol^{−1} per unit cell, this form can be expected to remain metastable at 300 K. Similarly, as it was done for the Al-fumarate, we computed that the free energy of the contracted phase increases from 7.2 kJ mol^{−1} per unit cell at 0 K to 15.7 kJ mol^{−1} per unit cell at 300 K with respect to the large pore phase. Since this increase of 8.5 kJ mol^{−1} per unit cell is not significantly larger than the barrier at 0 K (5 kJ mol^{−1}), we expect the barrier to remain at 300 K. As such, when pressure is applied and the structure contracts, the Ga-analogue will stay in the contracted phase after releasing the pressure. The presence of a well-defined energy minimum for the contracted phase resembles the experimentally observed trend of irreversible phase transition under applying an external pressure starting from the large pore phase.

An indicator of the higher structural rigidity of the Al-fumarate compared to the Ga-fumarate is the bulk modulus. This mechanical property is 4.1 GPa for Ga-fumarate obtained with a Vinet EOS fit,⁶⁴ while the Al-fumarate has a bulk modulus of 5.0 GPa (see ESI Fig. S6–S9†). This observation is consistent with a higher mechanical pressure required to induce the structural contraction of the Al-fumarate.

A further analysis of the elastic constants revealed that the anisotropy of the elastic properties of the materials under study was one order of magnitude lower than for the Al- and Ga-MIL-53-BDC (see ESI†).^{63,64}

Further qualitative insights into the differences between the two materials may be obtained by deriving a pressure *versus* volume profile from a polynomial fit to the *ab initio* energy profile by taking the negative derivative of it (details of this procedure can be found in the ESI†). The resulting pressure profiles (see Fig. S4†) illustrate that the large pore to contracted phase transition pressure is higher for Al-fumarate than for Ga-fumarate, in line with the Hg-intrusion experiments. By means of the QuickFF procedure,^{65,66} we traced the main source of difference in flexibility to the force constant of the M–O–C–C dihedral connecting the metal M (=Al/Ga) with the fumarate linker. This force constant is 10.4 kJ mol^{−1} for Ga-fumarate and 19.9 kJ mol^{−1} for Al-fumarate.

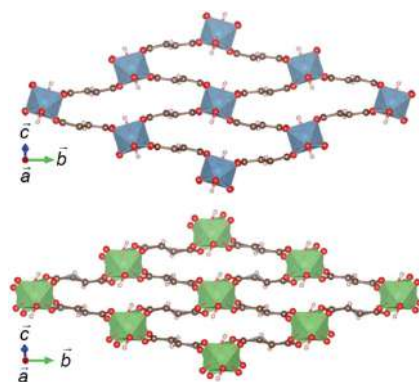


Fig. 7 The DFT-structure models for the contracted pore form of the Al- (up) and Ga- (down) fumarate along the pore channel-direction.

Finally, it can be noticed that the simulated contracted pore phases for Al- and Ga-fumarate slightly differ in unit cell parameters (see Table 2). While the DFT calculations reproduce well the cell dimensions of the large pore phases for both metals and the reversible/irreversible nature of the structural contraction of the Al- and Ga-fumarate respectively, it is noticeable that the contracted phases are predicted to be more closed for both metals than the experimental findings, the deviation being more pronounced for the Ga-material. The corresponding optimized crystal structures of the Al and Ga contracted phases are shown in Fig. 7. While the contraction of the Al-fumarate is partly mediated by a decrease in the C–C–C dihedral angle, in the Ga-fumarate it is entirely driven by the change of the Ga–O–C–C dihedral angle (see Table S8 in ESI†).

4. Conclusions

In summary, the synthesis and characterization of MIL-53(Ga)-FA, the Ga analogue of the commercially available Al fumarate or MIL-53(Al)-FA porous MOF, has been for the first time carried out. The mechanical behaviour of the dehydrated MIL-53(Ga)-FA has been investigated using a combination of Hg porosimetry, high-pressure XRPD experiments and DFT calculations. These studies indicated that the structural transition from the initial to the contracted phase in this solid is irreversible, which is in contrast with what has been observed previously for MIL-53(Al)-FA. These experimental trends were further rationalized by constructing *E* (*V*) curves at 0 K. For the Ga-fumarate material two well-defined minima were present whereas for the aluminium version only a very shallow contracted phase minimum was obtained. At finite temperatures, it may thus be expected that the Ga-fumarate material undergoes an irreversible transition. Although experimental and computational methods did not lead to a consistent conclusion regarding the degree to which the material contracted, the experimental trends regarding (i) the higher pressure required to induce the contraction of phase for the Al-material owing to its higher

degree of rigidity and (ii) the reversibility/irreversibility of the pressure-induced transition were reproduced by the simulations. When considering mechanical-energy related applications, the irreversible structural contraction upon applied pressure reveals that MIL-53(Ga)-FA could be used in shock absorber applications, similar to that envisaged for MIL-53(Al)-BDC, and complementary to the application previously envisioned for MIL-53(Al)-FA, MIL-53(Cr)-BDC and MIL-47(V^{IV}) as nano-dampers. The results obtained indicate that MIL-53(Ga)-FA and related solids have potential for various real-world mechanical energy-related applications.

Acknowledgements

The authors would like to thank the French National Agency for Research ANR "MODS" (ANR-12-BS10-0005) for its financial support. We acknowledge the French national synchrotron radiation source "Synchrotron Soleil" (Saint-Aubin, France) for providing access to the PSICHE beam-line. VVS, JW and LV acknowledge the Research Board of Ghent University (BOF), the Fund for Scientific Research Flanders (FWO), BELSPO in the frame of IAP/7/05 and the European Union's Horizon 2020 research and innovation program (consolidator ERC grant agreement No. 647755 – DYNPOR (2015–2020)). The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by the Hercules foundation and the Flemish Government – department EWI. G. M. thanks Institut Universitaire de France for its support.

Notes and references

- 1 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674, and references therein.
- 2 H.-C. Zhou and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415–5418, and references therein.
- 3 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
- 4 L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
- 5 R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650.
- 6 Q. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. Zhong, C. Serre, G. De Weireld and G. Maurin, *Angew. Chem., Int. Ed.*, 2013, **52**, 10316.
- 7 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
- 8 J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, 2011, **4**, 3030.
- 9 S. Vaesen, V. Guillermin, Q. Yang, A. D. Wiersum, B. Marszalek, B. Gil, A. Vimont, M. Daturi, T. Devic, P. L. Llewellyn, C. Serre, G. Maurin and G. De Weireld, *Chem. Commun.*, 2013, **49**, 10082.
- 10 B. Van de Voorde, D. Damasceno Borges, F. Vermoortele, R. Wouters, B. Bozbiyik, J. Denayer, F. Taulelle, C. Martineau, C. Serre, G. Maurin and D. De Vos, *ChemSusChem*, 2015, **8**, 3159.
- 11 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- 12 A. Cadiau, J. S. Lee, D. Damasceno Borges, P. Fabry, T. Devic, M. T. Wharmby, C. Martineau, D. Foucher, F. Taulelle, C.-H. Jun, Y. K. Hwang, N. Stock, M. F. De Lange, F. Kapteijn, J. Gascon, G. Maurin, J.-S. Chang and C. Serre, *Adv. Mater.*, 2015, **27**, 4775.
- 13 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.
- 14 C. Orellana-Tavra, E. F. Baxter, T. Tian, T. D. Bennett, N. K. H. Slater, A. K. Cheetham and D. Fairen-Jimenez, *Chem. Commun.*, 2015, **51**, 13878.
- 15 T. Kajiura, M. Higuchi, A. Yuasa, H. Higashimura and S. Kitagawa, *Chem. Commun.*, 2013, **49**, 10459.
- 16 D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 17105.
- 17 F. Vermoortele, M. Vandichel, B. Van de Voorde, R. Ameloot, M. Waroquier, V. Van Speybroeck and D. E. De Vos, *Angew. Chem., Int. Ed.*, 2012, **51**, 4887.
- 18 F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock and D. E. De Vos, *J. Am. Chem. Soc.*, 2013, **135**, 11465.
- 19 L. Ma, O. R. Evans, B. M. Foxman and W. Lin, *Inorg. Chem.*, 1999, **38**, 5837.
- 20 M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330.
- 21 M. Wriedt, A. A. Yakovenko, G. J. Halder, A. V. Prosvirin, K. R. Dunbar and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 4040.
- 22 M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.
- 23 D. Damasceno Borges, S. Devautour-Vinot, H. Jobic, J. Ollivier, F. Nouar, R. Semino, T. Devic, C. Serre, F. Paesani and G. Maurin, *Angew. Chem., Int. Ed.*, 2016, **55**, 3919.
- 24 P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913.
- 25 A. Clearfield, *Dalton Trans.*, 2016, **45**, 4100.
- 26 K. W. Chapman, G. J. Halder and P. J. Chupas, *J. Am. Chem. Soc.*, 2008, **130**, 10524.
- 27 S. A. Moggach, T. D. Bennett and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2009, **48**, 7087.
- 28 J.-C. Tan, T. D. Bennett and A. K. Cheetham, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 9938.
- 29 T. D. Bennett, J.-C. Tan, S. A. Moggach, R. Galvelis, C. Mellot-Draznicks, B. A. Reisner, A. Thirumugan, D. R. Allan and A. K. Cheetham, *Chem.-Eur. J.*, 2010, **16**, 10684.
- 30 P. Serra-Crespo, A. Dikhtiarenko, E. Stavitski, J. Juan-Alcaniz, F. Kapteijn, F.-X. Coudert and J. Gascon, *CrystEngComm*, 2015, **17**, 276.
- 31 Y. H. Hu and L. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 174103.
- 32 S. M. J. Rogge, J. Wieme, L. Vanduyfhuys, S. Vandenbrande, G. Maurin, T. Verstraelen, M. Waroquier and V. Van Speybroeck, *Chem. Mater.*, 2016, **28**, 5721.

- 33 T. D. Bennett, P. Simoncic, S. A. Moggach, F. Gozzo, P. Macchi, D. A. Keen, J.-C. Tan and A. K. Cheetham, *Chem. Commun.*, 2011, **47**, 7983.
- 34 I. Beurroies, M. Boulhout, P. L. Llewellyn, B. Kuchta, G. Férey, C. Serre and R. Denoyel, *Angew. Chem., Int. Ed.*, 2010, **49**, 7526.
- 35 Q. Ma, Q. Yang, A. Ghoufi, K. Yang, M. Lei, G. Férey, C. Zhong and G. Maurin, *J. Mater. Chem. A*, 2014, **2**, 9691.
- 36 P. G. Yot, Z. Boudene, J. Macia, D. Granier, L. Vanduyfhuys, T. Verstraelen, V. Van Speybroeck, T. Devic, C. Serre, G. Férey, N. Stock and G. Maurin, *Chem. Commun.*, 2014, **50**, 9462.
- 37 P. G. Yot, L. Vanduyfhuys, E. Alvarez, J. Rodriguez, J.-P. Itié, P. Fabry, N. Guillou, T. Devic, I. Beurroies, P. L. Llewellyn, V. Van Speybroeck, C. Serre and G. Maurin, *Chem. Sci.*, 2016, **7**, 446.
- 38 P. G. Yot, K. Yang, V. Guillermin, F. Ragon, V. Dmitriev, P. Parisiades, E. Elkaïm, T. Devic, P. Horcajada, C. Serre, N. Stock, J. P. S. Mowat, P. A. Wright, G. Férey and G. Maurin, *Eur. J. Inorg. Chem.*, 2016, **27**, 4424.
- 39 P. G. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghoufi, T. Devic, C. Serre, V. Dmitriev, G. Férey, C. Zhong and G. Maurin, *Chem. Sci.*, 2012, **3**, 1100.
- 40 C. L. Hobday, R. J. Marshall, C. F. Murphie, J. Sotelo, T. Richards, D. R. Allan, T. Düren, F.-X. Coudert, R. S. Forgan, C. A. Morrison, S. A. Moggach and T. D. Bennett, *Angew. Chem., Int. Ed.*, 2016, **55**, 2401.
- 41 P. G. Yot, K. Yang, F. Ragon, V. Dmitriev, T. Devic, P. Horcajada, C. Serre and G. Maurin, *Dalton Trans.*, 2016, **45**, 4283.
- 42 E. Alvarez, N. Guillou, C. Martineau, B. Bueken, B. van de Voorde, C. le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. Ho Cho, N. Ramsahye, T. Devic, M. Daturi, G. Maurin and C. Serre, *Angew. Chem., Int. Ed.*, 2015, **54**, 3664.
- 43 F. Jeremias, D. Fröhlich, C. Janiak and S. K. Henninger, *RSC Adv.*, 2014, **4**, 24073.
- 44 C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519.
- 45 A. S. Munn, A. J. Ramirez-Cuesta, F. Millange and R. I. Walton, *Chem. Phys.*, 2013, **427**, 30.
- 46 A. Boutin, M.-A. Springuel-Huet, A. Nossor, A. Gedeon, T. Loiseau, C. Volkringer, G. Férey, F.-X. Coudert and A. H. Fuchs, *Angew. Chem., Int. Ed.*, 2009, **48**, 8314.
- 47 A. Boutin, F.-X. Coudert, M.-A. Springuel-Huet, A. V. Neimark, G. Férey and A. H. Fuchs, *J. Phys. Chem. C*, 2010, **114**, 22237.
- 48 G. Weber, I. Bezverkhy, J.-P. Bellat, A. Ballandras, G. Ortiz, G. Chaplais, J. Patarin, F.-X. Coudert, A. H. Fuchs and A. Boutin, *Microporous Mesoporous Mater.*, 2016, **222**, 145.
- 49 R. S. Pillai, V. Benoit, A. Orsi, P. L. Llewellyn, P. A. Wright and G. Maurin, *J. Phys. Chem. C*, 2015, **119**, 23592.
- 50 A. S. Munn, R. S. Pillai, S. Biswas, N. Stock, G. Maurin and R. I. Walton, *Dalton Trans.*, 2016, **45**, 4162.
- 51 V. Petricek, M. Dusek and L. Palatinus, *Z. Kristallogr.*, 2014, **229**, 345.
- 52 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558.
- 53 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 14251.
- 54 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 55 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
- 56 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 57 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 58 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 59 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **132**, 1456.
- 60 D. E. P. Vanpoucke, K. Lejaeghere, V. Van Speybroeck, M. Waroquier and A. Ghysels, *J. Phys. Chem. C*, 2015, **119**, 23752.
- 61 P. Vinet, J. Ferrante, J. H. Rose and J. R. Smith, *J. Geophys. Res.*, 1987, **92**, 9319.
- 62 A. M. Walker, B. Civalieri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Román-Peréz, J. M. Soler and J. D. Gale, *Angew. Chem., Int. Ed.*, 2010, **49**, 7501.
- 63 A. U. Ortiz, A. Boutin, A. H. Fuchs and F.-X. Coudert, *Phys. Rev. Lett.*, 2012, **109**, 195502.
- 64 A. U. Ortiz, A. Boutin, A. H. Fuchs and F.-X. Coudert, *J. Chem. Phys.*, 2013, **138**, 174703.
- 65 L. Vanduyfhuys, S. Vandenbrande, T. Verstraelen, R. Schmid, M. Waroquier and V. Van Speybroeck, *J. Comput. Chem.*, 2015, **36**, 1015.
- 66 J. Wieme, L. Vanduyfhuys, S. M. J. Rogge, M. Waroquier and V. Van Speybroeck, *J. Phys. Chem. C*, 2016, **120**, 14934.

Paper III

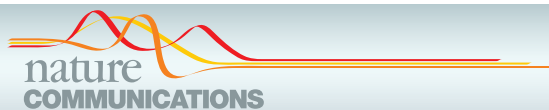
**Thermodynamic insight into stimuli–responsive
behaviour of soft porous crystals**

L. Vanduyfhuys, S.M.J. Rogge, J. Wieme, S. Vandenbrande,
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Nature Communications, **2018**, 9, 204

J. Wieme performed the DFT simulations and had a large contribution in the interpretation of the results as well as the preparation of the manuscript.

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DOI: 10.1038/s41467-017-02666-y

OPEN

Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals

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Knowledge of the thermodynamic potential in terms of the independent variables allows to characterize the macroscopic state of the system. However, in practice, it is difficult to access this potential experimentally due to irreversible transitions that occur between equilibrium states. A showcase example of sudden transitions between (meta)stable equilibrium states is observed for soft porous crystals possessing a network with long-range structural order, which can transform between various states upon external stimuli such as pressure, temperature and guest adsorption. Such phase transformations are typically characterized by large volume changes and may be followed experimentally by monitoring the volume change in terms of certain external triggers. Herein, we present a generalized thermodynamic approach to construct the underlying Helmholtz free energy as a function of the state variables that governs the observed behaviour based on microscopic simulations. This concept allows a unique identification of the conditions under which a material becomes flexible.

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NATURE COMMUNICATIONS | DOI: 10.1038/s41467-017-02666-y

At first, it might seem rather counterintuitive to connect flexibility and crystallinity. A crystalline phase is typically associated with a high degree of order and close packing of its components, which seemingly conflicts with softness or flexibility. However, new generations of materials have been discovered that, unlike most conventional inorganic crystals, possess a highly ordered network but are also able to structurally transform while retaining the same or similar topologies^{1–3}. Kitagawa and colleagues¹ coined the term ‘soft porous crystals’ (SPCs) for such materials, which show a bistable or multistable behaviour with long-range structural order. Since then, an enormous endeavour has been undertaken to understand this experimentally observed phenomenon^{4,5}. Prominent examples of such SPCs are flexible metal-organic frameworks (MOFs), built up from inorganic nodes or chains connected with organic linkers, which have the ability to undergo drastic changes in the unit cell volume upon external stimuli (Fig. 1)³. Initially, it was thought that framework flexibility could only be induced by adsorbing or desorbing guest molecules; however, various materials have been discovered that show stimuli-responsive behaviour under the influence of external triggers such as mechanical pressure, temperature, electric fields and light^{3,6}. The term ‘flexibility’ is a rather generic term and may imply different forms of structural changes such as ligand flipping, pore gating, breathing, etc. In this work, it will be used to refer to materials with the ability to undergo phase transformations accompanied by a substantial change in unit cell volume and for which the crystallographic space group of the different phases may change (schematically shown in Fig. 1)³. Frameworks exhibiting this type of flexibility have often been categorized as breathing materials. For more elaborate discussions on the terminology we refer to the review of Schneemann et al.³. The prototype flexible frameworks are the so-called MIL-53 materials (MIL = Matériaux de l’Institut Lavoisier) exhibiting a wine-rack topology

and capable of undergoing volume changes up to 40% upon exposure to external stimuli⁷. The observed macroscopic flexibility has been found to be critically dependent on the detailed composition of the framework and the building units making up the framework (Fig. 1)^{3,4}.

Experimentally, framework flexibility can be followed by monitoring the response of the material to the external stimulus (schematically shown in Fig. 2) with techniques such as mercury-intrusion porosimetry⁸, high-pressure X-ray diffraction⁹, differential scanning calorimetry¹⁰ or spectroscopic techniques¹¹. These approaches have been applied to a diverse set of soft porous materials and the observation of a sudden volume change at a given value of the external trigger uniquely identifies framework flexibility. Although the experimental profiles allow one to recognize the stimuli-responsive behaviour, they do not allow one to construct the underlying thermodynamic potential governing the observed behaviour. Indeed, during the breathing phenomenon, the material undergoes one or more irreversible structural transitions between (meta)stable equilibrium states, which are separated by a region of volume states, which are not equilibrated with the applied experimental conditions. These states are only visited during irreversible transitions and hence one cannot extract their equilibrium thermodynamic potential from experiment using basic equilibrium thermodynamics.

Yet, knowledge of the full thermodynamic potential in terms of the independent variables of the system is the key ingredient to understand the macroscopic conditions governing breathing. Within thermodynamics, a thermodynamic potential is defined as a function of certain variables characterizing the state of the system, having the property of being in a maximum or a minimum when the system is in equilibrium. Various thermodynamic potentials may be used such as the internal energy, the Helmholtz free energy and the Gibbs free energy. For systems characterized by the temperature, volume and number of particles as state

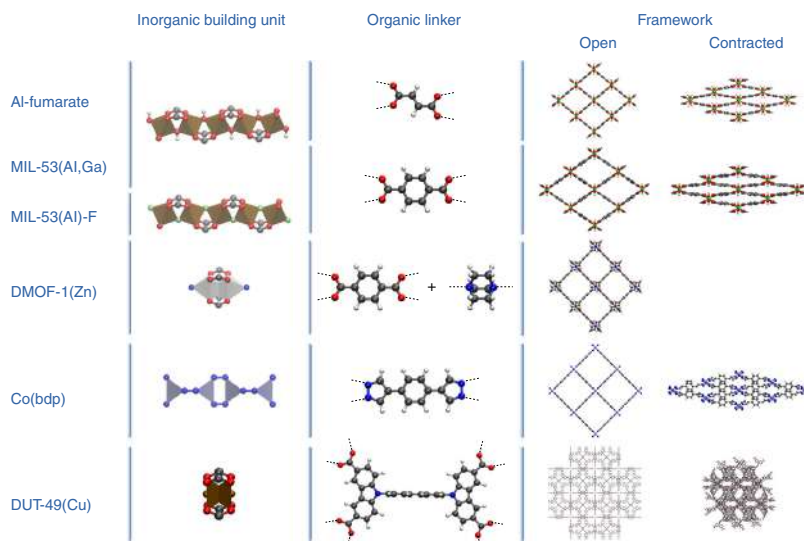


Fig. 1 Illustration of some metal-organic frameworks which show potential stimuli-responsive behaviour. All shown materials are MOFs built from a 0D or 1D inorganic moieties connected by organic linkers

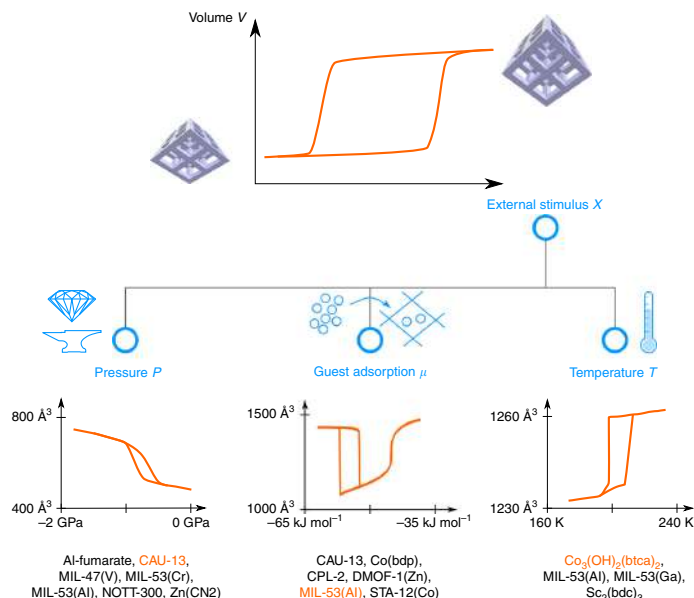


Fig. 2 Illustration of volume profiles for three types of external stimuli. The stimuli are mechanical pressure, chemical potential and temperature. Examples of soft porous materials for which such profiles have been determined are indicated in the bottom of the figure (Al-Fumarate¹⁷, CAU-13⁴⁸, MIL-47(V)¹⁸, MIL-53(Cr)⁴⁹, NOTT-300⁴⁸, Zn(CN)₂⁵⁰, Co(bdp)³⁵, CPL-2⁵¹, DMOF-1(Zn)³⁶, MIL-53(Al)^{12, 19, 52}, STA-12(Co)⁵³, Co₃(OH)₂(btca)₂⁵⁴, MIL-53(Ga)²⁶ and Sc₂(bdc)₃⁵⁵). The shown profiles correspond, from left to right, to CAU-13, MIL-53(Al) and Co₃(OH)₂(btca)₂. For each material, the chemical formula and building blocks are given in Supplementary Table 1

variables, the Helmholtz free energy is introduced as follows:

$$dF = -SdT - PdV + \sum_i \mu_i dN_i \quad (1)$$

However, one can transform one thermodynamic potential to another by means of a Legendre transformation¹².

Herein we present a microscopic approach based on classical molecular dynamics simulations to construct the Helmholtz free energy and to uniquely determine the macroscopic response of a material upon stimuli such as mechanical pressure, temperature and adsorbed guest molecules. The systematic thermodynamic approach allows for the identification of the macroscopic conditions under which a material is expected to undergo a structural transition. Some materials show rigidity in a certain window of state variables, while possessing intrinsic bistable or multistable behaviour characterized by a thermodynamic potential bearing one or more minima in terms of volume. Such materials may become flexible under another set of conditions. The approach is generic and may be applied directly to any SPC exhibiting long-range order. Materials for which the phase transition is accompanied by a loss of long-range order, such as amorphous MOFs¹³, cannot be straightforwardly simulated as the present approach relies on periodic boundary conditions. Effects such as amorphization under elevated pressures may however be detected both experimentally and theoretically by a broadening of the peaks in the radial distribution function¹⁴.

Results

Structural transitions induced by mechanical pressure. From a thermodynamic point of view two cases need to be distinguished: (i) structural transitions induced by a mechanical pressure P and (ii) structural transitions induced by another trigger $X \neq P$ ^{15, 16}. The thermodynamic approach is introduced for the case where structural transitions are induced by application of a mechanical pressure under fixed conditions of number of particles and temperature. As the volume is the conjugate variable of the pressure, this is thermodynamically the simplest case. In general, the experimental response of a material under a positive mechanical pressure can yield three profiles, as illustrated in Fig. 3^{17–21}. Negative pressures would correspond to pulling the crystal framework isotropically. Such conditions might become accessible experimentally by embedding the materials in a membrane; however we are not aware of the development of such a setup to test the material's behaviour at hand. In the first case (Type I in Fig. 3), the volume-versus-pressure profile shows no hysteresis and only a gradual decrease of the volume without structural transition is observed upon increasing pressure. The thermodynamic cycle is reversible upon exerting an external pressure and releasing it afterwards. The material behaves as an ideal spring, where both the material and the environment return to their initial state after the closed pressure cycle. Most conventional solids belong to this category in the elastic regime. In the second case (Type II in Fig. 3), the material suddenly switches towards a contracted pore phase but never returns to the original open pore phase even when releasing the pressure. The third case

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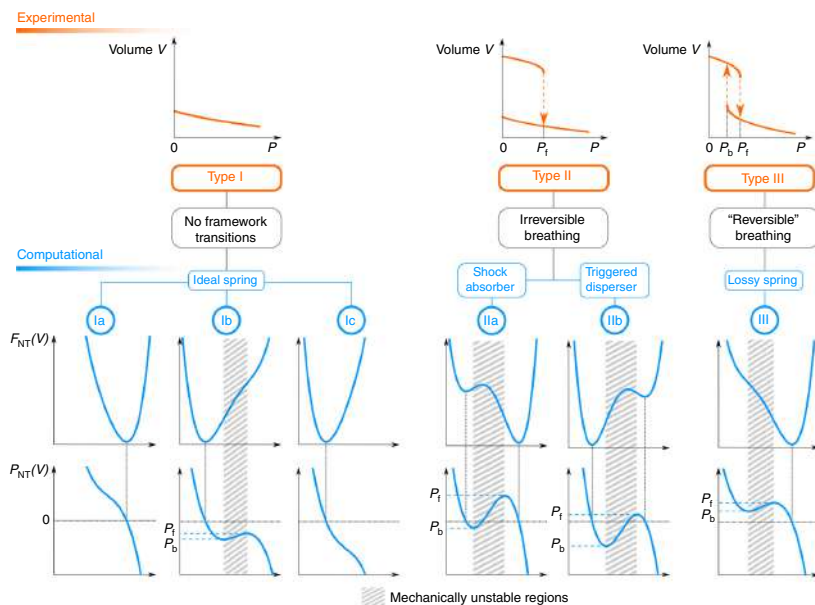


Fig. 3 Comparison of experimental response with corresponding hypothetical free energy. Top panel: illustration of the possible experimental responses of a material upon exerting a positive mechanical pressure^{17–21}. Bottom panel: hypothetical Helmholtz free energy $F_{NT}(V)$ and mechanical equation of state $P_{NT}(V)$, with N the number of particles and T the temperature, in terms of the volume. Shaded areas correspond to mechanically unstable regions

(Type III in Fig. 3) corresponds to a back-and-forth transition from one phase to another when increasing or releasing the pressure. In this case hysteresis is observed in the volume-versus-pressure profile. Although the sketched experimental $V(P)$ profiles unequivocally define the material's response to external pressure, they do not allow one to uniquely assess the underlying thermodynamic potential.

The same volume-versus-pressure profile may result from fundamentally different thermodynamic potentials, as it will be illustrated hereafter. For systems where only the PV work is relevant, i.e., isotropic or anisotropic systems exposed to a hydrostatic pressure, the state of the system is uniquely defined by the Helmholtz free energy F_{NT} as a function of the number of particles N , volume V and the temperature T . As the hydrostatic pressure is the negative volume derivative of the Helmholtz free energy, one can obtain the thermodynamic potential F_{NT} relative to some reference point using thermodynamic integration:

$$F_{NT}(V) - F_{NT}(V_{ref}) = \int_{V_{ref}}^V \frac{\partial F_{NT}(V')}{\partial V'} dV' = - \int_{V_{ref}}^V \langle P_{NT}(V') \rangle dV' \quad (2)$$

where P is the instantaneous hydrostatic pressure²². The latter quantity may be obtained from atomistic molecular dynamics simulations where the volume is constrained but the cell shape is allowed to fluctuate as explained in the Methods section. This procedure yields the mechanical equation of state $P_{NT}(V)$, for which six distinct profiles can be distinguished, as displayed in the bottom pane of Fig. 3. Via thermodynamic integration each subtype of $P_{NT}(V)$ results in a specific shape of the free energy

$F_{NT}(V)$. In all plots the shaded areas correspond to mechanically unstable regions, where $\frac{\partial P}{\partial V} > 0$ or, equivalently, with regions having a negative bulk modulus, which are not accessible experimentally. A given experimental response may originate from fundamentally different free energy curves, as schematically shown in Fig. 3. To properly understand the possible applications of the material under a given set of experimental conditions, it is crucial to distinguish between the various free energy profiles. For example, materials bearing a Type II behaviour may either be used as a shock absorber or a triggered disperser. We will now illustrate the approach to a series of MOFs, to predict their flexibility characteristics. For all materials, we constructed the thermodynamic potential from molecular dynamics simulations using in-house developed force fields (Methods section). The mechanical equations of state and the free energy profiles are shown in Fig. 4a.

UiO-66 and MIL-53(Ga) materials both behave as an ideal spring and show a volume-versus-pressure response of the Type I. UiO-66 is the prototype example of a very stable MOF under various conditions and is characterized by a Helmholtz free energy profile belonging to the Type Ia, as it has one stable minimum and no inflection points (see Supplementary Fig. 1)^{14,23–25}. Experimentally, the material shows a loss of crystallinity only at a hydrostatic pressure of about 1.4 GPa and the material is characterized by a high bulk modulus of about 17 GPa²⁰. MIL-53 (Ga) on the contrary belongs to the well-known MIL-53 series featuring a typical wine-rack framework which is a characteristic for many flexible materials^{21,26}. Structural transitions between an open pore and a contracted pore phase were observed under influence of temperature or guest adsorption, but the pressure response is to date unknown. A full tensorial analysis of the elastic

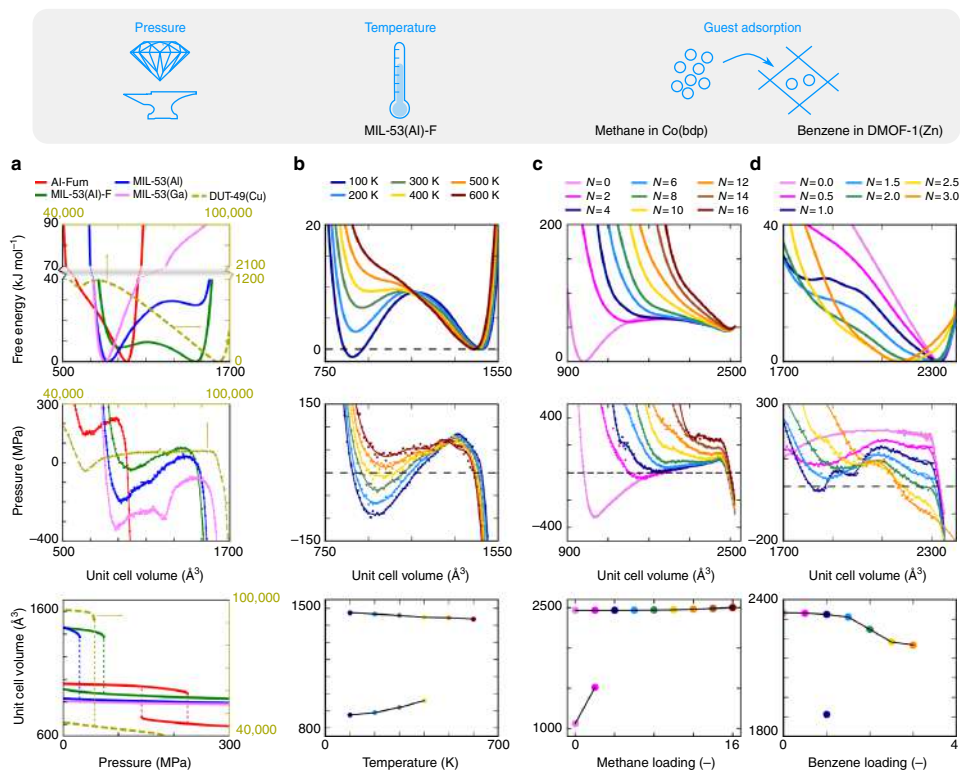


Fig. 4 Illustration of the mechanical equations of state for a variety of materials. Upper row: free energy profile; middle row: mechanical equations of state; bottom row: volume versus external trigger. **a** Free energies, mechanical equations of state $P_{HT}(V)$ and $V(P)$ profiles for Al-Fum, MIL-53(Al), MIL-53(Al)-F, MIL-53(Ga) and DUT-49(Cu) (DUT-49(Cu) axis are shown in olive green). **b** Free energies, mechanical equations of state $P_N(V;T)$ and $V(T)$ profiles for MIL-53(Al)-F. **c,d** Free energies, mechanical equations of state $P_T(V;N)$ and $V(N)$ profiles for methane@Co(bdp) and benzene@DMOF-1(Zn)

constants was performed by Ortiz et al.²⁷ They found a strong anisotropic behaviour of the Young modulus in various directions, which is an indicator for potential flexible behaviour. While such analysis of the anisotropy points towards potential bistable behaviour of a material, it does not reveal the conditions under which the material breathes²⁸. The thermodynamic potential—belonging to Type Ib—shows various inflection points, which is necessary for flexible behaviour. However, as the Helmholtz free energy reveals no stable minimum for the open pore phase, the material is predicted to remain in its contracted pore phase upon exerting positive pressure and releasing it back.

The functionality of the MIL-53 type of materials may be modulated by changing the linkers and/or metals. The MIL-53 (Al) and the MIL-53(Al)-F are both isorectical to the MIL-53 (Ga) but belong to the Type II class upon response to a positive mechanical pressure^{19,29}. MIL-53(Al) and MIL-53(Al)-F are both constructed with aluminum in the inorganic chains, but MIL-53 (Al) contains OH^- compensating anions, whereas MIL-53(Al)-F has F^- charge-compensating anions in the inorganic chains (Fig. 1)²⁹. These two materials are predicted to show an irreversible pressure-induced breathing. When increasing the pressure, the material, which is originally in its open pore phase,

will irreversibly transform to a contracted pore phase at a pressure P_f . When decreasing the pressure back to zero, the material relaxes reversibly to its contracted pore phase, but never returns to the open pore phase. According to the applied force fields, the Helmholtz free energy profiles are fundamentally different in both cases. For MIL-53(Al), the open pore phase is a metastable state (Type IIb) and the material behaves as a triggered disperser. During a compression/decompression cycle, the material releases part of its energy as heat to the environment, effectively increasing the entropy of the environment and as such also the universe. The pressure-induced open pore phase to contracted pore phase transition was experimentally observed at pressures of 13–18 MPa^{19,22}. The material also shows a large anisotropy of the Young modulus, which is a necessary criterion for breathing²⁷. Similar pressure-induced flexibility is predicted from our model for the Co(bdp) material, not belonging to the MIL-53 series³⁰. Current experimental procedures only allowed to synthesize a fully desolvated structure in the contracted pore phase, whereas our model predicts the existence of a large and contracted empty pore phase, which is only slightly less stable (45 kJ mol^{-1} at 300 K). This material might be interesting for further testing in a compression/decompression cycle. In contrast, MIL-

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53(Al)-F shows a free energy profile of Type IIa and behaves as a shock absorber and is potentially interesting for energy storage applications. Starting from the open pore phase and applying an external pressure, the material will also irreversibly contract towards the contracted pore phase, but in this particular case the material will absorb work resulting in an increase of the free energy ($\Delta F_{\text{MOF}} > 0$). According to the first and second law of thermodynamics, the total work performed on the MOF equals $W_{\text{MOF}} = \Delta F_{\text{MOF}} + T\Delta S_{\text{universe}} > \Delta F_{\text{MOF}}$ and it is larger than the change in free energy of the MOF, since the entropy of the universe will rise during an irreversible process. The ΔF_{MOF} is a lower bound for the work required to induce the open pore phase to the contracted pore phase transition. To maximize the stored mechanical energy, the MOF should preferentially exhibit a large volume difference between the two (meta)stable states and a high transition pressure. DUT-49(Cu) is another example of a potential shock absorber (Fig. 4a)³¹. According to our simulations, DUT-49(Cu) is predicted to have the ability to store more mechanical energy as MIL-53(Al)-F (57.8 J g⁻¹ vs 7.9 J g⁻¹). This might seem contradictory, as the transition pressure of DUT-49 (Cu) is lower; however, as explained in Supplementary Note 3, the larger volume variation (per gram material) is the main cause for the higher amount of absorbed mechanical energy.

As an example of a Type III material, we discuss the Aluminum fumarate MOF (Al-fumarate), which shows highly flexible behaviour. The material is isoreticular to the MIL-53(Al) but contains aliphatic fumarate linkers instead of the aromatic benzenedicarboxylate linkers (Fig. 1)^{17,32}. Our thermodynamic model predicts that, during a compression/decompression cycle, the material switches to its contracted pore phase once the pressure P_t is reached and returns to its open pore phase when releasing the pressures to values lower than P_b . This is fully consistent with the recent experimental observation which revealed that the reversible contraction of this material to the contracted pore phase occurs at a high transition pressure of about 120 MPa and returns back to the open pore phase upon releasing the pressure below 20 MPa¹⁷. The amount of mechanical energy that could be stored in one compression–decompression cycle was unprecedentedly high at that time with values estimated to be of the order of 40–60 J g⁻¹¹⁷. Within the class of porous solids, this material has large potential to be used as nano-dampener or lossy spring.

Structural transitions induced by a trigger $X \neq P$. The strength of our thermodynamic approach lies in the fact that it may also predict the response of the material upon other stimuli such as the temperature or the chemical potential, which are not conjugate variables of the volume. To investigate transitions induced by such an external trigger X , a series of pressure versus volume profiles $P_Y(V;X)$ for various values of the external trigger X need

to be constructed while the other state variables Y are kept constant (Fig. 5a). The principle is conceptually illustrated in Fig. 5. The volume response of the material upon the external stimulus X is obtained by determining for each X value of the volume V for which $P(V;X) = P_0$ and $\frac{\partial P}{\partial V} < 0$ from its mechanical equation of state. This is done by intersecting the mechanical equations of state at a given pressure $P = P_0$ (usually the atmospheric pressure), from which the $V(X)$ profiles are obtained (Fig. 5c). This $V(X)$ profile contains all information to deduce whether a material is expected to undergo a structural transformation under the influence of the external trigger X .

There are ample cases available for which breathing transitions were observed experimentally under influence of temperature and/or guest adsorption. For a selected set of materials, we constructed the mechanical equations of state in terms of various temperatures and/or guest loadings. The results are shown in panels b, c and d of Fig. 4. The thermo-responsive behaviour is illustrated for MIL-53(Al)-F in Fig. 4b. Experimentally, no temperature-induced transition to the contracted pore phase was observed, only a phase transition from an orthorhombic open pore phase to a monoclinic open pore phase at 175 K²⁹. A series of molecular dynamics simulations in the temperature window 100–600 K were performed to generate the $V(T)$ profile. Our thermodynamic approach reveals that the material exhibits two (meta)stable structures at temperatures below 400 K, whereas only one stable structure is found above 500 K. A transition to the contracted pore phase is predicted to be only possible if the open pore phase minimum in the free energy profile would disappear, according to the assumption of collective behaviour³³. Our model predicts that when starting from the contracted pore phase at low temperatures, a structural transition to an open pore phase would take place between 400 and 500 K. This experiment was not performed so far. Nanthamathee et al.²⁹ determined the volumetric thermal expansion coefficient $\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ in the temperature range 175–500 K, which was found to be negative for MIL-53(Al)-F in contrast to its -OH analogue. The $V(T)$ profile allows to directly deduce the thermal expansion coefficient in both the contracted and open pore phases. A negative coefficient is indeed found in the open pore phase, whereas the lower branch corresponding to the contracted pore phase is characterized by a positive thermal expansion coefficient. In fact, the volumetric thermal expansion coefficient α_V is a local descriptor of framework distortions but gives by itself no conclusive outcome on the potential phase transformations of the material in a given temperature window.

Guest-induced phase transformations are illustrated for xenon adsorption in MIL-53(Al) (Supplementary Fig. 2), methane adsorption in Co(bdp) (Fig. 4c) and benzene adsorption in DMOF-1(Zn) (Fig. 4d). We investigated the response of all these materials upon guest loading by constructing a series of $P_T(V; N)$

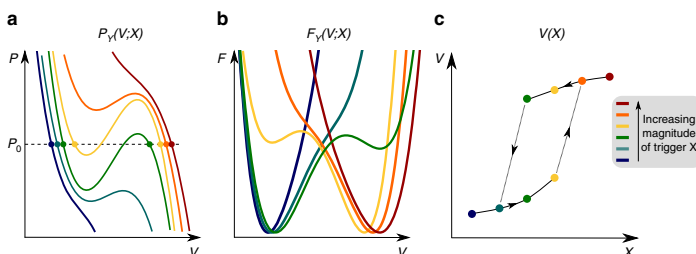


Fig. 5 Illustration of the structural transitions induced by a general state variable X . **a** Mechanical equation of state **b** free energy and **c** the response $V(X)$

mechanical equations of state for a fixed temperature but with a varying number of particles (see Methods section). Experimentally, one controls the chemical potential; however, computationally, it is easier to perform molecular dynamics simulations by controlling the number of particles. The obtained $P_T(V; N)$ profile can easily be transformed to a $P_T(V; \mu)$ equation of state by means of a Legendre transformation of the corresponding Helmholtz free energy to the grand canonical potential¹². By localizing the stable points at the intersection of the pressure profiles with a fixed mechanical pressure of 1 bar, the $V(N)$ response curve upon guest loading are constructed (Fig. 4c for methane@Co(bdp) and Supplementary Fig. 2 for xenon@MIL-53(Al)). For xenon adsorption in MIL-53(Al), our model predicts that the material undergoes a phase transition to an intermediate phase with a volume in between the contracted pore and open pore phases, when initially starting from the open pore phase, for a loading of one xenon particle per unit cell. Upon higher loading the volume gradually increases. These results agree well with the experiments of Boutin et al.³⁴, which evidenced breathing transitions in the measured xenon adsorption isotherms for MIL-53(Al) in the temperature range 195–323 K and earlier simulations based on a mean-field model^{12, 34}. For Co(bdp) we predict a transition from a contracted pore phase to an open pore phase for a methane loading varying between two and four molecules, which agrees well with the experiments of Mason et al.³⁵. The proposed model is versatile in the sense that not only phase transformations may be predicted but also continuous shrinking of the material as was observed for benzene adsorption in DMOF-1(Zn), which is a pillared layer MOF (Fig. 1)^{36, 37}. In this case a continuous shrinking of the open pore phase is observed upon loading with benzene molecules (Fig. 4d). The transition is observed from a loading from about 1.5 to 2 benzene molecules per unit cell. Our observations are in correspondence with the results of Grosch et al.³⁶ who performed a series of NPT simulations, but did not extract the full thermodynamic potential. The free energy determined here, reveals that a local minimum exists, which is, however, not sufficiently stabilized by the guest molecules to induce a phase transformation. Our thermodynamic model yields all necessary components to also explain unexpected effects such as negative gas adsorption, which was observed for DUT-49(Cu) upon exposure of methane, as explained in Supplementary Note 5³⁸. The approach proposed here, might be helpful to design materials with specific guest induced breathing in close collaboration with experimentalists³⁹.

Discussion

In conclusion, we presented a generalized thermodynamic approach to construct the Helmholtz free energy as a function of the state variables for SPCs based on microscopic simulations. The method relies on the construction of the mechanical equation of state $P_T(V; X)$ from molecular dynamics simulations for various natures and magnitudes of the external trigger X . In case the external stimulus is the mechanical pressure, the response of the material at a given temperature may be easily derived from one mechanical equation of state. For more general stimuli such as the temperature or the chemical potential of adsorbing guest molecules, which are not the conjugate variable of the volume, a series of mechanical equations of state at various values of X need to be determined. As such, one obtains the full thermodynamic potential in terms of the governing state variables and a complete characterization of the framework flexibility. The strength of the proposed thermodynamic model relies in the fact that it can predict a flexibility window for a given material in a generic way. We have shown that some materials, which show intrinsic bistable behaviour, may not adopt a flexible behaviour macroscopically.

This was the case for the MIL-53(Ga) for which local descriptors such as the anisotropy of Young modulus predict an intrinsic bistability, but which does not breathe under influence of pressure. Such local descriptors do not give a conclusive statement on the flexibility of the material under certain conditions. From an application point of view, knowledge of the thermodynamic potential is crucial, as it may allow the in silico anticipation of the selection of soft porous materials with adequate structural behaviour upon external stimuli, e.g., systems as shock absorbers or triggered dispersers when applying mechanical pressure.

Methods

Force field derivation. Molecular simulations for each MOF were performed using a force field specifically derived for each MOF. For DMOF-1(Zn), including the benzene guest molecules, the force field derived by Grosch et al.³⁶ was used. For MIL-53(Al), MIL-53(Al)-F, MIL-53(Ga), and Al-fumarate and Co(bdp), a force field was derived from periodic ab initio input using QuickFF, an in-house developed program to easily derive force fields for MOFs⁴⁰. The required ab initio input was obtained by performing periodic Density Functional Theory calculations with the Vienna Ab Initio Simulation Package⁴¹. These force fields consist of a covalent contribution defined by QuickFF, an electrostatic contribution described by Coulomb interactions between atomic charges estimated by means of the Minimal Basis Iterative Stockholder partitioning scheme and a van der Waals contribution taken from the MM3 force field^{42, 43}. More details on the construction of the force fields can be found in Supplementary Note 6. The thermodynamic model is in principle generic but relies on reliable force fields. As a typical illustration, we compared the results obtained for DMOF-1(Zn) with various force fields (Supplementary Note 7). For some materials such as one- and two-dimensional coordination polymers, force field development might be very challenging due to critical dependence on the non-bonding interactions between the layers or the chains and more dedicated research might be required to apply the methodology on these systems^{44, 45}.

Construction of free energy profiles. To construct the equation of state $P_{NVT}(V)$, several molecular dynamics simulations were run in the $(N, V, \sigma_x = 0, T)$ ensemble for various values of the unit cell volume, whereas the cell shape may fluctuate. Herein, σ_x is defined as the anisotropic contribution to the stress tensor. To mimic the experimental conditions of isotropic stress, we chose $\sigma_x = 0$, which is controlled by means of a Martyna–Tobias–Tuckerman–Klein barostat⁴⁶. The number of particles is kept fixed and the temperature is controlled using the Nosé–Hoover thermostat⁴⁷. From the output of such molecular dynamics simulations, the time average of the instantaneous hydrostatic pressure P_t was computed, which is defined at each time step as $P_t = \text{Tr}(\sigma_t)/3$ with σ_t the instantaneous, internal stress tensor resulting in $P(V)$ and $F(V)$ profiles. More information about the procedure can be found in the work of Rogge et al.²². The details of the computational setup of the molecular dynamics simulations can be found in Supplementary Note 8. For a selected set of materials, the separate contribution of internal energy and entropy was deduced from the simulations to obtain more insight into the effects contributing to the stabilization of one or the other phase (Supplementary Note 9). Alternatively, free energy profiles may be obtained in the quasi-harmonic approximation. This was done for some materials under study in this paper, more information can be found in Supplementary Note 10. Finally, the convergence of the free energy profiles in terms of the simulation time is investigated in Supplementary Note 11.

Data availability. The authors declare that all data supporting the findings of this study are available within the paper and the Supplementary Files, or available from the authors upon request (see Supplementary Note 12).

Received: 21 May 2017 Accepted: 18 December 2017

Published online: 15 January 2018

References

- Horike, S., Shimomura, S. & Kitagawa, S. Soft porous crystals. *Nat. Chem.* **1**, 695–704 (2009).
- Ferey, G. & Serre, C. Large breathing effects in three-dimensional porous hybrid matter: facts, analyses, rules and consequences. *Chem. Soc. Rev.* **38**, 1380–1399 (2009).
- Schneemann, A. et al. Flexible metal-organic frameworks. *Chem. Soc. Rev.* **43**, 6062–6096 (2014).
- Coudert, F.-X. Responsive metal-organic frameworks and framework materials: under pressure, taking the heat, in the spotlight, with friends. *Chem. Mat.* **27**, 1905–1916 (2015).

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NATURE COMMUNICATIONS | DOI: 10.1038/s41467-017-02666-y

5. Bennett, T. D., Cheetham, A. K., Fuchs, A. H. & Coudert, F.-X. Interplay between defects, disorder and flexibility in metal-organic frameworks. *Nat. Chem.* **9**, 11–16 (2017).
6. Ghofri, A., Benhamed, K., Boukdi-Hacene, L. & Maurin, G. Electrically induced breathing of the MIL-53(Cr) metal-organic framework. *ACS Cent. Sci.* **3**, 394–398 (2017).
7. Férey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **37**, 191–214 (2008).
8. Beurroies, L. et al. Using pressure to provoke the structural transition of metal-organic frameworks. *Angew. Chem. Int. Ed.* **49**, 7526–7529 (2010).
9. Hobday, C. L. et al. A computational and experimental approach linking disorder, high-pressure behavior, and mechanical properties in UiO frameworks. *Angew. Chem. Int. Ed.* **55**, 2401–2405 (2016).
10. Devautour-Vinot S. et al. Estimation of the breathing energy of flexible MOFs by combining TGA and DSC techniques. *Chem. Commun.* **0**, 2733–2735 (2009).
11. Titov, K. et al. Probing dielectric properties of metal-organic frameworks: MIL-53(Al) as a model system for theoretical predictions and experimental measurements via synchrotron far- and mid-infrared spectroscopy. *J. Phys. Chem. Lett.* **8**, 5035–5040 (2017).
12. Vanduyfhuys, L., Ghysels, A., Rogge, S. M. J., Demuyck, R. & Van Speybroeck, V. Semi-analytical mean-field model for predicting breathing in metal-organic frameworks. *Mol. Simulat.* **41**, 1311–1328 (2015).
13. Bennett, T. D. & Cheetham, A. K. Amorphous metal-organic frameworks. *Acc. Chem. Res.* **47**, 1555–1562 (2014).
14. Rogge, S. M. J. et al. Thermodynamic insight in the high-pressure behavior of UiO-66: effect of linker defects and linker expansion. *Chem. Mat.* **28**, 5721–5732 (2016).
15. Wieme, J., Vanduyfhuys, L., Rogge, S. M. J., Waroquier, M. & Van Speybroeck, V. Exploring the flexibility of MIL-47(V)-type materials using force field molecular dynamics simulations. *J. Phys. Chem. C* **120**, 14934–14947 (2016).
16. Evans, J. D., Bocquet, L. & Coudert, F.-X. Origins of negative gas adsorption. *Chem. Sci.* **1**, 873–886 (2016).
17. Yot, P. G. et al. Mechanical energy storage performance of an aluminum fumarate metal-organic framework. *Chem. Sci.* **7**, 446–450 (2016).
18. Yot, P. G. et al. Large breathing of the MOF MIL-47(V-IV) under mechanical pressure: a joint experimental-modelling exploration. *Chem. Sci.* **3**, 1100–1104 (2012).
19. Yot, P. G. et al. Metal-organic frameworks as potential shock absorbers: the case of the highly flexible MIL-53(Al). *Chem. Commun.* **50**, 9462–9464 (2014).
20. Yot, P. G. et al. Exploration of the mechanical behavior of metal organic frameworks UiO-66(Zr) and MIL-125(Ti) and their NH₂ functionalized versions. *Dalton T.* **45**, 4283–4288 (2016).
21. Chaplais, G. et al. IM-19: a new flexible microporous gallium based-MOF framework with pressure- and temperature-dependent openings. *Phys. Chem. Chem. Phys.* **11**, 5241–5245 (2009).
22. Rogge, S. M. J. et al. A comparison of barostats for the mechanical characterization of metal-organic frameworks. *J. Chem. Theory Comput.* **11**, 5583–5597 (2015).
23. Leus, K. et al. A systematic study of the chemical and hydrothermal stability of some “stable” Metal Organic Frameworks. *Micro. Mesopor. Mat.* **226**, 110–116 (2016).
24. Peterson, G. W. et al. Effects of pelletization pressure on the physical and chemical properties of the metal-organic frameworks Cu-3(BTC)(2) and UiO-66. *Micro. Mesopor. Mat.* **179**, 48–53 (2013).
25. Valenzano, L. et al. Disclosing the complex structure of UiO-66 metal organic framework: a synergic combination of experiment and theory. *Chem. Mater.* **23**, 1700–1718 (2011).
26. Volklinger, C. et al. XRD and IR structural investigations of a particular breathing effect in the MOF-type gallium terephthalate MIL-53(Ga). *Dalton T.* **0**, 2241–2249 (2009).
27. Ortiz, A. U., Boutin, A., Fuchs, A. H. & Coudert, F.-X. Anisotropic elastic properties of flexible metal-organic frameworks: how soft are soft porous crystals? *Phys. Rev. Lett.* **109**, 195502 (2012).
28. Serra-Crespo, P. et al. Experimental evidence of negative linear compressibility in the MIL-53 metal-organic framework family. *Crystengcomm* **17**, 276–280 (2015).
29. Nanthamath, C., Ling, S. L., Slater, B. & Atfield, M. P. Contradistinct thermoresponsive behavior of isostructural MIL-53 type metal-organic frameworks by modifying the framework inorganic anion. *Chem. Mater.* **27**, 85–95 (2015).
30. Choi, H. J., Dinca, M. & Long, J. R. Broadly hysteretic H₂ adsorption in the microporous metal-organic framework Co(1,4-benzenedipyrzolate). *J. Am. Chem. Soc.* **130**, 7848–7854 (2008).
31. Stoeck, U., Krause, S., Bon, V., Senkova, I. & Kaskel, S. A highly porous metal-organic framework, constructed from a cuboctahedral super-molecular building block, with exceptionally high methane uptake. *Chem. Commun.* **48**, 10841–10843 (2012).
32. Alvarez, E. et al. The structure of the aluminum fumarate metal-organic framework A520. *Angew. Chem. Int. Ed.* **54**, 3664–3668 (2015).
33. Ghysels, A. et al. On the thermodynamics of framework breathing: a free energy model for gas adsorption in MIL-53. *J. Phys. Chem. C* **117**, 11540–11554 (2013).
34. Boutin, A. et al. Breathing transitions in MIL-53(Al) metal-organic framework upon xenon adsorption. *Angew. Chem. Int. Ed.* **48**, 8314–8317 (2009).
35. Mason, J. A. et al. Methane storage in flexible metal-organic frameworks with intrinsic thermal management. *Nature* **527**, 357–361 (2015).
36. Grosch, J. S. & Paesani, F. Molecular-level characterization of the breathing behavior of the jungle-gym-type DMOF-1 metal-organic framework. *J. Am. Chem. Soc.* **134**, 4277–4215 (2012).
37. Dybtsev, D. N., Chun, H. & Kim, K. Rigid and flexible: a highly porous metal-organic framework with unusual guest-dependent dynamic behavior. *Angew. Chem. Int. Ed.* **43**, 5033–5036 (2004).
38. Krause, S. et al. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* **532**, 348–352 (2016).
39. Henke, S., Schneemann, A., Wutscher, A. & Fischer, R. A. Directing the breathing behavior of pillared-layered metal organic frameworks via a systematic library of functionalized linkers bearing flexible substituents. *J. Am. Chem. Soc.* **134**, 9464–9474 (2012).
40. Vanduyfhuys, L. et al. QuickFF: a program for a quick and easy derivation of force fields for metal-organic frameworks from ab initio input. *J. Comput. Chem.* **36**, 1015–1027 (2015).
41. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
42. Verstraeten, T. et al. Minimal basis iterative stockholder: atoms in molecules for force-field development. *J. Chem. Theory Comput.* **12**, 3894–3912 (2016).
43. Allinger, N. L., Yuh, Y. H. & Li, J. H. Molecular mechanics. The MM3 force field for hydrocarbons. *J. Am. Chem. Soc.* **111**, 8551–8566 (1989).
44. Ambrosetti, A., Ferri, N., DiStasio, R. A. & Tkatchenko, A. Wavelike charge density fluctuations and van der Waals interactions at the nanoscale. *Science* **351**, 1171–1176 (2016).
45. Bjorkman, T., Gulans, A., Krashenninnikov, A. V. & Nieminen, R. M. van der Waals bonding in layered compounds from advanced density-functional first-principles calculations. *Phys. Rev. Lett.* **108**, 235502 (2012).
46. Martyna, G. J., Tobias, D. J. & Klein, M. L. Constant pressure molecular dynamics algorithms. *J. Chem. Phys.* **101**, 4177–4189 (1994).
47. Martyna, G. J., Klein, M. L. & Tuckerman, M. Nosé-Hoover chains: the canonical ensemble via continuous dynamics. *J. Chem. Phys.* **97**, 2635–2643 (1992).
48. Ortiz, A. U., Boutin, A. & Coudert, F.-X. Prediction of flexibility of metal-organic frameworks CAU-13 and NOTT-300 by first principles molecular simulations. *Chem. Commun.* **50**, 5867–5870 (2014).
49. Neimark, A. V. et al. Structural transitions in MIL-53 (Cr): view from outside and inside. *Langmuir* **27**, 4734–4741 (2011).
50. Collings, I. E. et al. Homologous critical behavior in the molecular frameworks Zn(CN)(2) and Cd(imidazolate)(2). *J. Am. Chem. Soc.* **135**, 7610–7620 (2013).
51. Matsuda, R. et al. Guest shape-responsive fitting of porous coordination polymer with shrinkable framework. *J. Am. Chem. Soc.* **126**, 14063–14070 (2004).
52. Liu, Y. et al. Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **130**, 11813–11818 (2008).
53. Wharmby, M. T. et al. Synthesis and crystal chemistry of the STA-12 family of metal N,N'-piperazinebis(methylene phosphonate)s and applications of STA-12 (Ni) in the separation of gases. *Micro. Mesopor. Mater.* **157**, 3–17 (2012).
54. Lanza, A., Germann, L. S., Fisch, M., Casati, N. & Macchi, P. Solid-state reversible nucleophilic addition in a highly flexible MOF. *J. Am. Chem. Soc.* **137**, 13072–13078 (2015).
55. Mowat, J. P. S. et al. Structural chemistry, monoclinic-to-orthorhombic phase transition, and CO₂ adsorption behavior of the small pore scandium terephthalate, Sc-2(O₂CC₆H₄CO₂)(3), and its nitro- and amino-functionalized derivatives. *Inorg. Chem.* **50**, 10844–10858 (2011).

Acknowledgements

We acknowledge the Fund for Scientific Research—Flanders (FWO), the Research Board of Ghent University (BOF), BELSPO, in the frame of IAP/7/05 for financial support. V.V. S. acknowledges funding from the European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement number 647755-DYNPOR (2015–2020)). The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by the Hercules foundation and the Flemish Government—department EWI. We also thank J.D. Evans and F.-X. Coudert for providing us the data of the $F_T(V,N)$ profiles from their simulations of methane in DUT-49(Cu).

Author contributions

L.V., S.M.J.R., J.W., S.V., G.M. M.W., and V.V.S initiated the discussion and designed the paper. V.V.S. and L.V. wrote the manuscript with contributions of all authors. L.V., S.M. J.R., J.W., S.V., G.M., M.W. and V.V.S were involved in the discussion of the results and commented on the manuscript. J.W. performed the *ab initio* calculations. L.V. and J.W. constructed the force fields for all materials under study. L.V., S.M.J.R. and S.V. carried out the molecular dynamics simulations.

Additional information

Supplementary Information accompanies this paper at <https://doi.org/10.1038/s41467-017-02666-y>.

Competing interests: The authors declare no competing financial interests.

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Paper IV

Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/computational approach

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The Journal of Physical Chemistry C, **2018**, 122, 2734–2746

J. Wieme was one of the counsellors of A.E.J. Hoffman's master thesis and had a large contribution in the interpretation of the results.

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Elucidating the Vibrational Fingerprint of the Flexible Metal–Organic Framework MIL-53(Al) Using a Combined Experimental/Computational Approach

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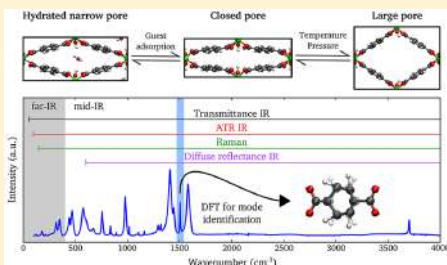
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Supporting Information

ABSTRACT: In this work, mid-infrared (mid-IR), far-IR, and Raman spectra are presented for the distinct (meta)stable phases of the flexible metal–organic framework MIL-53(Al). Static density functional theory (DFT) simulations are performed, allowing for the identification of all IR-active modes, which is unprecedented in the low-frequency region. A unique vibrational fingerprint is revealed, resulting from aluminum-oxide backbone stretching modes, which can be used to clearly distinguish the IR spectra of the closed- and large-pore phases. Furthermore, molecular dynamics simulations based on a DFT description of the potential energy surface enable determination of the theoretical Raman spectrum of the closed- and large-pore phases for the first time. An excellent correspondence between theory and experiment is observed. Both the low-frequency IR and Raman spectra show major differences in vibrational modes between the closed- and large-pore phases, indicating changes in lattice dynamics between the two structures. In addition, several collective modes related to the breathing mechanism in MIL-53(Al) are identified. In particular, we rationalize the importance of the trampoline-like motion of the linker for the phase transition.



1. INTRODUCTION

Metal–organic frameworks (MOFs) are an emerging class of porous crystalline materials consisting of metal-oxide clusters connected through organic linkers.^{1–3} The relatively easy synthesis procedure as well as the enormous number of existing⁴ and hypothetical⁵ MOFs make them promising materials for future industrial applications. Examples of such applications can be found in the fields of heterogeneous catalysis⁶ and gas separation,⁷ in which porous materials are ubiquitous. However, the chemical versatility of MOFs also allows for their use in applications such as drug delivery,⁸ lighting,⁹ and chemical sensing.¹⁰ An important subclass of MOFs consists of flexible MOFs,¹¹ some of which can undergo a phase transition upon external stimuli. This behavior is called breathing when the phase transition induces a drastic change in unit cell volume.^{11,12}

A prototypical example of a breathing MOF is MIL-53(Al), first synthesized by Férey and co-workers.¹³ The structure is composed of infinite chains of corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra connected through 1,4-benzenedicarboxylate linkers, which results in 1D diamond-shaped channels. After activation, MIL-53(Al) was originally reported to occur in two different phases. The low-temperature phase represents a narrow-pore

structure containing adsorbed water molecules and has a monoclinic crystal system. The high-temperature phase has a much larger pore volume without guest molecules and is orthorhombic. In the following, both phases will be indicated by NP-h and LP, where the abbreviation is used for the narrow- and large-pore phases, respectively, and the suffix h refers to hydration. Transitions between the two phases can be induced by adsorption and desorption of guest molecules,¹⁴ and at first it was believed that the presence of guest molecules is essential to observe the phase transition in MIL-53(Al). However, Liu et al.¹⁵ reported that under vacuum a third phase of MIL-53(Al) is present, which exhibits the same monoclinic structure as the NP-h phase but with a slightly smaller pore volume and in absence of guest molecules. Therefore, we will refer to this phase as the closed-pore (CP) phase. It was shown that reversible transitions between the different phases of MIL-53(Al) occur not only under the influence of guest adsorption,¹⁶ but also by changing the temperature^{15,17,18} or by applying pressure.¹⁹ As a consequence, the origin of

Received: November 8, 2017

Revised: December 29, 2017

Published: January 8, 2018



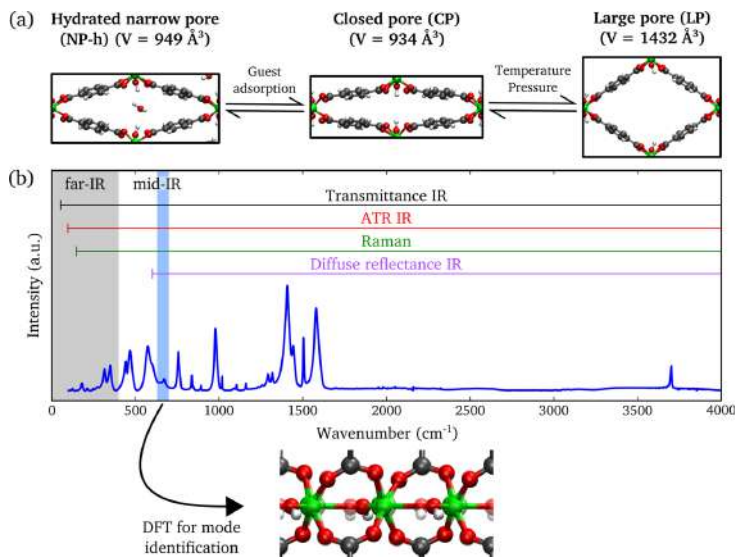


Figure 1. (a) Illustration of the different crystal structures of MIL-53(Al) with corresponding unit cell volumes (volumes were taken from refs 18 and 21). (b) Schematic representation of the applied experimental techniques with respective spectral ranges that can be probed by these techniques. Static and dynamic DFT simulations have been used to identify the observed IR- and Raman-active vibrational modes, respectively.

breathing in MIL-53(Al) cannot solely be explained by the presence of guest molecules, but it is also an intrinsic property of the framework.²⁰ We remark that, depending on the source, different nomenclatures are used to represent the various phases. In Figure 1a, we provide an overview of the different phases of MIL-53(Al) with the nomenclature adopted in this work.

To understand the flexibility of breathing MOFs on a molecular scale, vibrational spectroscopy can be used to characterize the different phases as it provides a fingerprint of the structure.^{22,23} In the past, several experimental investigations using infrared (IR) or Raman spectroscopy have been performed on materials of the MIL-53 family in order to reveal the vibrational spectra of the CP, NP-h, and LP phases.^{13,14,17,24–32} The reported results were mostly limited to the mid-IR range (400–4000 cm^{-1}). From these studies, differences between the NP-h and CP spectra were assigned to spectral bands of the adsorbed water molecules and shifts of the stretch and bend modes of the hydroxyl group.^{13,17,29} The vibrational spectra of the CP and LP phases differed mainly because of spectral shifts, of which the shift of the ν_{18a} ring mode^{14,29,31} appeared to be the most prominent one. Here, we adopt the nomenclature on aromatic ring vibrations as introduced by Wilson.³³ The spectral bands in the mid-IR range belong to vibrations of specific functional groups within the structure, and their shifts do not provide much insight into the breathing phenomenon. To improve the understanding of the mechanisms resulting in the phase transition, it is necessary to study the collective dynamics of the structure with corresponding vibrational modes in the far-IR region,²² which presents several challenges.

A first challenge that arises is the difficulty of experimentally obtaining a high-quality IR spectrum (high signal-to-noise ratio) in the far-IR range. Recent studies of far-IR spectra of MOFs^{22,23,32} benefited from the high brilliance of synchrotron sources to improve signal intensity in the far-IR, where absorption by ambient atmosphere is very strong. The far-IR spectrum of MIL-53(Al) has recently been explored by means of specular reflectance spectroscopy using synchrotron radiation.³²

A second challenge concerns the microscopic identification of certain low-frequency modes. This is not straightforward as these modes no longer originate from known localized vibrations of functional groups. Therefore, computer simulations are necessary to elucidate the modes in the far-IR range.^{22,23} Although a lot of theoretical research has been performed on MIL-53, computational studies regarding the IR spectra of the structure are less numerous,^{29,32} and a simulated Raman spectrum has, to the best of our knowledge, not been reported.

In this work, we use Fourier transform infrared (FTIR) and Raman spectroscopy to investigate the complete (mid- and far-IR range) vibrational spectrum of the different phases of MIL-53(Al). Figure 1b shows a schematic representation of the applied experimental techniques with respective spectral ranges. By application of both static and dynamic *ab initio* calculations, we obtain the corresponding theoretical IR and Raman spectra. Excellent agreement between experimental and simulated spectra is observed, which allows for the identification of all optically active peaks in the range of 100–4000 cm^{-1} . We reveal a unique vibrational fingerprint that distinguishes between the CP and LP phase spectra. Furthermore, we

investigate the low-frequency modes of MIL-53(Al) in order to elucidate the breathing mechanism in the structure.

2. EXPERIMENTAL DETAILS

The material synthesis and activation were carried out as previously reported by Nevjestic et al.²¹ In particular, a solvent extraction method consisting of three steps was employed for activation.³⁴ First, a heating step at 425 K in dimethylformamide in a Teflon-lined autoclave for 24 h was executed. Afterward, the material was washed at 395 K in methanol for 72 h. A last step consisted of drying at 475 K for 2 h under vacuum. With in situ powder X-ray diffraction as a function of air pressure and temperature (see Figure S1 in the Supporting Information) it was verified that the NP-h, CP, and LP phases of MIL-53(Al) could be obtained in (nearly) pure form.

Nevertheless, obtaining a targeted and pure crystallographic phase of MIL-53(Al) inside of a spectrometer remains a challenging task. Therefore, recording the FTIR spectra of the three phases (NP-h, CP, and LP) of MIL-53(Al) required multiple setups and measurement modes, as schematically shown in Figure 1b. The IR spectrum of the NP-h phase was recorded in transmission mode with a Bruker Vertex 80v vacuum FTIR spectrometer equipped with a DLATGS detector, a globar source, and a KBr or Mylar multilayer beamsplitter for mid- or far-IR measurements, respectively. The transmission spectra were obtained from pellet samples with less than 1 wt % MIL-53(Al) powder diluted in KBr or polyethylene, which are IR-inactive in the mid- and far-IR ranges, respectively. It was verified that the influence of the matrix material on MIL-53(Al) in the NP-h phase was negligible (see section S1.2 in the Supporting Information). The spectra were recorded under vacuum conditions (1–2 mbar) with a resolution of 0.5 cm⁻¹, accumulating 40 scans. While free-standing MIL-53(Al) powder dehydrates fast under vacuum conditions, the sample inside of the pellet remains hydrated because the out-diffusion of water is hindered.

The IR spectrum of the CP phase could not be measured completely in transmission mode because the presence of polyethylene in the pellet significantly affects the far-IR spectrum (see Figures S3 and S4 in the Supporting Information). Therefore, the IR spectrum of the CP phase was recorded in the attenuated total reflection (ATR) mode using a single-bounce ATR accessory (PLATINUM ATR) with a diamond crystal in the Bruker Vertex 80v FTIR spectrometer. MIL-53(Al) powder was placed on top of the diamond crystal and pressed by a small lever in order to provide good contact. Afterward, the sample chamber was pumped to 1–2 mbar, and IR spectra were recorded with a resolution of 1 cm⁻¹, accumulating 10–40 scans, depending on the quality of the spectrum. An ATR correction was performed on the resulting spectrum mainly to take into account the larger beam penetration depth into the sample at lower frequencies. Comparison of the corrected ATR IR spectrum of the CP phase with the transmission spectrum in the mid-IR range demonstrated a small shift in several peak positions, mainly caused by the additional pressure delivered by the lever, resulting in a slightly compressed structure in the ATR mode (see Figures S5 and S6 in the Supporting Information).

The only practical way to obtain the LP phase is by heating the sample above 370 K (see section S1.1 in the Supporting Information). The lack of an in situ heating device for the Bruker Vertex 80v FTIR spectrometer prohibited measurements of the LP phase with this setup. Therefore, a Nicolet

6700 diffuse reflectance infrared Fourier transform (DRIFT) spectrometer was used, equipped with a liquid-nitrogen-cooled MCT-A detector, an ETC IR source, and a KBr beamsplitter. The optics of the spectrometer limited the spectral range to >600 cm⁻¹, which made far-IR measurements impossible. The powdered sample was prepared by diluting it in KBr and placing it in a small cup inside of a Graseby Specac diffuse reflectance cell with an external vacuum connection. DRIFT spectra of the CP and LP phases were recorded with a resolution of 2 cm⁻¹, accumulating 1000 scans. The DRIFT spectrum of the CP phase qualitatively matches the ATR IR spectrum. However, due to the Kubelka–Munk transformation, used to convert the DRIFT spectra to absorption spectra, slight intensity differences between spectra obtained by DRIFT and ATR IR exist (see Figure S5 in the Supporting Information). The CP-to-LP transition was obtained by heating the sample to 400 K under vacuum conditions. It was verified that the transformation had actually taken place by cooling the sample under vacuum back to room temperature, after which the spectral changes remained.

The Raman spectra were collected with a NXR FT-Raman spectrometer equipped with an InGaAs detector, a KBr beamsplitter, and a Nd:YVO₄ laser with a wavelength of 1064 nm and a power of 2.5 W. During the experiments, the MIL-53(Al) powder was kept in a glass flask under vacuum conditions. After recording the spectra for the CP phase, the sample was heated to induce a transition to the LP phase. The Raman spectra were measured in the frequency range of 150–4000 cm⁻¹ with a resolution of 2 cm⁻¹, accumulating 500 scans.

3. COMPUTATIONAL DETAILS

Static and dynamic density functional theory (DFT) simulations were performed on structures in the CP and LP phases to determine the theoretical IR and Raman spectra of MIL-53(Al). Theoretical IR and Raman spectra of the NP-h phase were not calculated because the interactions of water inside of MIL-53(Al) are complex³⁵ and difficult to deal with correctly by DFT calculations.²⁹ Static DFT simulations were executed with the Vienna Ab initio Simulation Package (VASP)³⁶ using the PBE exchange-correlation functional,³⁷ a projector-augmented plane wave basis set³⁸ with a cutoff energy of 500 eV, and a Monkhorst–Pack k-mesh³⁹ with 2 × 6 × 6 k-points for the CP phase and 2 × 6 × 2 k-points for the LP phase. Grimme's D3 corrections with Becke–Johnson damping were used to describe the long-range dispersion interactions.^{40,41} Initially, the structure was optimized by ionic relaxation using the conjugate-gradient algorithm, allowing for changes in the cell shape but keeping the volume fixed. The ionic relaxation was assumed to be converged when the change in the total energy decreased below 10⁻⁷ eV between two ionic steps. The lattice parameters of the optimized geometries of the CP and LP phases are in good agreement with the experimental values (see Table S1 of the Supporting Information). Moreover, we obtain an energy difference between both phases of $\Delta E_{\text{LP-CP}} = 26.7 \text{ kJ mol}^{-1}$ per unit cell at the PBE-D3(BJ) level of theory, which falls in the range of the results obtained by Walker et al.²⁰

The vibrational frequencies and corresponding IR intensities of the optimized structures were calculated using density functional perturbation theory (DFPT)^{42,43} and the Berry phase approach.^{44,45} Both methods are incorporated in VASP and calculate the Born effective charge tensor and the dynamical matrix at the gamma point. The DFPT method uses linear response techniques to efficiently determine the

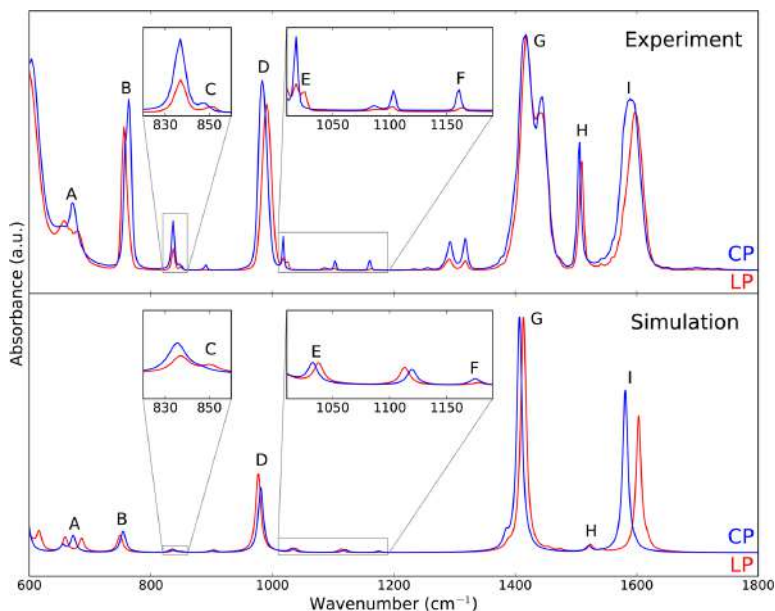


Figure 2. Comparison of DRIFT spectra (top) and theoretical IR spectra obtained by static DFT calculations (bottom) for the CP (blue) and LP (red) phases in the range of 600–1800 cm^{-1} . Both theoretical spectra were blue-shifted with a scaling factor of 1.025 and received a Lorentzian line shape with a FWHM of 10 cm^{-1} . The spectral differences between the experimental CP and LP phases are indicated by capital letters.

required data, but these calculations have to be executed without dispersion corrections. The Berry phase approach uses finite differences to obtain the necessary tensors and can include dispersion corrections, but it is computationally more demanding. We have verified that both approaches give almost exactly the same spectra (see Figure S7 in the Supporting Information), which is why we opted for the computationally cheaper DFPT method. From static DFT calculations, the vibrational modes with their corresponding IR activity are retrieved, but information on the bandwidth is not provided. In order to facilitate comparison with the experimental spectra, we applied a Lorentzian line shape with full width at half-maximum (FWHM) of 10 cm^{-1} to all calculated delta peaks, which is a common procedure in the literature.²³

To investigate the effect of temperature and anharmonicities on the vibrational spectra of MIL-53(Al), ab initio molecular dynamics (AIMD) simulations were performed using the CP2K software with the DFT Quickstep module.^{46,47} Calculations were executed at the PBE level of theory with Grimme's D3 corrections.⁴⁰ The Gaussian and plane waves (GPW) method was used with atom-centered Gaussian orbitals complemented with auxiliary plane waves. The Gaussian basis sets were of the TZVP2 type for all atoms except aluminum, for which the DZVP basis set was used. They were picked from the MOLOPT basis set. The cutoff for the auxiliary plane waves was set at 400 and 600 Ry for AIMD simulations on the CP and LP phases, respectively. The difference in cutoff originates from the computationally more expensive calculations for the CP phase. In addition, GTH pseudopotentials⁴⁸ were applied to take into account the core electrons. The dynamic simulations

were executed in the NVT ensemble with cell shape and volume fixed at the optimized cell with VASP. Both the CP and LP structures were equilibrated for 3 ps. The equations of motion were evaluated with a time step of 0.5 fs, and total simulation times of 10 and 20 ps were reached for the CP and LP phases, respectively. The temperature of 300 K was controlled by a Nosé–Hoover chain thermostat^{49–52} with three beads and a time constant of 100 fs.

From an AIMD simulation, the IR spectrum can be determined by taking the Fourier transform of the autocorrelation function of the dipole moment.⁵³ Therefore, the dipole moment was calculated every 2.5 fs using the Berry phase approach implemented in the CP2K code. As the dynamic IR spectrum shows only minor differences with the static IR spectrum, its discussion is found in section S3.1 of the Supporting Information. Besides IR spectra, we also determined Raman spectra from the MD trajectory. The calculation of the Raman spectrum from an AIMD simulation occurs in an analogous way as the calculation of the IR spectrum. It is performed by adding Fourier transforms of autocorrelation functions of the components of the polarizability tensor.⁵³ Due to the limited simulation time, these Fourier transforms could only be executed on relatively small data blocks, limiting the spectral resolution to 6.5 cm^{-1} . One possible way to obtain the polarizability tensor is by linear response techniques, but this approach is computationally very intensive.⁵⁴ Therefore, a faster though less accurate method was employed, whereby an electric field was applied to each configuration of the standard MD trajectory. Three different simulations were performed with an electric field of 257 $\text{MV}\cdot\text{m}^{-1}$ in each of the three Cartesian

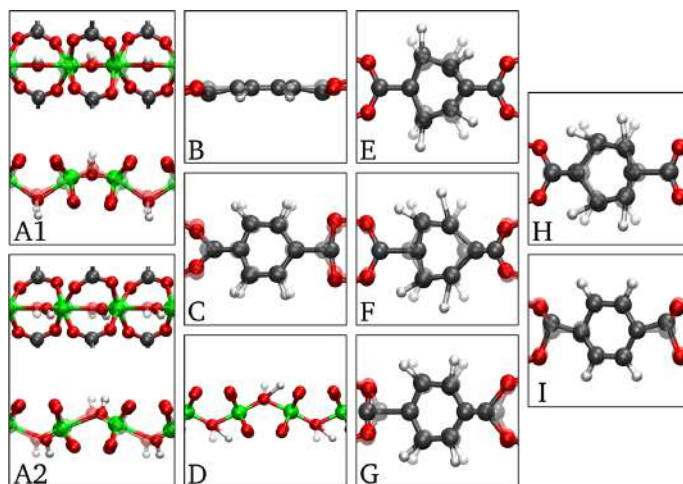


Figure 3. Illustration of the vibrational modes indicated in Figure 2. (A1) Symmetric stretch of the aluminum-oxide backbone. (A2) Antisymmetric stretch of the aluminum-oxide backbone. (B) Out-of-plane vibration of hydrogen atoms on the aromatic ring (ν_{11}). (C) Bend of the carboxyl group + bend of the aromatic ring. (D) Rocking of the hydroxyl group. (E) Bending of the aromatic ring + rocking of hydrogen atoms on the aromatic ring (ν_{18a}). (F) Stretch between the aromatic ring and carboxyl group + rocking of hydrogen atoms on the aromatic ring (ν_{18a}). (G) Symmetric stretch of the carboxyl group. (H) Stretch between the aromatic ring and carboxyl group + rocking of hydrogen atoms on the aromatic ring (ν_{19a}). (I) Antisymmetric stretch of the carboxyl group. Videos of these modes are available in the [Supporting Information](#).

directions. The dipole moment was calculated with and without an electric field, and subsequently, the components of the polarizability tensor were approximated by dividing the difference of the resulting dipole moments by the intensity of the electric field. In this way, a Raman spectrum was obtained with limited additional computational cost given the rather short simulation time. In contrast, calculation of the Raman spectra using a static DFT approach was exceedingly expensive as this required determination of the derivatives of the polarizability tensor with respect to all vibrational modes.⁵⁵

4. RESULTS AND DISCUSSION

In this section, we will first verify the correspondence between the IR spectra of MIL-53(Al) obtained by static DFT simulations and experiments in the mid-IR range. These results test the ability of the DFT calculations to reproduce the experimentally observed spectral differences between the CP and LP phases, showcasing the validity of our computational approach. Afterward, this approach is applied to study the far-IR spectra of MIL-53(Al). We assign the IR-active modes of the CP phase observed in the experiment with the help of our theoretical results. Subsequently, the spectral differences of the LP and NP-h phases with the CP phase are identified and rationalized. Furthermore, the theoretical Raman spectra of the CP and LP phases of MIL-53(Al) are determined by AIMD simulations and compared with the experimental spectra. Finally, we examine several low-frequency vibrations obtained by static DFT simulations and identify whether there is a correspondence with the breathing behavior in MIL-53(Al).

4.1. Comparison of the Mid-IR Spectra of MIL-53(Al) CP and LP. Figure 2 compares the experimental DRIFT spectra of the CP and LP phases of MIL-53(Al) in the range of 600–1800 cm^{-1} with the predicted static DFT results, which

are blue-shifted with a scaling factor in order to obtain the best possible agreement with experiment. A quantitative measure for this correspondence can be obtained by evaluation of the similarity index, which is a measure of the correlation between two spectra^{56,57}

$$\text{similarity index} = \frac{\int f(\sigma)g(\sigma) d\sigma}{\sqrt{\int f^2(\sigma) d\sigma \int g^2(\sigma) d\sigma}}$$

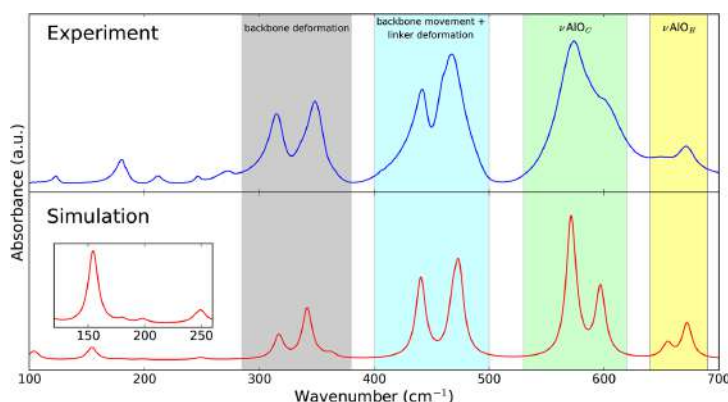
Here, $f(\sigma)$ and $g(\sigma)$ represent the intensities of the simulated and experimental spectra at frequency σ . A similarity index of 0 means absolutely no correspondence between the two spectra, while a similarity index of 1 indicates that the spectra are identical. Using the optimal scaling factor and line shape for the theoretical spectra, we calculated a similarity index as high as 0.86 for the CP phase and 0.84 for the LP phase (see [section S2.3](#) of the Supporting Information). We derived an optimal scaling factor of 1.025, in agreement with earlier DFT calculations using the PBE functional in which an optimal scaling factor of approximately 1.03 was predicted.^{58–61} Although the correspondence after scaling generally improves for the modes below 1700 cm^{-1} , it deteriorates correspondence with the C–H and O–H stretching modes located at higher frequencies, as is common in the literature⁵⁸ (see [Figure S9](#) in the Supporting Information).

From Figure 2 and the respective similarity indices, it is clear that our simulations are able to predict the experimental spectrum accurately. The DFT calculation allowed us to assign vibrational modes to all peaks except for the two at around 1300 cm^{-1} (see [Table S4](#) in the Supporting Information for complete mode identification). In general, we observe a good match in the positions of the peaks. The relative intensities are often well predicted, except for the symmetric (G) and

Table 1. Experimental and Theoretical Frequencies (Static) of the Vibrational Modes Characteristic of the CP-to-LP Transition Indicated in Figure 2 along with the Spectral Shifts between the Two Phases

vibrational mode	assignment ^a	experiment (cm ⁻¹)			simulation ^b (cm ⁻¹)		
		CP	LP	Δ_{LP-CP}	CP	LP	Δ_{LP-CP}
A1	$\nu\text{AlOAl}_{\text{sym}}$	653	657	4	655	659	4
A2	$\nu\text{AlOAl}_{\text{as}}$	671	680	9	672	686	14
B	ωCH (ν_{11})	764	756	-8	755	750	-5
C	$\delta\text{CCC} + \delta\text{CO}_2$	847	851	4	847	851	4
D	δOH	983	991	8	981	977	-4
E	$\delta\text{CCC} + \delta\text{CH}$ (ν_{18a})	1018	1026	8	1033	1038	5
F	$\nu\text{CC} + \delta\text{CH}$ (ν_{18a})	1160	1163	3	1176	1178	2
G	$\nu_{\text{sym}}\text{CO}_2$	1415	1418	3	1407	1413	6
H	$\nu\text{CC} + \delta\text{CH}$ (ν_{19a})	1505	1509	4	1521	1523	2
I	$\nu_{\text{as}}\text{CO}_2$	1589	1597	8	1581	1603	22

^aWe used the following spectroscopic notation: ν = stretching, δ = bending or in-plane rocking, and ω = out-of-plane wagging. The abbreviations sym and as stand for symmetric and antisymmetric, respectively. The nomenclature of ring modes is added between brackets where appropriate. ^bThe values are multiplied by a scaling factor of 1.025.

**Figure 4.** Comparison of the far-IR spectrum (100–700 cm⁻¹) of the CP phase of MIL-53(Al) obtained by FTIR spectroscopy using the single-bounce diamond ATR device (top) and by static DFT calculations (bottom). The theoretical spectrum was blue-shifted with a scaling factor of 1.025 and received a Lorentzian line shape with a FWHM of 10 cm⁻¹. The regions with the most IR-active vibrational modes are indicated.

antisymmetric (I) stretching modes of the carboxyl group, which are overestimated in our model, and the ν_{19a} ring mode (H), which is underestimated (see Figure 3 for a visualization of the modes). This results partially from the single broadening factor that we used, not accounting for the different line widths observed experimentally for different modes. However, most importantly, the spectral shifts between the CP and LP phases as observed from DFT simulations coincide with the ones observed from experiments, except for the mode that is indicated with D. In Table 1, all spectral shifts noticed in the DRIFT measurements are listed, along with their simulated values. For frequencies higher than 750 cm⁻¹ (B–I), the magnitude of the shifts is rather limited and they do not change the general shape of the spectrum. In contrast, a unique vibrational fingerprint is revealed at lower frequencies, which is substantially different in the CP and LP phase (labeled A). The peaks that characterize this fingerprint are assigned to the symmetric (A1) and antisymmetric (A2) stretch modes of the aluminum-oxide backbone (see Figure 3). Bourrelly et al.²⁷ already employed the metal-oxide backbone stretching mode in the chromium analogue to estimate the amount of large-pore

structure in the sample, but here we show that this major change in the IR spectrum specifically originates from a large blue shift of the antisymmetric stretch mode from the CP to the LP phase. As this spectral feature is still in the range of most IR spectrometers, it can be employed in routine measurements to distinguish between the CP and LP phases even at low resolutions. However, care should be taken when using this fingerprint in the presence of guest molecules as the aluminum-oxide backbone stretching modes may overlap with the vibrations of certain guest species, such as CO₂.

In contrast to the large shift in the stretching modes of the aluminum-oxide backbone, earlier investigations used the more subtle shifts in the ν_{18a} ring modes (E and F) (see Figure 3) to determine the fraction of large-pore phase in the sample.^{14,31} In our experimental spectrum of the LP phase, an additional low-intensity peak in the region of mode E indicates that the measured sample still contained traces of the CP phase. Nevertheless, as clear from the lower pane of Figure 2, the theoretical spectrum is able to predict the shifts of the ν_{18a} ring modes accurately. The only characterizing mode, listed in Table 1, for which the shift differs is the δOH mode (D). Finally, we

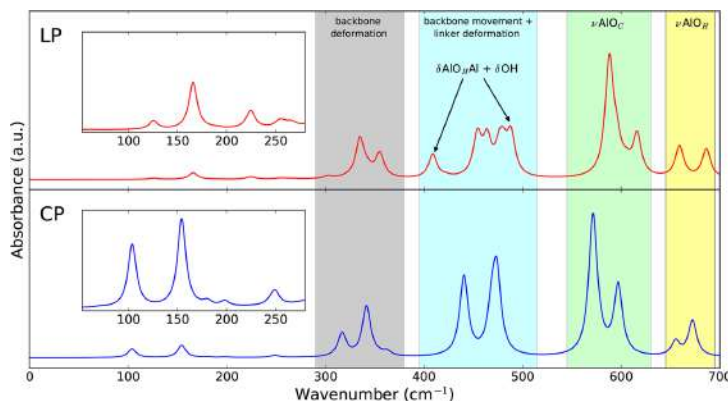


Figure 5. Comparison of the theoretical far-IR spectrum (0–700 cm^{-1}) of the CP and LP phases of MIL-53(Al). The spectra were blue-shifted with a scaling factor of 1.025 and received a Lorentzian line shape with a FWHM of 10 cm^{-1} .

want to mention the general decrease in intensity of the peaks from the CP to the LP phase observed in the measurements. A possible explanation is the higher symmetry of the LP phase structure, which reduces the change in dipole moment induced by the modes leading to a smaller IR activity. This decrease is not captured in our static DFT simulations.

In conclusion, the correspondence between the simulated and experimental spectra of the CP and LP phases in the mid-IR range confirms the validity of our theoretical approach and allowed us to uniquely characterize the aluminum-oxide backbone stretching modes as a clear fingerprint to distinguish between the modes of the CP and LP phases of MIL-53(Al).

4.2. Far-IR Spectrum of the CP and LP Phases of MIL-53(Al). **4.2.1. CP Phase.** Besides DRIFT measurements, we also performed ATR IR measurements on the CP phase of MIL-53(Al), allowing us to obtain high-quality spectra in the far-IR range down to 100 cm^{-1} . Assigning the vibrational modes based on tabulated data of functional group vibrations is no longer possible in this region, revealing the importance of our static DFT calculations, which proved to perform well in the mid-IR range. In the literature, mode identification was performed before by Salazar et al. for modes with frequencies above 400 cm^{-1} .²⁹ However, below 700 cm^{-1} , their assignment becomes unreliable as they were unable to identify the aluminum-oxide backbone stretching modes correctly. From Figure 4, we see that the resemblance of our model to the experimental spectrum in the range of 100–700 cm^{-1} is striking. This can also be concluded from the similarity index, which yields 0.96 with an optimal scaling factor and line shape.

Between 300 and 700 cm^{-1} , four different regions of vibrations appear (see Figure S11 in the Supporting Information for visualization). Above 640 cm^{-1} , we already discussed the presence of stretching modes of the aluminum-oxide backbone. Within the region of 520–620 cm^{-1} , stretching modes of the aluminum atom with the oxygen atoms of the carboxyl group emerge. Between 400 and 500 cm^{-1} , we find in-plane and out-of-plane movements of the ring structure (ν_{16b} ring mode) coupled with rocking of the aluminum atom, inducing a bend in the metal-oxide backbone. The last frequency region with intense peaks is observed within the 280–380 cm^{-1} range and mainly contains modes inducing

deformations of the metal-oxide backbone. Below 280 cm^{-1} , we distinguish between five IR-active modes, which are slightly red-shifted by 20–40 cm^{-1} in the simulation when compared with experiment. These modes are made up of combinations of scissoring modes ($\delta\text{O}_C\text{AlO}_C$) and linker rocking mostly coupled with δOH vibrations inducing a change in dipole moment.

4.2.2. Comparison between the Simulated CP and LP Phases. Our model proved to be very accurate in the mid-IR range (similarity index of 0.84), and also, the simulated far-IR spectrum of the CP phase showed excellent agreement with experiment (similarity index of 0.96). Therefore, even though the experimental far-IR data for the LP phase are missing, it is interesting to inspect the differences with the CP phase spectrum predicted by static DFT calculations. In Figure 5, we compare the simulated far-IR spectrum of the LP phase with the CP phase.

A first remarkable difference between the two spectra is the general blue shift of the vibrational frequencies in the LP phase compared with the CP phase. This effect was already slightly visible for some functional group vibrations in the mid-IR range, but it becomes much more pronounced in the far-IR range. We believe that the lower frequencies in the CP phase are a result of the stronger dispersion interactions in the denser structure.²⁰ This weakens the forces between neighboring atoms, yielding lower covalent and ionic bond strengths.^{62,63}

Besides the frequency shift, two IR-active modes arise in the spectrum of the LP phase, which were not present in the CP phase spectrum. These modes can be identified as bending modes of the metal-oxide backbone. In the LP structure, these bending modes are coupled with a δOH vibration, which makes them IR-active. In the CP structure, the stronger hydrogen bond interactions between opposite aluminum-oxide backbones inhibit this coupling with δOH vibrations, and as a result, the modes remain optically inactive (see Figure S12 in the Supporting Information for visualization).

Above 300 cm^{-1} , most of the modes appearing in the CP phase have their counterparts in the LP phase. At lower frequencies, this one-to-one correspondence between modes is no longer present as these low-frequency modes correspond to collective motions that may differ between the CP and LP

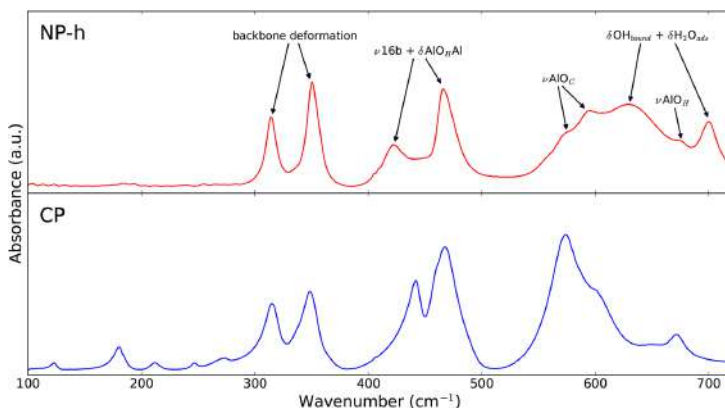


Figure 6. Comparison of the experimental far-IR spectrum (100–700 cm^{-1}) of the CP and NP-h phase of MIL-53(Al). The CP phase was recorded with a single-bounce ATR device, while the NP-h phase was obtained in transmittance mode.

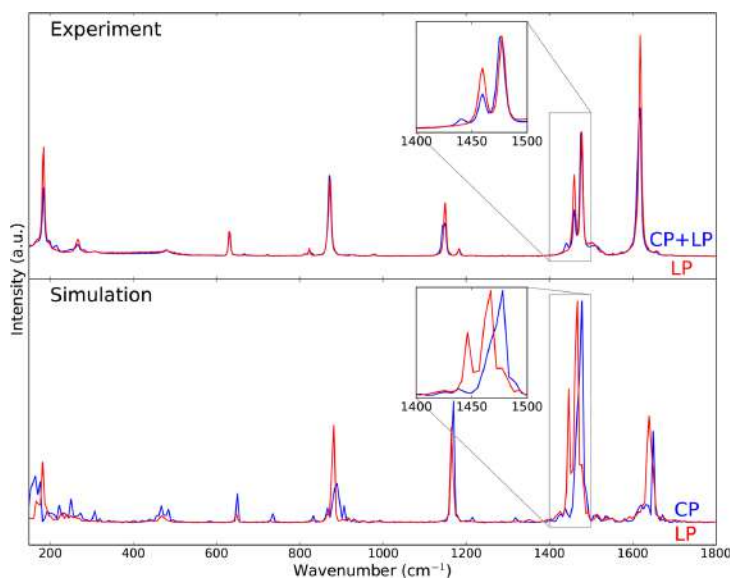


Figure 7. Comparison of the experimental (top) and theoretical (bottom) Raman spectra of the CP (blue) and LP (red) phases of MIL-53(Al) in the range of 150–1800 cm^{-1} . The theoretical Raman spectra were blue-shifted with a scaling factor of 1.035.

structures. In section 4.4, we specifically discuss those low-frequency modes describing the breathing transition in MIL-53(Al).

4.2.3. Comparison between the Experimental NP-h and CP Phases. Under atmospheric conditions, MIL-53(Al) is usually present in the NP-h phase. Therefore, it is important to have a notion of its characterizing vibrational modes. As the mid-IR spectrum has been reported numerous times,^{13,17,29} we will restrict ourselves to a discussion of the IR spectrum in the range of 100–700 cm^{-1} . Experimentally, this spectrum was

obtained in transmittance mode. As mentioned in section 3 on computational details, a theoretical IR spectrum was not calculated. In Figure 6, we compare the experimental IR spectrum of the NP-h phase with the one of the CP phase.

Above 500 cm^{-1} , we observe important differences between both spectra, caused by additional rocking modes of adsorbed water molecules in the NP-h phase.²⁹ Between 300 and 500 cm^{-1} , these modes are not present and we recognize similar bands in the NP-h phase spectrum as in the CP phase spectrum. The most striking difference in this frequency range

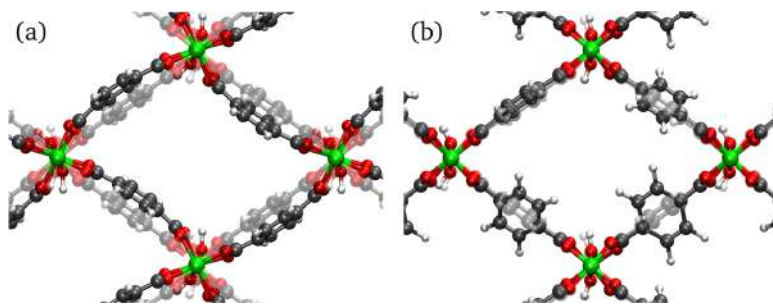


Figure 8. (a) Rotation of the metal-oxide backbone inducing a trampoline-like motion of the linker (11 cm^{-1} in CP phase, 15 cm^{-1} in LP phase). (b) Linker rotation (69 cm^{-1} in CP phase, 54 cm^{-1} in LP phase). Videos of these modes are available in the [Supporting Information](#).

is a red shift of one of the bands that represent a combination of the in-plane and out-of-plane movement of the aromatic ring with bending of the metal-oxide backbone. This shift may be caused by hydrogen bonds weakening the forces coupled with the in-plane movement of the aromatic ring. Below 300 cm^{-1} , the intensities of the bands in the NP-h phase spectrum are much lower than those in the CP phase spectrum. One of the reasons is the use of the transmission mode instead of the ATR mode applied for the CP phase spectrum. The latter highlights low-frequency modes. Another reason could be broadening of the bands due to the presence of adsorbed water molecules. Furthermore, the use of a pellet in transmission mode results in an interference pattern, which becomes clearly visible below 130 cm^{-1} .

4.3. Raman Spectrum of MIL-53(Al). To acquire a more complete view of the vibrational modes of MIL-53(Al), we supplemented our IR spectroscopy with Raman spectroscopy, which results in active modes complementary to the IR spectrum. Experimentally, we measured the Raman spectra of the LP phase on the one hand and a mixture of the CP and LP phase on the other hand. Measurement of the Raman spectrum of the pure CP phase was not possible due to laser heating of the sample. In [Figure 7](#), the experimental results in the range of $150\text{--}1800\text{ cm}^{-1}$ are compared by the theoretical spectra of the CP and LP phases obtained by AIMD simulations (see [Figure S10](#) in the [Supporting Information](#) for the Raman spectra in the range of $2800\text{--}4000\text{ cm}^{-1}$). The simulated spectra are shifted with a scaling factor of 1.035 (see [section S2.3](#) in the [Supporting Information](#)), which differs from the scaling factor used for the static simulations, mainly due to the use of a different basis set. Nevertheless, this scaling factor is still in agreement with results found in the literature.^{58–61} We observe that the experimental spectra look similar for wavenumbers above 400 cm^{-1} , except at around 1450 cm^{-1} , where one of the CO_2 symmetric stretch peaks undergoes a shift upon transition from the CP to the LP phase. This spectral difference was also observed by Hamon et al.²⁵ In the same frequency range, the theoretical Raman spectra show satisfactory agreement with the experimental results. All peaks observed in the measurements do appear in the simulation, albeit with different intensities. Notably, the characterizing difference in the Raman spectra of the CP and LP phases at around 1450 cm^{-1} is clearly captured in the simulation. At wavenumbers lower than 300 cm^{-1} , we note more Raman-active peaks in the experimental spectrum of the mixture of CP and LP phases than that in the pure LP

phase spectrum, indicating differences in collective vibrations. This feature is also predicted by our AIMD simulation, although it becomes increasingly difficult to match the theoretical Raman spectrum of the CP phase with experiment at such low frequencies. This difficulty is related to the limited simulation time for these expensive simulations, causing insufficient sampling of the low-frequency modes. To the best of our knowledge, this is the first time that experimental and theoretical Raman spectra of MIL-53(Al) are reported in the range of $150\text{--}4000\text{ cm}^{-1}$. The results obtained here are very rewarding and open perspectives to simulate Raman spectra of other complex nanostructured materials.

4.4. Collective Vibrations with Impact on the Breathing Mechanism. From the preceding discussion, it is clear that our static DFT simulations are very well suited to describe the vibrational modes of the CP and LP phases of MIL-53(Al). We pointed out specific fingerprint modes that distinguish between the spectra of the CP and LP phases in the mid-IR range, which were related to shifts of the aluminum-oxide backbone stretch modes (IR-active) and of one of the symmetric stretch modes of the carboxyl group (Raman-active). In the far-IR range, the spectra of both phases were more distinct, primarily in the low-frequency region (below 300 cm^{-1}). In this respect, the collective vibrations, which affect the lattice as a whole, are of particular interest. These modes are predominantly located at frequencies below 100 cm^{-1} . The LP phase has 12 modes in this frequency range, whereas we find only 7 modes for the CP phase, excluding the 3 modes of almost zero frequency representing translations of the complete structure (see [Tables S5 and S6](#) in the [Supporting Information](#)). The deficit of very low frequency modes in the CP phase can be attributed to the constrained movement, which shifts modes to higher frequencies. In the following, we will discuss the modes that are of importance for the breathing mechanism.

The lowest-frequency mode appearing in both the CP (11 cm^{-1}) and LP (15 cm^{-1}) phase concerns the opposite rotation of neighboring metal-oxide backbones inducing a weak trampoline motion of the organic linker ([Figure 8a](#)). This mode is of minor importance for the CP-to-LP transition, but in MIL-53(Sc), it is assumed to be the driving mechanism in the transition of the CP phase to an even denser structure.⁶⁴

At slightly higher frequencies, multiple modes are present inducing rotation of the organic linker ([Figure 8b](#)). In the LP phase, four of these modes can be observed. A single mode, located at 47 cm^{-1} , consists of a complete linker rotation

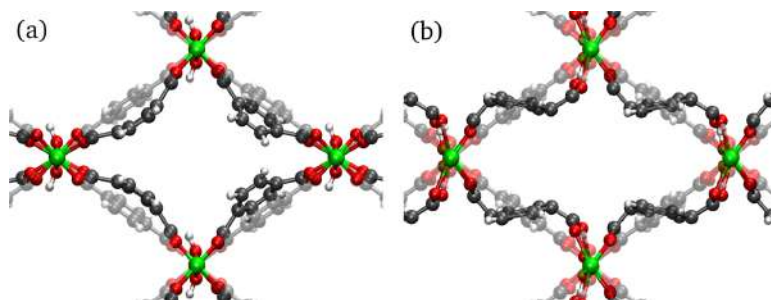


Figure 9. Low-frequency vibrations of the LP phase possibly affecting the breathing mechanism. (a) Trampoline-like motion of the linker (59 cm^{-1}). (b) Scissoring of the octahedra (181 cm^{-1}). Videos of these modes are available in the [Supporting Information](#).

induced by alternating rotation of the octahedra on the metal-oxide backbone. A triply degenerate mode, located at 54 cm^{-1} , gives rise to rotations of the aromatic ring only. In contrast, we identified only a double-degenerate mode with linker rotations below 100 cm^{-1} in the CP phase. In addition, the frequency of the modes is blue-shifted to 69 cm^{-1} . This shift was already reported by Liu et al.¹⁵ and was assumed to result from the constrained motion in the CP phase. This observation leads to the speculation that linker rotations trigger breathing of the structure. Moreover, Walker et al.²⁰ argued that the larger number of very low frequency modes associated with linker rotations in the LP phase drives the CP-to-LP transition at higher temperatures because of the increased entropy. The lack of modes inducing linker rotations in the CP phase in the frequency region below 100 cm^{-1} is compensated by a doubly degenerate mode inducing linker rotation located at 151 cm^{-1} , again due to a heavily constrained motion.

Besides linker rotations, we discovered several other low-frequency modes that give rise to enhanced π - π interactions and, subsequently, can trigger breathing in MIL-53(Al). These modes were found to be different in the CP and LP phases. For the LP phase, the first two modes are located at 59 and 60 cm^{-1} and contain a trampoline-like motion of the organic linker (Figure 9a). Although the trampoline mode itself does not include changes in the unit cell volume because it represents a normal mode with fixed unit cell, it can be expected to be related to volume-changing breathing modes as it brings the organic linkers closer together. As a result, stronger π - π interactions can be present between opposite linkers. These interactions play a significant role in the CP phase. At low temperatures, they favor the presence of the CP phase over the LP phase,²⁰ and in MIL-53(Fe), they hinder the occurrence of the LP phase even at higher temperatures.⁶⁵ Therefore, we can assume that the modes containing trampoline-like motions trigger the LP-to-CP transition. Furthermore, at 181 cm^{-1} , a mode consisting of synchronous scissoring of the metal octahedra inducing a seesaw motion of the organic linker was identified (Figure 9b). Within this motion, the opposite linkers tend to align, which again gives rise to increased π - π interactions and a possible contraction of the pores.

As the linkers in the CP phase are already closely packed, the trampoline-like motion is heavily constrained. As a consequence, the modes containing trampoline-like motions are shifted to higher wavenumbers compared to the LP phase. The first "breathing mode" in the CP phase is located at 123 cm^{-1}

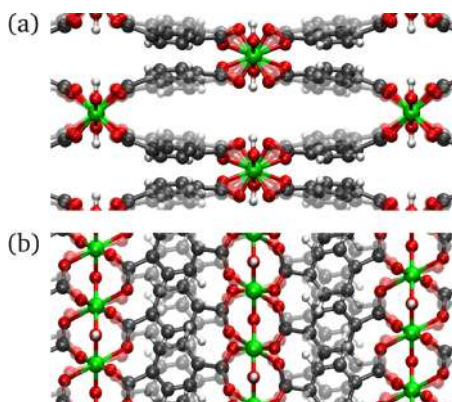


Figure 10. Low-frequency vibration of the CP phase located at 123 cm^{-1} possibly affecting the breathing mechanism. (a) View of the diamond-shaped channel showing the trampoline-like motion of the linker and the rotation of the octahedra. (b) View along the aluminum-oxide backbone showing the translation of the linker. Videos of this mode are available in the [Supporting Information](#).

and consists of a trampoline-like motion of the linker in combination with translation of the linker along the aluminum-oxide backbone and rotation of the octahedra (Figure 10). Other trampoline-like motions that are able to open the pore are found at 138 , 139 , and 143 cm^{-1} . These modes weaken the strong π - π interactions and can lead to a transition to the LP phase.

5. CONCLUSIONS

In this paper, we examined the phase transition in MIL-53(Al) by a combination of experimental and computational vibrational spectroscopy. Experimentally, we applied a variety of techniques to record high-quality IR and Raman spectra of the CP, NP-h, and LP phases of MIL-53(Al) in the mid- and far-IR range. This revealed a unique vibrational fingerprint in the IR spectrum related to the stretching modes of the aluminum-oxide backbone, which is very well suited to identify breathing in the structure. Further insight into the breathing phenomenon was obtained by static and dynamic DFT calculations. We

performed static DFT simulations to determine the theoretical IR spectra of the CP and LP phases of MIL-53(Al). These calculations were able to correctly predict all but one of the characterizing vibrational shifts of the CP-to-LP transition in the mid-IR range, including the aluminum-oxide backbone stretching modes. The almost one-to-one correspondence of our static DFT calculations with the experimental spectrum in the far-IR allowed for a detailed description of the IR-active low-frequency modes, which is unprecedented for a material of the MIL-53 family. Furthermore, we determined the theoretical Raman spectra of the MIL-53(Al) CP and LP phases for the first time using ab initio molecular dynamics simulations and obtained satisfactory agreement with the experimental spectra. Finally, we highlighted several collective vibrations that may trigger breathing in MIL-53(Al). Of particular interest are the collective vibrations showing a trampoline-like deformation of the linker as these increase π - π interactions, resulting in contraction of the pore.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11031.

Powder X-ray diffraction patterns, investigation of the influence of dilution on the spectra, comparison of the different experimental techniques, computational and experimental lattice parameters, comparison of DFPT and Berry phase approach, quantification of correspondence of experimental and theoretical spectra, IR spectra obtained by AIMD simulations, experimental and theoretical IR and Raman spectra in the range of 2800–4000 cm^{-1} , complete mode identification, visualization of IR-active modes, and description of low-frequency vibrations in CP and LP phases (PDF)
Videos of all modes discussed in this paper (ZIP)

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Fund for Scientific Research Flanders (FWO), the Research Board of the Ghent University (BOF), and BELSPO in the frame of IAP/7/05. V.V.S. acknowledges funding from the European Union's Horizon 2020 research and innovation programme [consolidator ERC Grant Agreement No. 647755 - DYNPOR (2015–2020)]. H.V. acknowledges funding from the Hercules Foundation and the Research Foundation - Flanders (FWO) [FT-IMAGER - AUGE/13/16 and Project Grant No. G0048.13N]. Computational resources (Stevin Supercomputer Infrastructure) and services were provided by Ghent University.

■ REFERENCES

- (1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444.
- (2) Kitagawa, S. Future porous materials. *Acc. Chem. Res.* **2017**, *50*, 514–516.
- (3) Maurin, G.; Serre, C.; Cooper, A.; Férey, G. The new age of MOFs and of their porous-related solids. *Chem. Soc. Rev.* **2017**, *46*, 3104–3107.
- (4) Moghadam, P. Z.; Li, A.; Wiggins, S. B.; Tao, A.; Maloney, A. G.; Wood, P. A.; Ward, S. C.; Fairen-Jimenez, D. Development of a Cambridge structural database subset: a collection of metal-organic frameworks for past, present, and future. *Chem. Mater.* **2017**, *29*, 2618–2625.
- (5) Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q. Large-scale screening of hypothetical metal-organic frameworks. *Nat. Chem.* **2012**, *4*, 83–89.
- (6) Rogge, S. M. J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivio-Suarez, A. I.; Sepúlveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kapteijn, F.; et al. Metal-organic and covalent organic frameworks as single-site catalysts. *Chem. Soc. Rev.* **2017**, *46*, 3134–3184.
- (7) Li, J.-R.; Sculley, J.; Zhou, H.-C. Metal-organic frameworks for separations. *Chem. Rev.* **2012**, *112*, 869–932.
- (8) Horcajada, P.; Serre, C.; Maurin, G.; Ramsahye, N. A.; Balas, F.; Vallet-Regi, M.; Sebban, M.; Taulelle, F.; Férey, G. Flexible porous metal-organic frameworks for a controlled drug delivery. *J. Am. Chem. Soc.* **2008**, *130*, 6774–6780.
- (9) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Luminescent functional metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 1126–1162.
- (10) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyn, R. P.; Hupp, J. T. Metal-organic framework materials as chemical sensors. *Chem. Rev.* **2012**, *112*, 1105–1125.
- (11) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible metal-organic frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062–6096.
- (12) Depaauw, H.; Nevjestic, I.; Wang, G.; Leus, K.; Callens, F.; De Canck, E.; De Buysser, K.; Vrielinck, H.; Van Der Voort, P. Discovery of a novel, large pore phase in a bimetallic Al/V metal-organic framework. *J. Mater. Chem. A* **2017**, *5*, 24580–24584.
- (13) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. *Chem.-Eur. J.* **2004**, *10*, 1373–1382.
- (14) Serre, C.; Bourrelly, S.; Vimont, A.; Ramsahye, N. A.; Maurin, G.; Llewellyn, P. L.; Daturi, M.; Filinchuk, Y.; Leynaud, O.; Barnes, P.; et al. An explanation for the very large breathing effect of a metal-organic framework during CO₂ adsorption. *Adv. Mater.* **2007**, *19*, 2246–2251.
- (15) Liu, Y.; Her, J.-H.; Dailly, A.; Ramirez-Cuesta, A. J.; Neumann, D. A.; Brown, C. M. Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **2008**, *130*, 11813–11818.
- (16) Boutin, A.; Springuel-Huet, M.-A.; Nossou, A.; Gédéon, A.; Loiseau, T.; Volklinger, C.; Férey, G.; Coudert, F.-X.; Fuchs, A. H. Breathing transitions in MIL-53(Al) metal-organic framework upon xenon adsorption. *Angew. Chem., Int. Ed.* **2009**, *48*, 8314–8317.
- (17) Volklinger, C.; Loiseau, T.; Guillou, N.; Férey, G.; Elkaim, E.; Vimont, A. XRD and IR structural investigations of a particular breathing effect in the MOF-type gallium terephthalate MIL-53(Ga). *Dalton Trans.* **2009**, 2241–2249.
- (18) Nevjestic, I.; Depaauw, H.; Gast, P.; Tack, P.; Deduytsche, D.; Leus, K.; Van Landeghem, M.; Goovaerts, E.; Vincze, L.; Detavernier, C.; et al. Sensing the framework state and guest molecules in MIL-53(Al) via the electron paramagnetic resonance spectrum of V^{IV} dopant ions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 24545–24554.
- (19) Yot, P. G.; Boudene, Z.; Macia, J.; Granier, D.; Vanduyfhuys, L.; Verstraelen, T.; Van Speybroeck, V.; Devic, T.; Serre, C.; Férey, G.; et al. Metal-organic frameworks as potential shock absorbers: the case

of the highly flexible MIL-53(Al). *Chem. Commun.* **2014**, 50, 9462–9464.

(20) Walker, A. M.; Civalieri, B.; Slater, B.; Mellot-Draznicks, C.; Cora, F.; Zicovich-Wilson, C. M.; Román-Pérez, G.; Soler, J. M.; Gale, J. D. Flexibility in a metal–organic framework material controlled by weak dispersion forces: the bistability of MIL-53(Al). *Angew. Chem., Int. Ed.* **2010**, 49, 7501–7503.

(21) Nevjestic, I.; Depauw, H.; Leus, K.; Rampelberg, G.; Murray, C. A.; Detavernier, C.; Van Der Voort, P.; Callens, F.; Vrielinck, H. In situ electron paramagnetic resonance and X-ray diffraction monitoring of temperature-induced breathing and related structural transformations in activated V-doped MIL-53(Al). *J. Phys. Chem. C* **2016**, 120, 17400–17407.

(22) Ryder, M. R.; Civalieri, B.; Bennett, T. D.; Henke, S.; Rudić, S.; Cinque, G.; Fernandez-Alonso, F.; Tan, J.-C. Identifying the role of terahertz vibrations in metal–organic frameworks: from gate-opening phenomenon to shear-driven structural destabilization. *Phys. Rev. Lett.* **2014**, 113, 215502.

(23) Ryder, M. R.; Civalieri, B.; Cinque, G.; Tan, J.-C. Discovering connections between terahertz vibrations and elasticity underpinning the collective dynamics of the HKUST-1 metal–organic framework. *CrystEngComm* **2016**, 18, 4303–4312.

(24) Vimont, A.; Travert, A.; Bazin, P.; Lavalley, J.-C.; Daturi, M.; Serre, C.; Férey, G.; Bourrelly, S.; Llewellyn, P. L. Evidence of CO₂ molecule acting as an electron acceptor on a nanoporous metal–organic-framework MIL-53 or Cr³⁺(OH)(O₂C–C₆H₄–CO₂). *Chem. Commun.* **2007**, 3291–3293.

(25) Hamon, L.; Llewellyn, P. L.; Devic, T.; Ghoufi, A.; Clet, G.; Guillermin, V.; Pirngruber, G. D.; Maurin, G.; Serre, C.; Driver, G.; et al. Co-adsorption and separation of CO₂/CH₄ mixtures in the highly flexible MIL-53(Cr) MOF. *J. Am. Chem. Soc.* **2009**, 131, 17490–17499.

(26) Ravon, U.; Chaplais, G.; Chizallet, C.; Seyyedi, B.; Bonino, F.; Bordiga, S.; Bats, N.; Farrusseng, D. Investigation of acid centers in MIL-53(Al, Ga) for Brønsted-type catalysis: in situ FTIR and ab initio molecular modeling. *ChemCatChem* **2010**, 2, 1235–1238.

(27) Bourrelly, S.; Moulin, B.; Rivera, A.; Maurin, G.; Devautour-Vinot, S.; Serre, C.; Devic, T.; Horcajada, P.; Vimont, A.; Clet, G.; et al. Explanation of the adsorption of polar vapors in the highly flexible metal–organic framework MIL-53(Cr). *J. Am. Chem. Soc.* **2010**, 132, 9488–9498.

(28) Boutin, A.; Bousquet, D.; Ortiz, A. U.; Coudert, F.-X.; Fuchs, A. H.; Ballandras, A.; Weber, G.; Bezverkhyy, I.; Bellat, J.-P.; Ortiz, G.; et al. Temperature-induced structural transitions in the gallium-based MIL-53 metal–organic framework. *J. Phys. Chem. C* **2013**, 117, 8180–8188.

(29) Salazar, J.; Weber, G.; Simon, J.; Bezverkhyy, I.; Bellat, J. Characterization of adsorbed water in MIL-53(Al) by FTIR spectroscopy and ab-initio calculations. *J. Chem. Phys.* **2015**, 142, 124702.

(30) Mihaylov, M.; Andonova, S.; Chakarova, K.; Vimont, A.; Ivanova, E.; Drenchev, N.; Hadjiivanov, K. An advanced approach for measuring acidity of hydroxyls in confined space: a FTIR study of low-temperature CO and ¹⁵N₂ adsorption on MOF samples from the MIL-53(Al) series. *Phys. Chem. Chem. Phys.* **2015**, 17, 24304–24314.

(31) Andonova, S. M.; Ivanova, E.; Yang, J.; Hadjiivanov, K. I. Adsorption forms of CO₂ on MIL-53(Al) and MIL-53(Al)-OH_x as revealed by FTIR spectroscopy. *J. Phys. Chem. C* **2017**, 121, 18665–18673.

(32) Titov, K.; Zeng, Z.; Ryder, M. R.; Chaudhari, A.; Civalieri, B.; Kelley, C. S.; Frogley, M. D.; Cinque, G.; Tan, J.-C. Probing dielectric properties of metal–organic frameworks: MIL-53(Al) as a model system for theoretical predictions and experimental measurements via synchrotron far- and mid-infrared spectroscopy. *J. Phys. Chem. Lett.* **2017**, 8, 5035–5040.

(33) Wilson, E. B., Jr The normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule. *Phys. Rev.* **1934**, 45, 706.

(34) Rallapalli, P.; Patil, D.; Prasanth, K. P.; Somani, R. S.; Jasra, R. V.; Bajaj, H. C. An alternative activation method for the enhancement

of methane storage capacity of nanoporous aluminum terephthalate, MIL-53(Al). *J. Porous Mater.* **2010**, 17, 523–528.

(35) Férey, G. Swelling hybrid solids. *Z. Anorg. Allg. Chem.* **2012**, 638, 1897–1909.

(36) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54, 11169.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, 3865.

(38) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 50, 17953.

(39) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1976**, 13, 5188.

(40) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, 27, 1787–1799.

(41) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, 32, 1456–1465.

(42) Giannozzi, P.; Baroni, S. Vibrational and dielectric properties of C₆₀ from density-functional perturbation theory. *J. Chem. Phys.* **1994**, 100, 8537–8539.

(43) Baroni, S.; De Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **2001**, 73, S15.

(44) King-Smith, R.; Vanderbilt, D. Theory of polarization of crystalline solids. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47, 1651.

(45) Resta, R. Macroscopic polarization in crystalline dielectrics: the geometric phase approach. *Rev. Mod. Phys.* **1994**, 66, 899.

(46) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **2005**, 167, 103–128.

(47) Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. CP2K: atomistic simulations of condensed matter systems. *WIREs Comput. Mol. Sci.* **2014**, 4, 15–25.

(48) Goedecker, S.; Teter, M.; Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54, 1703.

(49) Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Mod. Phys.* **1984**, 52, 255–268.

(50) Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **1984**, 81, 511–519.

(51) Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A: At, Mol, Opt. Phys.* **1985**, 31, 1695.

(52) Martyna, G. J.; Klein, M. L.; Tuckerman, M. Nosé–Hoover chains: the canonical ensemble via continuous dynamics. *J. Chem. Phys.* **1992**, 97, 2635–2643.

(53) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row, 1976.

(54) Luber, S.; Iannuzzi, M.; Hutter, J. Raman spectra from ab initio molecular dynamics and its application to liquid S-methylxirane. *J. Chem. Phys.* **2014**, 141, 094503.

(55) Fonari, A.; Stauffer, S. vasp_raman.py. <https://github.com/raman-sc/VASP/> (2013).

(56) Debie, E.; De Gussem, E.; Dukor, R. K.; Herrebout, W.; Nafie, L. A.; Bultinck, P. A confidence level algorithm for the determination of absolute configuration using vibrational circular dichroism or Raman optical activity. *ChemPhysChem* **2011**, 12, 1542–1549.

(57) Covington, C. L.; Polavarapu, P. L. Similarity in dissymmetry factor spectra: a quantitative measure of comparison between experimental and predicted vibrational circular dichroism. *J. Phys. Chem. A* **2013**, 117, 3377–3386.

(58) Merrick, J. P.; Moran, D.; Radom, L. An evaluation of harmonic vibrational frequency scale factors. *J. Phys. Chem. A* **2007**, 111, 11683–11700.

(59) Paulechka, Y. U.; Kabo, G. J.; Blokhin, A. V.; Shaplov, A. S.; Lozinskaya, E. I.; Golovanov, D. G.; Lyssenko, K. A.; Korlyukov, A. A.; Vygodskii, Y. S. IR and X-ray study of polymorphism in 1-alkyl-3-

methylimidazolium bis(trifluoromethanesulfonyl)imides. *J. Phys. Chem. B* **2009**, *113*, 9538–9546.

(60) Alecu, I.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational thermochemistry: scale factor databases and scale factors for vibrational frequencies obtained from electronic model chemistries. *J. Chem. Theory Comput.* **2010**, *6*, 2872–2887.

(61) Duan, S.; Fang, P.-P.; Fan, F.-R.; Broadwell, I.; Yang, F.-Z.; Wu, D.-Y.; Ren, B.; Amatore, C.; Luo, Y.; Xu, X.; et al. A density functional theory approach to mushroom-like platinum clusters on palladium-shell over Au core nanoparticles for high electrocatalytic activity. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5441–5449.

(62) Schindler, W.; Jonas, J. Solvent effects on vibrational phase relaxation and frequency shifts in isobutylene. *J. Chem. Phys.* **1980**, *73*, 3547–3552.

(63) Centrone, A.; Siberio-Pérez, D. Y.; Millward, A. R.; Yaghi, O. M.; Matzger, A. J.; Zerbi, G. Raman spectra of hydrogen and deuterium adsorbed on a metal–organic framework. *Chem. Phys. Lett.* **2005**, *411*, 516–519.

(64) Mowat, J. P. S.; Seymour, V. R.; Griffin, J. M.; Thompson, S. P.; Slawin, A. M. Z.; Fairen-Jimenez, D.; Düren, T.; Ashbrook, S. E.; Wright, P. A. A novel structural form of MIL-53 observed for the scandium analogue and its response to temperature variation and CO₂ adsorption. *Dalton Trans.* **2012**, *41*, 3937–3941.

(65) Férey, G.; Serre, C. Large breathing effects in three-dimensional porous hybrid matter: facts, analyses, rules and consequences. *Chem. Soc. Rev.* **2009**, *38*, 1380–1399.

Paper V

**Tuning the balance between dispersion and entropy
to design temperature-responsive flexible
metal-organic frameworks**

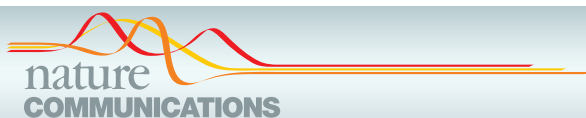
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Nature Communications, **2018**, 9, 4899

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J. Wieme performed the DFT simulations and had a large contribution in the interpretation of the results as well as the preparation of the manuscript.

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ARTICLE

DOI: 10.1038/s41467-018-07298-4

OPEN

Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks

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Temperature-responsive flexibility in metal-organic frameworks (MOFs) appeals to the imagination. The ability to transform upon thermal stimuli while retaining a given crystalline topology is desired for specialized sensors and actuators. However, rational design of such shape-memory nanopores is hampered by a lack of knowledge on the nanoscopic interactions governing the observed behavior. Using the prototypical MIL-53(Al) as a starting point, we show that the phase transformation between a narrow-pore and large-pore phase is determined by a delicate balance between dispersion stabilization at low temperatures and entropic effects at higher ones. We present an accurate theoretical framework that allows designing breathing thermo-responsive MOFs, based on many-electron data for the dispersion interactions and density-functional theory entropy contributions. Within an isorecticular series of materials, MIL-53(Al), MIL-53(Al)-FA, DUT-4, DUT-5 and MIL-53(Ga), only MIL-53(Al) and MIL-53(Ga) are proven to switch phases within a realistic temperature range.

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ARTICLE

NATURE COMMUNICATIONS | DOI: 10.1038/s41467-018-07298-4

The recent discovery of flexible porous materials ushered in an intriguing new era in science^{1–4}. Their combination of cooperative structural transformability and crystallinity was initially perceived as counterintuitive. For some metal-organic frameworks (MOFs)^{3,6}, such as the wine-rack-topology MIL-53 materials, phase transformations were observed between a narrow-pore (np) and large-pore (lp) phase (Fig. 1a)^{7,8}. Such a phase transformation—also called breathing—is typically accompanied by large volume changes of about 40% and may be induced by external stimuli such as temperature, mechanical pressure, and adsorption of guest molecules^{7,9–12}. These features are promising for applications such as controlled drug release¹³, gas adsorption and separation^{10,14,15}, and sensors¹⁶. A particularly captivating case is that of temperature-responsive breathing. The search for a new generation of temperature-controlled smart materials attracts much interest^{17–19}, in which thermally triggered breathing MOFs may play a pivotal role. Unfortunately, MOFs exhibiting this flexibility are rare^{20–26}. Indeed, rational design of MOFs with shape-memory nanopores remains a formidable challenge^{27,28}. Nowadays their discovery is based on

serendipity, since the nanoscopic interactions and transition mechanisms governing the flexible behavior are not properly understood. Motivated by this lack of understanding, we investigate in this contribution the intrinsic physical origin of temperature-responsive breathing using thermodynamic considerations and state-of-the-art electronic-structure calculations.

Experimentally, framework flexibility can be followed by monitoring the response of a material as a function of an applied external stimulus. A breathing transition yields a sudden volume change at a given value of the external trigger. The principle is illustrated in Fig. 1 for MIL-53(Al), a material for which Liu et al.⁷ observed a reversible phase transformation as a function of temperature. A significant temperature hysteresis was found (Fig. 1b): the transition from the lp to the np structure occurs in a temperature window around T_2 , while the transition from the np to the lp structure takes place around T_4 . For MIL-53(Al), the experimental transition temperatures lie between 125–150 K and between 325–375 K, respectively. The experiments enable to unambiguously detect stimulus-responsive behavior, but they do not allow the construction of the underlying thermodynamic

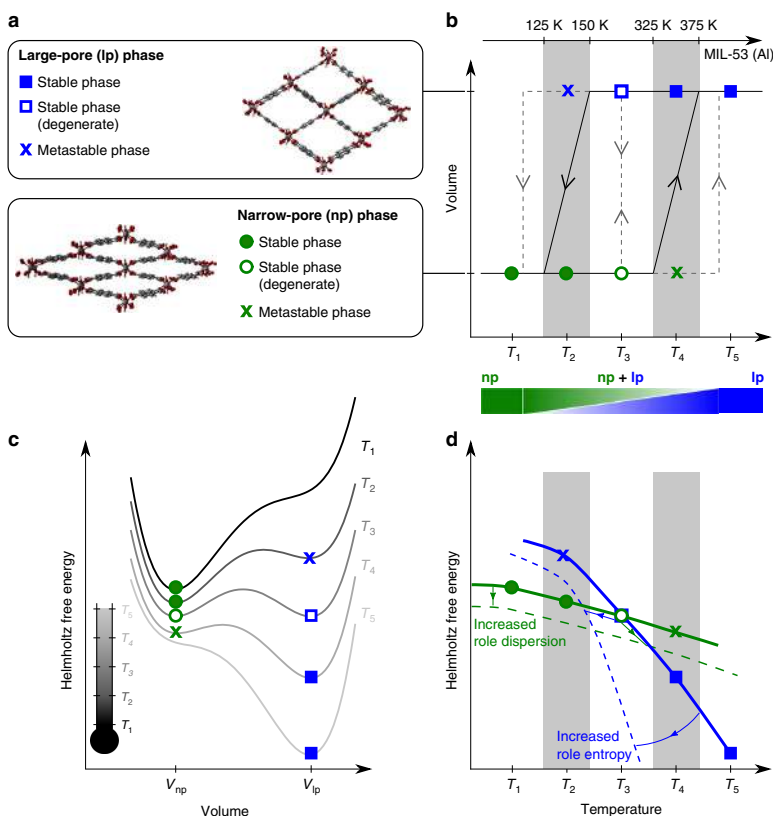


Fig. 1 Temperature-induced breathing of a flexible MOF. The definition of the blue and green symbols is indicated in the top left panel. **a** Two (meta)stable phases of MIL-53(Al). **b** Thermo-responsive behavior of MIL-53(Al) as measured by experiment. The system switches as a function of temperature between the np and lp phase with a hysteresis loop. Different transition regimes are indicated with arrows (see main text). The gray shaded areas correspond to the experimentally measured transition regions⁷. **c** Hypothetical Helmholtz free energy curves as a function of volume at different temperatures (T_1 , T_2 , T_3 , T_4 , T_5) as an explanation for the observed experimental behavior. **d** Hypothetical evolution of the Helmholtz free energy for the np and lp phase as a function of temperature. The gray shaded areas correspond to the experimentally measured transition regions⁷

potential⁴ governing the observed behavior, like the Helmholtz free energy F . The experimental observations do, however, suggest that low-temperature Helmholtz free energies favor the np phase, whereas at higher temperature the lp phase prevails. Apart from that the observations provide little guidance for the development of new thermo-responsive materials.

A thorough understanding of the thermodynamic potential is critical for design of dedicated applications, e.g., tuning the transition temperatures for sensors and actuators. Some hypothetical Helmholtz free energy profiles in terms of the volume are shown in Fig. 1c for various temperatures. The low- (T_1) and high-temperature (T_5) profiles are extreme cases and a broad temperature window with bistable behavior is expected (T_2 – T_4), as suggested by the observed hysteresis. The relative Helmholtz free energy difference between the two phases determines the possibility of a phase transformation as a function of temperature. Based on the hypothetical curves in Fig. 1c, the temperature dependence of the Helmholtz free energy of both phases (F_{np} and F_{lp}) is sketched in Fig. 1d. To obtain an np-to-lp transition at T_4 and an lp-to-np transition at T_2 , F_{np} needs to be lower than F_{lp} for temperatures below T_2 and F_{lp} needs to be lower than F_{np} for temperatures higher than T_4 . Such behavior requires a critical crossing temperature of the two curves (T_{cross}) at T_3 , i.e., between T_2 and T_4 .

Theoretical investigations are indispensable to pinpoint the microscopic factors controlling the shape of the thermodynamic potential. Moreover, theory can overcome some puzzling dependences on the experimental synthesis procedure. Some groups found non-breathing MIL-53(Al) frameworks when procedures other than standard hydrothermal synthesis were used, for example^{29–33}. These experiments indicate that the material could be trapped in a metastable phase due to interactions with the solvent³⁴. Theoretical calculations are not hampered by such a critical experimental sensitivity and may therefore advance understanding and development of flexible MOFs. Ideally, theory can even predict materials properties of yet to be synthesized MOFs and stimulate the discovery of new flexible MOFs. Various groups explored computer-aided design by screening hypothetical MOFs for several desired properties and functions^{35–38}.

Previous theoretical studies have suggested that the lp-np relative stability of MIL-53(Al) is dependent on two factors: long-range dispersion interactions and vibrational entropy^{39,40}. Dispersion is related to the attractive part of a van der Waals-type nonbonding interaction, while vibrational entropy connects to the amount of freedom the atoms have to move. Walker et al.⁴⁰ showed using density-functional theory (DFT) that long-range dispersion is critical to obtain the np phase at low temperatures, as it is mainly stabilized by π – π stacking interactions between the organic linkers. The strength of the dispersion interactions is,

however, very method dependent (Supplementary Table 4); stronger dispersion interactions shift the F_{np} curve down with respect to F_{lp} , yielding a higher T_{cross} (Fig. 1d). To date, there is no clear understanding on the impact of the chosen dispersion method on the observed thermo-responsive behavior. The stabilization of the lp phase at higher temperatures is caused by entropy⁴¹, as the linkers have more freedom to move in this phase. An increase of the entropic part of the Helmholtz free energy stabilizes the lp phase, yielding lower critical temperatures for the transition.

Herein, we critically assess the impact of dispersion interactions and thermal effects on the breathing behavior of MIL-53(Al) using state-of-the-art theoretical calculations. To ensure an accurate account of the 0 K lp-np relative stability, we present the first many-electron treatment of a flexible MOF by applying the random-phase approximation to the correlation energy (RPA). Our results provide unprecedented insight into the mechanism behind temperature-induced breathing, which enables formulating some minimal design rules for tailoring flexible MOFs with a temperature switch in a desired window. We demonstrate for a series of isorecticular materials that rational design of flexible MOFs is now within reach. In addition, our high-level computational approach shows some deficiencies in commonly used electronic-structure methods which may stimulate the theoretical community to investigate hybrid materials like flexible MOFs as a novel test bed for future theory development.

Results

Temperature-dependent stability of the np and lp phases. We calculated the harmonic Helmholtz free energy difference between np and lp MIL-53(Al) as a function of temperature using various exchange-correlation (XC) functionals and dispersion schemes. Table 1 lists the differences at 130 and 350 K, which are situated in the experimental transition windows⁷. None of the methods reproduce the expected relative stability for both phases. Because the np phase remains the most stable structure at both temperatures, the expected crossing point (Fig. 1d) is situated at too high temperatures (410–1474 K). As mentioned above, the relative position of the Helmholtz free energy curves of both phases is expected to be dictated by a delicate balance between dispersion and entropy. The individual contributions to the energy difference are given in Table 1 and show that the electronic energy is the dominating term for most methods in the experimental temperature window. There is a substantial theoretical spread on this energy (30 kJ mol^{–1}), which confirms the strongly scattered DFT data in literature (Supplementary Table 4). The entropic contribution to the Helmholtz free energy at 300 K varies to a lesser extent (7 kJ mol^{–1}). Getting the

Table 1 Helmholtz free energy, energy and entropy difference between the lp and np phase of MIL-53(Al) for different methods

	ΔF_{lp-np} at 130 K (kJ mol ^{–1})	ΔF_{lp-np} at 350 K (kJ mol ^{–1})	T_{cross} (K)	ΔE_{lp-np}^{el} (kJ mol ^{–1})	ΔE_{lp-np}^{vib} at 240 K (kJ mol ^{–1})	$-T\Delta S_{lp-np}^{vib}$ at 240 K (kJ mol ^{–1})
PBE + D2	10.9	2.4	410	15.7	0.5	–9.4
PBE + MBD	20.8	13.3	735	24.5	0.3	–8.3
SCAN + rVV10	25.7	14.0	799	28.3	0.3	–10.3
vdW-DF2	31.2	21.0	799	35.5	2.6	–11.3
PBE + MBD/FI	15.0	11.3	1034	16.4	0.8	–4.2
PBE + D3(BJ)	24.1	19.1	1201	26.1	0.4	–5.5
PBEsol + D3(BJ)	41.4	34.6	1474	44.2	1.3	–7.5

The Helmholtz free energy difference ΔF_{lp-np} was calculated via the harmonic approximation for different DFT methods in the np-to-lp (at 130 K) and lp-to-np (at 350 K) transition range. The crossing temperature T_{cross} , i.e., when both phases are in thermodynamic equilibrium ($\Delta F_{lp-np} = 0$), is also given. The different contributions to the Helmholtz free energy are given in the last three columns: the electronic energy difference ΔE_{lp-np}^{el} , the vibrational energy difference ΔE_{lp-np}^{vib} and the entropic contribution $-T\Delta S_{lp-np}^{vib}$. The latter two depend on temperature and are given for a value in the middle of the experimental hysteresis loop

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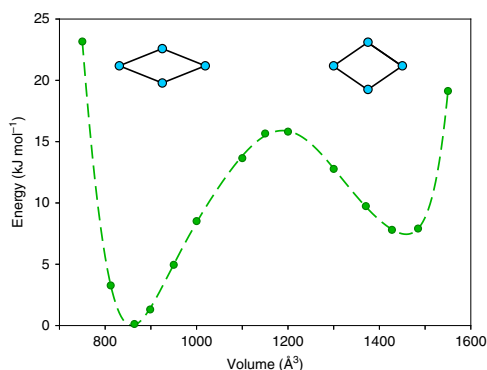


Fig. 2 RPA + SE electronic energy profile as a function of volume for MIL-53(Al)

electronic energy difference right is therefore essential to accurately determine the overall position of T_{cross} .

This knowledge motivated us to construct high-accuracy data for the electronic energies using the random-phase approximation. This many-body perturbative approach to the correlation energy goes beyond the state of the art with respect to the computational treatment of flexible porous materials. It seamlessly integrates long-range dispersion effects with short-range interactions. Although beyond-RPA contributions may improve the performance even further (see Methods section), it already results in an excellent agreement with experimental data for various systems^{42–45}. Because of the importance of single-excitation (SE) effects for molecular solids^{46–48}, this contribution was moreover included and found to be crucial for our system as well (Supplementary Figure 5 in Supplementary Note 7). The energy-versus-volume profile of MIL-53(Al) at the RPA + SE level of theory is shown in Fig. 2. The energy difference between the lp and np phase amounts to only 7.4 kJ mol^{-1} . Furthermore, a barrier of more than 8 kJ mol^{-1} is found in both directions, facilitating the existence of a metastable lp state even at 0 K.

Using these high-accuracy data for the electronic energies, we reassessed the position of T_{cross} . Because current computational resources do not yet allow to calculate RPA + SE thermal corrections for large systems like MOFs, Fig. 3 shows $\Delta F_{\text{lp-np}}(T)$ with thermal corrections at various DFT levels (Table 1) on top of the RPA + SE electronic energy difference. It was previously shown that the specific choice of the XC functional and dispersion scheme could influence the thermal corrections and relative stability at room temperature in, for example, molecular crystals⁴⁹. The orange region in Fig. 3 delimits the method dependence of the zero-point, vibrational and entropic contributions. Starting from the RPA + SE-favored np at 0 K, most methods change sign in the experimentally determined temperature window between T_2 and T_4 . Combining an accurate electronic energy difference with standard DFT vibrational entropy contributions hence yields a crossing temperature in accordance with experiment^{7,50} and thermodynamic models^{51,52}.

As RPA + SE is computationally too demanding to be employed on a scale required for materials design, it is important to identify cheaper DFT methods with a similar predictive quality⁵³. We therefore compared our DFT data to the RPA + SE benchmark and extended the set of assessed DFT methods to more advanced XC and dispersion schemes. Table 2 confirms that despite the omnipresent use of DFT in materials science, flexible

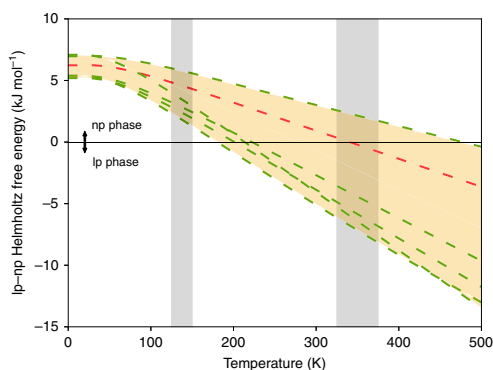


Fig. 3 Helmholtz free energy difference between the lp and np phase of MIL-53(Al) as a function of temperature. This Helmholtz free energy difference was calculated with the harmonic approximation. An accurate electronic energy difference between the lp and np phase was obtained using RPA + SE. The displayed spread (orange shaded area) is obtained using predictions of the evolution of the Helmholtz free energy difference with various density-functional theory methods (Table 1). The red curve indicates the corrections at the PBE + D3(BJ) level of theory, while the green curves represent the other levels of theory (from bottom to top starting from the right: vdW-DF2, SCAN + rVV10, PBE + D2, PBE + MBD, PBEsol + D3(BJ) and PBE + MBD/FI). The individual Helmholtz free energy curves are shown in more detail in Supplementary Note 6 (Supplementary Figure 4). The gray shaded areas correspond with the experimentally measured transition regions⁷

MOFs are a challenging case for common DFT-based methods, which should be used with caution. Nonetheless, several interesting trends can be extracted. While dispersion corrections are necessary to stabilize the np phase, most methods overbind it, some even to the extent that they fail to find a metastable lp state. Although a rather large spread is observed on the equilibrium volumes too, we show in Supplementary Note 3 (Supplementary Figures 2 and 3, Supplementary Tables 7–15) that the structural differences affect the lp-np energy difference only to a limited extent. The deviations are mostly due to the used dispersion model. Many popular methods, such as the Grimme D2 and D3 schemes, describe dispersion by means of purely pairwise atomic interactions. However, higher-order corrections to the dispersion interaction were reported to play an important role in some other materials^{54–57}, and are now found to be crucial to get the relative phase stability of MIL-53(Al) right. Indeed, many-body effects (MBD vs TS and D3(BJ)^{ATM} vs. D3(BJ)) destabilize the np phase and bring relative energy differences much closer to the benchmark value. This is also reflected in the equilibrium volumes of both phases, which are in general too small, but improve for schemes beyond pairwise atomic interactions. We further note that a recent adaptation of the promising MBD scheme, MBD/FI, performs better than the original. This can probably be ascribed to the revised description of the polarizability for systems with a strongly ionic character, relevant for the one-dimensional metal-oxide chain in MIL-53(Al).

Overall PBE + D3(BJ)^{ATM} yields an energy difference of 6.2 kJ mol^{-1} in closest agreement with the reference RPA + SE value for this particular system. One should nevertheless be cautious to extrapolate the good performance of this dispersion method to other materials. A key problem lies in the choice of the dispersion model parameters and the coupling with the XC functional. For van der Waals-type bonding, dispersion corrections are designed

Table 2 The electronic energy difference between the lp and np phase of MIL-53(Al) with different methods				
	V_{np} (Å ³)	V_{lp} (Å ³)	ΔE_{lp-np}^l (kJ mol ⁻¹)	$\Delta E_{lp-np}^{l,s}$ (kJ mol ⁻¹)
Experiment (77 K) ⁷	864	1419 ^a	–	–
RPA + SE	860	1455	7.4	7.7 ± 3.5 ^b
PBE	np unstable	1489	np unstable	-118.5
PBE + D2	808	1457	15.7	12.8
PBE + D3(BJ)	843	1426	26.6	26.1
PBE + D3(BJ) ^{ATM}	874	1448	5.8	6.2
HSE06 + D3(BJ)	825	lp unstable	lp unstable	42.3
HSE06 + D3(BJ) ^{ATM}	850	1389	22.3	22.4
B3LYP + D3(BJ)	789	lp unstable	lp unstable	58.9
B3LYP + D3(BJ) ^{ATM}	806	1405	43.8	39.0
PBE + TS	793	lp unstable	lp unstable	74.2
PBE + MBD	828	1425	25.8	24.5
PBE + MBD/FI	851	1439	16.4	16.4
SCAN	np unstable	1430	np unstable	-43.6
SCAN + rVV10	803	1384	31.2	28.3
vdW-DF2	869	1456	34.8	35.5
MO6-L	829	lp unstable	lp unstable	36.6

ΔE_{lp-np}^l is the 0 K electronic energy difference at the equilibrium volumes of both phases (V_{np} and V_{lp}) relaxed with the specific method (or PBE + D3(BJ) for RPA + SE, see Methods). $\Delta E_{lp-np}^{l,s}$ is the 0 K electronic energy difference at fixed structures (864 Å³ (np) and 1427 Å³ (lp)). The lp and np structures are provided in Supplementary Data 1 and 2. Generalized gradient approximation (GGA), meta-GGA and hybrid XC functionals were included together with dispersion models ranging from pairwise (D2, D3(BJ), TS) to many-body schemes (D3(BJ)^{ATM}, MBD, MBD/FI). Three XC functionals inherently including long-range dispersion were also tested, i.e., SCAN + rVV10, vdW-DF2 and MO6-L. A full list of references to these methods is included in the Methods section

^aThe sample was going towards the np phase on a longer time scale than the measurement⁷

^bThe error bar on the RPA + SE result reflects the uncertainty due to numerical convergence effects. More information on how this error bar was determined can be found in the Methods section

to yield results largely independent of the parent functional for a set of reference molecules. Even though MOFs are not included in this set, after adding dispersion corrections, the energy difference between the lp and np becomes reasonably independent on the parent functional. This compensation is indeed observed for TS and MBD, but it is less effective for D3-derived methods (Supplementary Tables 16 and 17). This might explain why the success of PBE + D3(BJ)^{ATM} does not transfer to HSE06 + D3(BJ)^{ATM}. In addition the SCAN functional yields results that are less satisfactory than one might hope^{58,59}. As we show in Supplementary Note 4 (Supplementary Table 16), this effect is related to the nontrivial coupling between the SCAN functional and dispersion schemes⁶⁰. A meticulous choice of both the XC functional and the dispersion scheme is therefore of utmost importance to obtain reliable energy values for flexible MOFs, which are prone to subtle long-range interactions. The above discussion underlines the complex physics in MIL-53(Al) and the challenge of correctly capturing it. The PBE + D3(BJ)^{ATM} method serves as a convenient and cheap solution for the system at hand, although this might be somewhat accidentally.

Transition mechanism and barrier between np and lp. The approach used so far identifies the thermodynamically preferred phase at various temperatures. Indeed, bistable behavior is a necessary condition for breathing. However, bistability alone is not sufficient to guarantee temperature-responsive flexibility. The transition mechanism determines whether it is possible to reversibly switch between the two phases. Two limiting scenarios may be distinguished, as schematically shown in Fig. 1b. If the stability of the two phases were the only criterion, both the forward and backward transition would occur at the temperature T_3 where the two phases become isoenergetic, and no hysteresis would be found. In the other extreme case, a phase transition would only take place when the barrier between the two (meta) stable states fully disappears and only one minimum is present in the Helmholtz free energy curve. This mechanism corresponds to the hypothesis of collective behavior, where the entire framework

must transform in a collective fashion. Even the smallest barrier in the thermodynamic potential of a single unit cell then translates to a huge barrier for the entire system⁶¹. Under this assumption the transition would happen between T_4 and T_5 for np to lp, and between T_2 and T_1 for lp to np (Fig. 1d).

Our high-accuracy RPA + SE data in Figs. 2 and 3 suggest an intermediate transition scenario. The experimentally observed hysteresis confirms the importance of the barrier between lp and np, but the RPA + SE barrier is too high to completely disappear within a reasonable temperature range. Fully collective behavior is therefore unrealistic. This conclusion is corroborated by Mendt et al., who found a fraction of lp material at temperatures down to 9 K³⁰. Instead, the transition may be facilitated by surfaces or lattice imperfections, which serve as nucleation sites. Recent experimental studies showed that guest-responsive breathing of several MOFs is critically affected by the number of defects^{27,62,63}. Larger crystals, which contain more defects, kinetically promote the phase transition yet maintain the center of the hysteresis loop²⁷. Triguero et al. proposed a theoretical layer-by-layer transition model, which assumes that a collective lp-np transformation only occurs in a single layer of MIL-53(Al) at a time⁶⁴. This idea is supported by first-principles molecular dynamics of guest-induced breathing in MIL-53(Sc)⁶⁵. The temperature-induced transition of a framework may therefore nucleate through a combination of defects, temperature fluctuations and strains, after which the locally increased stress causes the transformation to propagate further through the lattice in a layer-by-layer fashion. In view of this suggested complex transition mechanism, the RPA + SE barrier should be considered as one of several parameters determining the experimental transition temperature.

Design of temperature-induced flexibility. Our analysis of MIL-53(Al) identified the mechanisms underlying temperature-dependent breathing, putting particular emphasis on the shift from long-range dispersion stabilization at low temperature to entropic stabilization at higher temperatures. We can use this

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knowledge to rationalize changes in the crossing temperature for materials isorecticular to MIL-53(Al). Inspired by the good correspondence with RPA + SE for MIL-53(Al), we consider a series of materials with very similar structural characteristics and apply PBE + D3(BJ)^{ATM} for the electronic energy difference in combination with thermal corrections at the PBE + D3(BJ) level. Note that if flexible MOFs with a more different make-up would be considered, the most appropriate levels of theory for this procedure may vary and need to be rechecked. As an initial design strategy, we modulate the framework by changing the organic linkers. MIL-53(Al)-FA⁶⁶, DUT-4^{67,68}, and DUT-5⁶⁷ have a similar inorganic chain as MIL-53(Al) but are connected with fumaric acid, biphenyl and naphthalene dicarboxylate linkers, respectively (see also Supplementary Table 19 in Supplementary Note 8).

Figure 4 shows the electronic energy profiles at 0 K (Fig. 4c) and the Helmholtz free energy differences between the lp and np phase as a function of temperature (Fig. 4a). The lack of π - π stacking interactions limits the dispersion stabilization of the np

phase in MIL-53(Al)-FA, while on the contrary, the extended linkers in the case of DUT-4 and DUT-5 stabilize it excessively. The Helmholtz free energy moreover varies more rapidly for DUT-5 as a function of temperature due to the mobility of the biphenyl linker in the lp phase. The easy rotation of the phenyl rings relative to each other gives rise to an increased lp-np entropy difference compared to the rigid naphthalene linker in DUT-4, for example. However, none of the considered frameworks is expected to display temperature-induced breathing. MIL-53(Al)-FA assumes an lp structure over the entire temperature range, and the stability of the np phase of DUT-4 and DUT-5 will never be compensated by entropy effects at temperatures for which the material remains stable. Changing the organic linkers thus results in a large shift of the Helmholtz free energy difference, which leaves little room for fine-tuning the temperature window for applications in these types of frameworks.

To achieve a subtler effect, we modified the inorganic chain by replacing aluminum with gallium^{69,70}. As the coordination

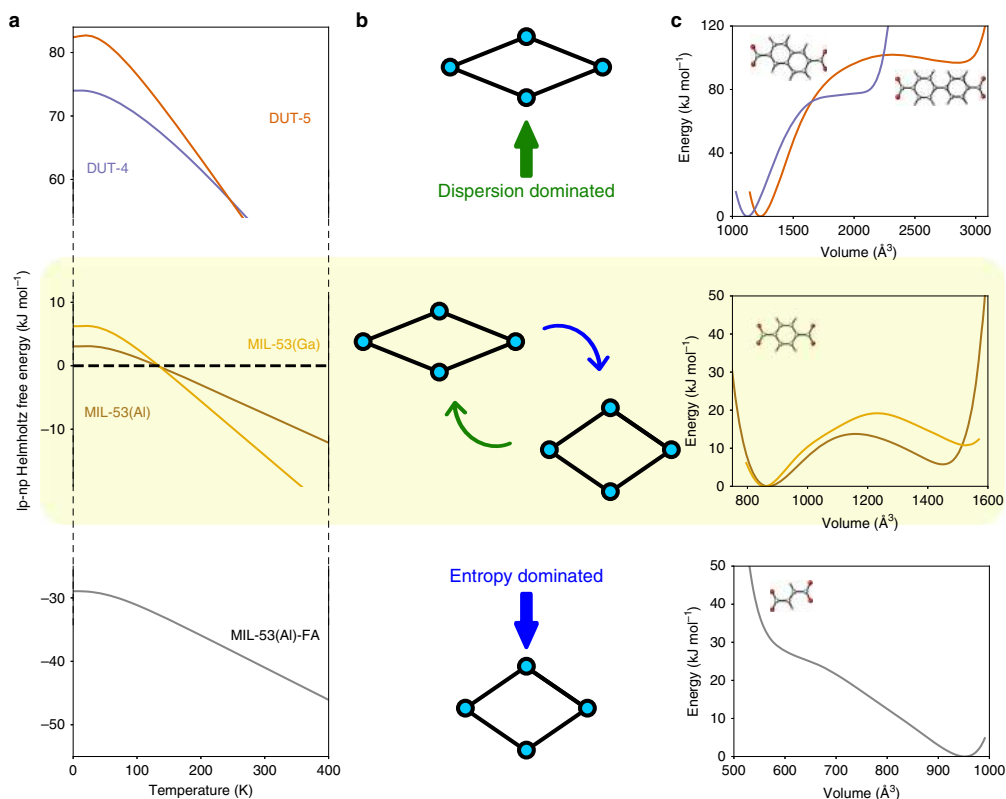


Fig. 4 Design of temperature-dependent flexibility in isorecticular MIL-53 materials. Several experimentally synthesized materials are considered: MIL-53(Al)-FA (or A520)⁶⁶, MIL-53(Al)⁸, MIL-53(Ga)⁶⁹ (or IM-19⁷⁰), DUT-4⁶⁷ (or MIL-69⁶⁸), and DUT-5⁶⁷. The yellow shaded area highlights the desired temperature-responsive case. **a** Helmholtz free energy difference between the lp and np phase as a function of temperature for the series of isorecticular MIL-53 frameworks. The harmonic temperature corrections were calculated at the PBE + D3(BJ) level of theory, and were added on top of the 0 K PBE + D3(BJ)^{ATM} electronic energy difference. **b** Schematic depiction of the (meta)stable phases and the dominating contributions. **c** Electronic energy profiles as a function of the volume for different materials at the PBE + D3(BJ)^{ATM} level of theory. The corresponding organic linkers are indicated in the different panels

environment around gallium is more diffuse, it can deform more easily. This in turn enables the framework to reduce the strain energy penalty in the distorted dispersion-dominated dense phase, yielding an overall np stabilization. On the other hand, the entropy of the lp phase is also raised with respect to the np phase, overall compensating the effect on T_{cross} for MIL-53(Ga) and resulting in an only negligible shift (Fig. 4a).

Our findings for this series of materials are validated by the limited available experimental literature (see also Supplementary Table S20). MIL-53(Al)-FA resides in the lp phase at room temperature, and was only reported to reversibly breathe under influence of pressure^{71,72}. DUT-4 has been hydrothermally synthesized in an np phase—also called MIL-69⁶⁸—and remains nonporous up to more than 600 K, after which the structure decomposes. Note that although DUT-4 and DUT-5 could also be synthesized in an lp phase using DMF⁶⁷, similar to MIL-53(Al)³⁰, they were trapped in this metastable state. They do not show intrinsic flexibility as, for instance, lp DUT-4 could not be converted to its stable nonporous state. Finally, MIL-53(Ga) was experimentally found to be in a nonporous np phase at room temperature and undergoes a phase transition to the lp phase between 450 and 520 K^{69,70,73}. This is consistent with our crossing temperature, even if a quantitative prediction of the transition range would require more insight in the transition mechanism, as discussed above.

Discussion

As evidenced by our study of MIL-53-type MOFs, temperature-induced breathing can only be achieved when a delicate balance between several constraints is fulfilled. It suggests why thus far only a limited number of materials were found with this feature. To design a material with temperature-induced breathing behavior, at least two (meta)stable phases should exist, which are required to change relative stability as a function of temperature. The np phase should be stabilized at low temperatures by supramolecular interactions, while entropic contributions to the Helmholtz free energy drive the relative stability towards the lp phase with increasing temperature. The stability switch needs to occur at temperatures for which the material is still thermally stable. The exact transition temperature is dependent on the transition mechanism but the change of sign of the lp-np Helmholtz free energy difference is a necessary condition to obtain a temperature-dependent phase switch. These clear design rules could stimulate experimentalists to develop the next-generation of thermo-responsive MOFs.

A theoretical assessment of the above constraints only becomes possible when a sufficiently accurate level of theory is used. DFT calculations may be ubiquitous in materials science, but for flexible MOFs most common DFT approaches fall short. The XC functional and dispersion scheme need to be selected carefully as they largely determine the Helmholtz free energy difference for these materials. We took a major step forward by accurately determining the phase stability of the prototypical breathing material, MIL-53(Al), using computationally demanding high-level RPA + SE calculations. Comparison with various commonly used electronic-structure methods revealed some interesting physical trends, and exposed at the same time some issues with popular XC functionals and dispersion corrections. This will hopefully stimulate the community developing functionals to investigate the case of flexible MOFs carefully. Because the cheaper PBE + D3(BJ)^{ATM} method reasonably reproduced the benchmark results for MIL-53(Al), we were able to extend the discussion to a broader set of isorectical materials, where we could possibly benefit from error compensation. However, care must be taken to extend this level of theory towards widely

different materials as a sensible selection of the best functional is certainly system dependent. Future refinement of temperature effects may be obtained via more advanced estimates for the entropy, e.g., using molecular dynamics simulations⁷⁴.

Temperature-induced breathing has the potential to define an entirely new class of temperature-triggered sensors and actuators, provided materials can be designed with a tunable switch in the desired temperature window. Np-to-lp phase transitions can be tuned by finding the right balance between dispersive and entropic effects. One option for modification exists in changing the organic linkers. The modified dispersion interaction hugely impacts the relative stability and thus the operation temperature window. Alternative and more subtle pathways include linker functionalization and local changes to the metal coordination. In these cases, shifts in electron density and changes in framework rigidity affect the np stabilization less directly. Additionally, entropic design may exploit linkers with larger mobility to enhance lp stability and decrease transition temperatures. The insights obtained here show that dispersive and entropic effects need to be tuned appropriately and pave the way to design thermo-responsive MOFs for desired applications.

Methods

General settings. All calculations of MIL-53(Al) were carried out with the Vienna Ab initio Simulation Package (VASP)⁷⁵ using the projector-augmented wave (PAW) method^{66,77}. The computational unit cell contains four organic linkers and thus 76 atoms in total. We employed the recommended GW-ready PBE PAW potentials for all elements and exchange-correlation (XC) functionals (v5.4). For the Al atoms, 3s and 3p electrons were explicitly included. For the C and O atoms, the 2s and 2p electrons were considered as valence electrons. For the H atoms, the 1s electron was explicitly treated. The specific settings for the density-functional theory (DFT) and random-phase approximation (RPA) simulations are listed below.

DFT calculations. All DFT calculations on MIL-53(Al) were performed with a plane-wave kinetic-energy cutoff of 600 eV and using Gaussian smearing with a smearing width of 0.05 eV. Projection operators were evaluated in reciprocal space. A $2 \times 6 \times 6 / 2 \times 6 \times 2$ Monkhorst-Pack k-grid was used for the np/lp phase⁷⁸. The real-space Fast Fourier Transform (FFT) grid was able to describe wavevectors up to two times the maximum wavevector present in the basis set. An augmentation grid that is twice as large was used to avoid wrap-around errors in order to obtain accurate forces. The electronic (ionic) convergence criterion was set to 10^{-8} (10^{-7}) eV, except for the hybrid XC functionals where it was slightly lowered to 10^{-6} (10^{-5}) eV. The Hartree-Fock (HF) kernel for the latter was evaluated on a k-grid reduced by a factor of two in each reciprocal direction, which we found to be possible without a loss of accuracy⁷⁹.

We considered GGA (generalized gradient approximation)^{80–82}, meta-GGA^{83,84} and hybrid^{85–87} XC functionals, combined with dispersion schemes ranging from pairwise additive^{88–91} to many-body approaches^{92–95}. In addition, we included XC functionals in which some long-range dispersion is inherently captured, such as vdW-DF2⁸⁰, M06-L⁸⁴, and SCAN + rVV10⁸⁹. Most DFT simulations executed in this work consist of fixed-volume relaxations in which the positions and cell shape were optimized. The equilibrium volumes were obtained by constructing a local energy profile as a function of the volume, and by fitting a Rose-Vinet equation of state to the profile (Supplementary Figure 1)^{78,96}. Only for the DFT-D3 schemes including Axilrod-Teller-Muto (ATM)^{97,98} contributions (DFT-D3^{ATM}), optimizations were performed at the DFT-D3 level. ATM corrections were calculated with the DFT-D3 program and added a posteriori to the energy, as they have not yet been implemented in VASP. This is justified by the typically small corrections to the geometry⁹⁷. An overview of the different methodologies used in this work is given in Supplementary Note 1 (Supplementary Tables 1–3). An overview of the available experimental information (Supplementary Note 2) and our DFT optimized structures (Supplementary Note 3) is given in Supplementary Tables 5, 6, 8 and 9.

Furthermore, we considered other materials isorectical to MIL-53(Al). We mostly used the same computational settings for the DFT calculations on MIL-53(Al)-FA, MIL-53(Ga), DUT-4 and DUT-5. Only for the last two materials, the k-point grid of the np phase was lowered to a $1 \times 6 \times 6$ mesh. The computational unit cell contains four linkers for all materials. We also employed the recommended GW-ready PAW potential for the Ga atoms, which includes the 3d, 4s, and 4p electrons explicitly.

We calculated the Helmholtz free energy using the harmonic approximation for some well-known methods predicting a bistable material. To this end, we determined the dynamical matrix using 0.01 Å displacements for all atomic coordinates in a $1 \times 2 \times 1$ supercell. We only included Γ -point phonons, such that

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the expressions for the energy, entropy and the Helmholtz free energy in the harmonic approximation simplify to:

$$E(T) = E^{\text{el}} + \sum_{i=1}^{3N} \left(\frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} \right) \quad (1)$$

$$= E^{\text{el}} + E^{\text{ZPE}} + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}$$

$$S(T) = k_B \sum_{i=1}^{3N} \left(\frac{\hbar\omega_i}{k_B T} \frac{1}{e^{\beta\hbar\omega_i} - 1} - \ln \left(1 - e^{-\frac{\hbar\omega_i}{k_B T}} \right) \right) \quad (2)$$

$$F(T) = E(T) - TS(T) = E^{\text{el}} + \sum_{i=1}^{3N} \left(\frac{\hbar\omega_i}{2} + k_B T \ln \left(1 - e^{-\frac{\hbar\omega_i}{k_B T}} \right) \right) \quad (3)$$

The post-processing of the results was performed with phonopy⁹⁹.

RPA calculations. For the RPA calculations on MIL-53(Al), we applied a cubically scaling algorithm proposed and implemented in VASP by Kalktak et al.^{100,101} Such calculations combine the HF energy and RPA correlation energy using non-self-consistent calculations on top of DFT Kohn-Sham orbitals. These orbitals were generated using the SCAN meta-GGA functional^{58,83}, which was proven to provide a good starting point for non-self-consistent RPA¹⁰². We moreover included single-excitation contributions by calculating the difference between the exact exchange energy calculated using frozen SCAN orbitals and the energy obtained by a single diagonalization of the Hartree-Fock Hamiltonian set up using the SCAN orbitals¹⁰². As shown in ⁴⁷ this is practically equivalent to the singles of Ren and coworkers⁴⁸.

All RPA calculations were performed with a plane-wave kinetic-energy cutoff of 600 eV and using Gaussian smearing with a smearing width of 0.05 eV. Both for the semilocal parts and the exchange energy (EXX), the real-space FFT grid was able to describe wavevectors up to 3/2 times the maximum wavevector present in the basis set and two times as many for the grid representing the augmentation charges. Projection operators were evaluated in reciprocal space. The RPA correlation energy was determined for a $2 \times 3 \times 3$ (750–1150 Å³) or $2 \times 3 \times 2$ Γ-centered k-grid (1200–1550 Å³), while higher k-point settings were needed for the EXX energy: $3 \times 8 \times 8$ for the smaller cells and $3 \times 8 \times 5$ for the larger cells. Singles contributions were calculated at $3 \times 5 \times 5$ and $3 \times 5 \times 3$ k-grid respectively. For the RPA correlation energies, the long-wavelength contribution was neglected, which is a good approximation in case of sufficiently dense k-grids¹⁰³. In addition, the response function was expanded into plane waves up to several values of the wavevector, after which the correlation energy was extrapolated to the asymptotic limit of infinite cutoffs^{103,104}. Integration of the response function over frequency space¹⁰⁰ was performed using eight frequency points. For the contribution of single excitations, we needed to optimize wavefunctions, which were determined by means of a blocked Davidson iteration scheme using up to 10 iterations per band. Convergence was assumed as soon as the change in energy eigenvalue had decreased by a factor 1000.

Using the above settings, we estimate the numerical error bar on our RPA lp-np energy difference to be 3.5 kJ mol⁻¹. Increasing the number of k-points for the MIL-53(Al) lp EXX energy from $3 \times 8 \times 5$ to $4 \times 10 \times 6$ yielded a difference of only 6 μeV, and going from $2 \times 3 \times 3 / 2 \times 3 \times 2$ to $2 \times 5 \times 5 / 2 \times 5 \times 3$ (with a cutoff of 400 eV) changed the RPA correlation energy difference between the lp and the np phase by 8 meV. Singles contributions were found to display a similar convergence behavior as the EXX energy, leading to an estimated 0.2 meV difference between $3 \times 5 \times 5 / 3 \times 5 \times 3$ and $3 \times 8 \times 8 / 3 \times 8 \times 5$ k-grids. Raising the cutoff energy did not significantly change the relative stability of the lp and np phase: going from 600 eV to 700 eV changed the EXX energy difference by 2 meV, the RPA energy difference by 0.5 meV and the singles energy difference by 0.01 eV. The largest influence was found to be the reference determinant for the non-self-consistent RPA calculations. Changing the starting orbitals from SCAN to PBE affects the lp-np energy difference by 0.03 eV and the singles contribution by 0.015 eV. The latter error bar also captures deviations due to using a Davidson optimization rather than an exact diagonalization. Differences due to this approach were not larger than 2 meV in the neighborhood of the np volume. When assuming all error contributions to be largely independent, we arrive at a total of 36 meV or 3.5 kJ mol⁻¹ on the energy difference between the lp and np phase.

Note that the proposed error bar of 3.5 kJ mol⁻¹ only captures numerical effects and does not consider the limitations of the RPA + SE theory itself. From the viewpoint of many-body perturbation theory, RPA only sums ring diagrams which describe the nonlocal coupling between quantum charge fluctuations. This gives rise to a systematic underbinding¹⁰⁵. Several methods have therefore been proposed to include other diagrammatic contributions (e.g., ^{106,107}). Specifically, different approaches exist to account for the effect of single excitations^{47,48}. This may give rise to additional uncertainty. Unfortunately, it is difficult to estimate the magnitude of these errors for MIL-53(Al). Since DFT polarizabilities are typically within a few percent of experimental data and coupled-cluster results¹⁰⁸, the

leading RPA error is expected to stem from an overestimation of the Pauli repulsion due to the use of DFT orbitals for the exchange, which we captured by taking into account single excitations. A rough estimate of the residual error can be obtained by comparing our results to the hybrid approach proposed by Ren et al., which involves calculating the Hartree-Fock exchange fully self-consistently⁴⁸. This results in a 10.8 kJ mol⁻¹ lp-np energy difference, i.e., a 3.1 kJ mol⁻¹ difference from our previously reported RPA + SE result. We therefore expect theory-based errors to be of the same order as the numerical errors. The limited size of the total error is also corroborated by the good agreement of the predicted lp-np crossing temperatures compared to experiment when an RPA + SE reference is used (see Table 1 and Fig. 3).

Although it has recently become possible to calculate RPA forces within the VASP PAW formalism¹⁰⁹, structural relaxations of the MIL-53(Al) unit cell are still beyond the capabilities of current computing infrastructures. We have therefore performed single-point RPA + SE calculations on top of DFT-optimized crystal structures. We selected PBE + D3(BJ) for crystal structure generation (Supplementary Data 1 and 2) as this method not only yields good geometries, but also provides reasonable lp-np energy differences and volumes at an acceptable cost (Supplementary Data 1 and 2). We investigated the sensitivity of the RPA + SE lp-np energy difference by testing lp and np geometries from vdW-DF2 and HS060 + D3(BJ) and the influence on the relative stability was within the RPA + SE error bar (Supplementary Table 18 in Supplementary Note 5).

Code availability. The VASP code can be licensed from the University of Vienna (see the FAQ section on <https://www.vasp.at/>).

Data availability

The authors declare that all data supporting the findings of this study are available within the paper and the Supplementary Files, or available from the authors upon request.

Received: 15 February 2018 Accepted: 25 October 2018

Published online: 21 November 2018

References

- Schneemann, A. et al. Flexible metal-organic frameworks. *Chem. Soc. Rev.* **43**, 6062–6096 (2014).
- Coudert, F.-X. Responsive metal-organic frameworks and framework materials: under pressure, taking the heat, in the spotlight, with friends. *Chem. Mater.* **27**, 1905–1916 (2015).
- Horike, S., Shimomura, S. & Kitagawa, S. Soft porous crystals. *Nat. Chem.* **1**, 695–704 (2009).
- Vanduythuys, L. et al. Thermodynamic insight into stimuli-responsive behavior of soft porous crystals. *Nat. Commun.* **9**, 204 (2018).
- Furukawa, H., Cordova, K. E., O’Keeffe, M. & Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **341**, 1230444 (2013).
- Slater, A. G. & Cooper, A. I. Porous materials. Function-led design of new porous materials. *Science* **348**, aaa8075 (2015).
- Liu, Y. et al. Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **130**, 11813–11818 (2008).
- Loiseau, T. et al. A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. *Chem. Eur. J.* **10**, 1373–1382 (2004).
- Carrington, E. J. et al. Solvent-switchable continuous-breathing behaviour in a diamondoid metal-organic framework and its influence on CO₂ versus CH₄ selectivity. *Nat. Chem.* **9**, 882–889 (2017).
- Mason, J. A. et al. Methane storage in flexible metal-organic frameworks with intrinsic thermal management. *Nature* **527**, 357–361 (2015).
- Yot, P. G. et al. Metal-organic frameworks as potential shock absorbers: the case of the highly flexible MIL-53(Al). *Chem. Commun.* **50**, 9462–9464 (2014).
- Yot, P. G. et al. Large breathing of the MOF MIL-47(V^{IV}) under mechanical pressure: a joint experimental-modelling exploration. *Chem. Sci.* **3**, 1100–1104 (2012).
- Horcajada, P. et al. Metal-organic frameworks in biomedicine. *Chem. Rev.* **112**, 1232–1268 (2012).
- Li, J. R., Sculley, J. & Zhou, H. C. Metal-organic frameworks for separations. *Chem. Rev.* **112**, 869–932 (2012).
- Kim, J. Y. et al. Selective hydrogen isotope separation via breathing transition in MIL-53(Al). *J. Am. Chem. Soc.* **139**, 17743–17746 (2017).
- Kreno, L. E. et al. Metal-organic framework materials as chemical sensors. *Chem. Rev.* **112**, 1105–1125 (2012).
- Sambe, L. et al. Programmable polymer-based supramolecular temperature sensor with a memory function. *Angew. Chem. Int. Ed.* **53**, 5044–5048 (2014).
- Brites, C. D. S. et al. Thermometry at the nanoscale. *Nanoscale* **4**, 4799–4829 (2012).

19. Mura, S., Nicolas, J. & Couvreur, P. Stimuli-responsive nanocarriers for drug delivery. *Nat. Mater.* **12**, 991–1003 (2013).
20. Henke, S., Schneemann, A. & Fischer, R. A. Massive anisotropic thermal expansion and room-responsive breathing in metal-organic frameworks modulated by linker functionalization. *Adv. Funct. Mater.* **23**, 5990–5996 (2013).
21. Huang, Y.-G. et al. Superior thermoelasticity and shape-memory nanopores in a porous supramolecular organic framework. *Nat. Commun.* **7**, 11564 (2016).
22. Matsuda, R. et al. Temperature responsive channel uniformity impacts on highly guest-selective adsorption in a porous coordination polymer. *Chem. Sci.* **1**, 315–321 (2010).
23. Zhang, J.-P., Lin, Y.-Y., Zhang, W.-X. & Chen, X.-M. Temperature- or guest-induced drastic single-crystal-to-single-crystal transformations of a nanoporous coordination polymer. *J. Am. Chem. Soc.* **127**, 14162–14163 (2005).
24. Collings, I. E. et al. Homologous critical behavior in the molecular frameworks $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{imidazolate})_2$. *J. Am. Chem. Soc.* **135**, 7610–7620 (2013).
25. Wharmby, M. T. et al. Extreme flexibility in a zeolitic imidazolate framework: porous to dense phase transition in desolvated ZIF-4. *Angew. Chem. Int. Ed.* **54**, 6447–6451 (2015).
26. Schneemann, A. et al. Different breathing mechanisms in flexible pillared-layered metal-organic frameworks: impact of the metal center. *Chem. Mater.* **30**, 1667–1676 (2018).
27. Sakata, Y. et al. Shape-memory nanopores induced in coordination frameworks by crystal downsizing. *Science* **339**, 193–196 (2013).
28. Shivanna, M. et al. Readily accessible shape-memory effect in a porous interpenetrated coordination network. *Sci. Adv.* **4**, eaq1636 (2018).
29. Joaristi, A. M., Juan-Alcañiz, J., Serra-Crespo, P., Kapteijn, F. & Gascon, J. Electrochemical synthesis of some archetypal Zn^{2+} , Cu^{2+} , and Al^{3+} metal organic frameworks. *Cryst. Growth Des.* **12**, 3489–3498 (2012).
30. Mounfield, W. P. III & Walton, K. S. Effect of synthesis solvent on the breathing behavior of MIL-53(Al). *J. Colloid Interface Sci.* **447**, 33–39 (2015).
31. Moran, C. M., Joshi, J. N., Marti, R. M., Hayes, S. E. & Walton, K. S. Structured growth of metal-organic framework MIL-53(Al) from solid aluminum carbide precursor. *J. Am. Chem. Soc.* **140**, 9148–9153 (2018).
32. Fischer, M., Schwegler, J., Paula, C., Schulz, P. S. & Hartmann, M. Direct synthesis of non-breathing MIL-53(Al)(ht) from a terephthalate-based ionic liquid as linker precursor. *Dalton Trans.* **45**, 18443–18446 (2015).
33. Liu, D. et al. Impact of moderate ligand hydrolysis on morphology evolution and the morphology-dependent breathing effect performance of MIL-53(Al). *CrystEngComm* **20**, 2102–2111 (2018).
34. Cheetham, A. K., Kieslich, G. & Yeung, H. H. Thermodynamic and kinetic effects in the crystallization of metal-organic frameworks. *Acc. Chem. Res.* **51**, 659–667 (2018).
35. Wilmer, C. E. et al. Large-scale screening of hypothetical metal-organic frameworks. *Nat. Chem.* **4**, 83–89 (2012).
36. Moghadam, P. Z. et al. Computer-aided discovery of a metal-organic framework with superior oxygen uptake. *Nat. Commun.* **9**, 1378 (2018).
37. Vogiatzis, K. D. et al. Accelerated computational analysis of metal-organic frameworks for oxidation catalysts. *J. Phys. Chem. C* **120**, 18707–18712 (2016).
38. Simon, C. M. et al. Materials genome in action: identifying the performance limits for methane storage. *Energy Environ. Sci.* **8**, 1190–1199 (2015).
39. Coudert, F.-X., Boutin, A. & Fuchs, A. H. A thermodynamic description of the adsorption-induced structural transitions in flexible MIL-53 metal-organic framework. *Mol. Phys.* **112**, 1257–1261 (2014).
40. Walker, A. M. et al. Flexibility in a metal-organic framework controlled by weak dispersion forces: the bistability of MIL-53(Al). *Angew. Chem. Int. Ed.* **49**, 7501–7503 (2010).
41. Bennett, T. D., Cheetham, A. K., Fuchs, A. H. & Coudert, F.-X. Interplay between defects, disorder and flexibility in metal-organic frameworks. *Nat. Chem.* **9**, 11–16 (2017).
42. Eshuis, H., Bates, J. E. & Furche, F. Electron correlation methods based on the random phase approximation. *Theor. Chem. Acc.* **131**, 1084 (2012).
43. Harl, J. & Kresse, G. Accurate bulk properties from approximate many-body techniques. *Phys. Rev. Lett.* **103**, 056401 (2009).
44. Ren, X., Rinke, P., Joas, C. & Scheffler, M. Random-phase approximation and its applications in computational chemistry and materials science. *J. Mater. Sci.* **47**, 7447–7471 (2012).
45. Schimka, L., Gaudoin, R., Klimeš, J., Marsman, M. & Kresse, G. Lattice constants and cohesive energies of alkali, alkaline-earth, and transition metals: random phase approximation and density functional theory results. *Phys. Rev. B* **87**, 214102 (2013).
46. Klimeš, J. Lattice energies of molecular solids from the random phase approximation with singles correction. *J. Chem. Phys.* **145**, 094506 (2016).
47. Klimeš, J., Kaltak, M., Maggio, E. & Kresse, G. Singles correlation energy contributions in solids. *J. Chem. Phys.* **143**, 102816 (2015).
48. Ren, X., Tkatchenko, A., Rinke, P. & Scheffler, M. Beyond the random-phase approximation for the electron correlation energy: the importance of single excitations. *Phys. Rev. Lett.* **106**, 153003 (2011).
49. Reilly, A. M. & Tkatchenko, A. Role of dispersion interactions in the polymorphism and entropic stabilization of the aspirin crystal. *Phys. Rev. Lett.* **113**, 055701 (2014).
50. Mendt, M. et al. Structural phase transitions and thermal hysteresis in the metal-organic framework compound MIL-53 as studied by electron spin resonance spectroscopy. *J. Phys. Chem. C* **114**, 19443–19451 (2010).
51. Boutin, A. et al. Breathing transitions in MIL-53(Al) metal-organic framework upon xenon adsorption. *Angew. Chem. Int. Ed.* **48**, 8314–8317 (2009).
52. Boutin, A. et al. The behavior of flexible MIL-53(Al) upon CH_4 and CO_2 adsorption. *J. Phys. Chem. C* **114**, 22237–22244 (2010).
53. Bokdam, M., Lahnsteiner, J., Ramberger, B., Schäfer, T. & Kresse, G. Assessing density functionals using many body theory for hybrid perovskites. *Phys. Rev. Lett.* **119**, 145501 (2017).
54. Liu, X., Hermann, J. & Tkatchenko, A. Communication: many-body stabilization of non-covalent interactions: structure, stability, and mechanics of $\text{Ag}_2\text{Co}(\text{CN})_6$ framework. *J. Chem. Phys.* **145**, 241101 (2016).
55. Reilly, A. M. & Tkatchenko, A. van der Waals dispersion interactions in molecular crystals: beyond pairwise additive. *Chem. Sci.* **6**, 3289–3301 (2015).
56. von Lilienfeld, O. A. & Tkatchenko, A. Two- and three-body interatomic dispersion energy contributions to binding in molecules and solids. *J. Chem. Phys.* **132**, 234109 (2010).
57. Moellmann, J. & Grimme, S. DFT-D3 study of some molecular crystals. *J. Phys. Chem. C* **118**, 7615–7621 (2014).
58. Sun, J. et al. Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional. *Nat. Chem.* **8**, 831–836 (2016).
59. Peng, H., Yang, Z.-H., Perdew, J. P. & Sun, J. Versatile van der Waals density functional based on a meta-generalized gradient approximation. *Phys. Rev. X* **6**, 041005 (2016).
60. Hermann, J. & Tkatchenko, A. Electronic exchange and correlation in van der Waals systems: balancing semilocal and nonlocal energy contributions. *J. Chem. Theory Comput.* **14**, 1361–1369 (2018).
61. Vanduythuys, L., Ghysels, A., Rogge, S. M. J., Demuyck, R. & Van Speybroeck, V. Semi-analytical mean-field model for predicting breathing in metal-organic frameworks. *Mol. Simulat.* **41**, 1311–1328 (2015).
62. Kavoozi, N. et al. Tailoring adsorption induced phase transitions in the pillared-layer type metal-organic framework DUT-8(Ni). *Dalton Trans.* **46**, 4685–4695 (2017).
63. Krause, S. et al. The effect of crystallite size on pressure amplification in switchable porous solids. *Nat. Commun.* **9**, 1573 (2018).
64. Triguero, C., Coudert, F.-X., Boutin, A., Fuchs, A. H. & Neimark, A. V. Mechanism of breathing transitions in metal-organic frameworks. *J. Phys. Chem. Lett.* **2**, 2033–2037 (2011).
65. Chen, L. et al. Elucidating the breathing of the metal-organic framework MIL-53(Sc) with ab initio molecular dynamics simulations and in situ X-ray powder diffraction experiments. *J. Am. Chem. Soc.* **135**, 15763–15773 (2013).
66. Alvarez, E. et al. The structure of the aluminum fumarate metal-organic framework A520. *Angew. Chem. Int. Ed.* **54**, 3664–3668 (2015).
67. Senkovska, I. et al. New highly porous aluminum based metal-organic frameworks: $\text{Al}(\text{OH})(\text{ndc})$ ($\text{ndc} = 2,6$ -naphthalene dicarboxylate) and $\text{Al}(\text{OH})(\text{bpdc})$ ($\text{bpdc} = 4,4'$ -biphenyl dicarboxylate). *Microporous Mesoporous Mater.* **122**, 93–98 (2009).
68. Loiseau, T. et al. Hydrothermal synthesis and crystal structure of a new three-dimensional aluminum-organic framework MIL-69 with 2,6-naphthalenedicarboxylate (ndc), $\text{Al}(\text{OH})(\text{ndc})\cdot\text{H}_2\text{O}$. *C. R. Chim.* **8**, 765–772 (2005).
69. Volkinger, C. et al. XRD and IR structural investigations of a particular breathing effect in the MOF-type gallium terephthalate MIL-53(Ga). *Dalton Trans.* **0**, 2241–2249 (2009).
70. Chaplais, G. et al. IM-19: a new flexible microporous gallium based-MOF framework with pressure- and temperature-dependent openings. *Phys. Chem. Chem. Phys.* **11**, 5241–5245 (2009).
71. Ramaswamy, P. et al. Mechanical properties of a gallium fumarate metal-organic framework: a joint experimental-modelling exploration. *J. Mater. Chem. A* **5**, 11047–11054 (2017).
72. Yot, P. G. et al. Mechanical energy storage performance of an aluminum fumarate metal-organic framework. *Chem. Sci.* **7**, 446–450 (2016).
73. Boutin, A. et al. Temperature-induced structural transitions in the gallium-based MIL-53 metal-organic framework. *J. Phys. Chem. C* **117**, 8180–8188 (2013).
74. Demuyck, R. et al. Efficient construction of free energy profiles of breathing metal-organic frameworks using advanced molecular dynamics simulations. *J. Chem. Theory Comput.* **13**, 5861–5873 (2017).
75. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).

ARTICLE

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76. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
77. Lejaeghere, K. et al. Reproducibility in density functional theory calculations of solids. *Science* **351**, 1415 (2016).
78. Vanpoucke, D. E. P., Lejaeghere, K., Van Speybroeck, V., Waroquier, M. & Ghysels, A. Mechanical properties from periodic plane wave quantum mechanical codes: the challenge of the flexible nanoporous MIL-47(V) framework. *J. Phys. Chem. C* **119**, 23752–23766 (2015).
79. Paier, J., Marsman, M., Hummer, K. & Kresse, G. Screened hybrid density functional applied to solids. *J. Chem. Phys.* **124**, 154709 (2006).
80. Lee, K., Murray, E. D., Kong, L., Lundqvist, B. I. & Langreth, D. C. Higher-accuracy van der Waals density functional. *Phys. Rev. B* **82**, 081101 (2010).
81. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
82. Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.* **100**, 136406 (2008).
83. Sun, J., Ruzsinszky, A. & Perdew, J. P. Strongly constrained and appropriately normed semilocal density functional. *Phys. Rev. Lett.* **115**, 036402 (2015).
84. Zhao, Y. & Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **125**, 194101 (2006).
85. Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **38**, 3098–3100 (1988).
86. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **125**, 224106 (2006).
87. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).
88. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787–1799 (2006).
89. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **132**, 15104 (2010).
90. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456–1465 (2011).
91. Tkatchenko, A. & Scheffler, M. Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.* **102**, 073005 (2009).
92. Ambrosetti, A., Reilly, A. M., DiStasio, R. A. Jr. & Tkatchenko, A. Long-range correlation energy calculated from coupled atomic response functions. *J. Chem. Phys.* **140**, 18A508 (2014).
93. Bučko, T., Lebègue, S., Gould, T. & Ángyán, J. G. Many-body dispersion corrections for periodic systems: an efficient reciprocal space implementation. *J. Phys. Condens. Matter* **28**, 045201 (2016).
94. Gould, T., Lebègue, S., Ángyán, J. G. & Bučko, T. A fractionally ionic approach to polarizability and van der Waals many-body dispersion calculations. *J. Chem. Theory Comput.* **12**, 5920–5930 (2016).
95. Tkatchenko, A., DiStasio, R. A. Jr., Car, R. & Scheffler, M. Accurate and efficient method for many-body van der Waals interactions. *Phys. Rev. Lett.* **108**, 236402 (2012).
96. Vinet, P., Ferrante, J., Rose, J. H. & Smith, J. R. Compressibility of solids. *J. Geophys. Res.* **92**, 9319–9325 (1987).
97. Axilrod, B. M. & Teller, E. Interaction of the van der Waals type between three atoms. *J. Chem. Phys.* **11**, 299–300 (1943).
98. Muto, Y. Force between nonpolar molecules. *Proc. Phys. Math. Soc. Jpn.* **17**, 629–631 (1943).
99. Togo, A. & Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **108**, 1–5 (2015).
100. Kalkt, M., Klimeš, J. & Kresse, G. Low scaling algorithms for the random phase approximation: imaginary time and Laplace transformations. *J. Chem. Theory Comput.* **10**, 2498–2507 (2014).
101. Kalkt, M., Klimeš, J. & Kresse, G. Cubic scaling algorithm for the random phase approximation: self-interstitials and vacancies in Si. *Phys. Rev. B* **90**, 054115 (2014).
102. Bates, J. E., Mezei, P. D., Csonka, G. I., Sun, J. & Ruzsinszky, A. Reference determinant dependence of the random phase approximation in 3d transition metal chemistry. *J. Chem. Theory Comput.* **13**, 100–109 (2017).

103. Harl, J., Schimka, L. & Kresse, G. Assessing the quality of the random phase approximation for lattice constants and atomization energies of solids. *Phys. Rev. B* **81**, 115126 (2010).
104. Harl, J. & Kresse, G. Cohesive energy curves for noble gas solids calculated by adiabatic connection fluctuation-dissipation theorem. *Phys. Rev. B* **77**, 045136 (2008).
105. Furche, F. Molecular tests of the random phase approximation to the exchange-correlation energy functional. *Phys. Rev. B* **64**, 195120 (2001).
106. Ren, X., Rinke, P., Scuseria, G. E. & Scheffler, M. Renormalized second-order perturbation theory for the electron correlation energy: concept, implementation, and benchmarks. *Phys. Rev. B* **88**, 035120 (2013).
107. Maggio, E. & Kresse, G. Correlation energy for the homogeneous electron gas: exact Bethe-Salpeter solution and an approximate evaluation. *Phys. Rev. B* **93**, 235113 (2016).
108. Hait, D. & Head-Gordon, M. How accurate are static polarizability predictions from density functional theory? An assessment over 132 species at equilibrium geometry. *Phys. Chem. Chem. Phys.* **20**, 19800–19810 (2018).
109. Ramberger, B., Schäfer, T. & Kresse, G. Analytic interatomic forces in the random phase approximation. *Phys. Rev. Lett.* **118**, 106403 (2017).

Acknowledgements

This work is supported by the Fund for Scientific Research Flanders (FWO). V.V.S. acknowledges funding from the European Union's Horizon 2020 research and innovation program (consolidator ERC grant agreement No. 647755 - DYNPOR (2015–2020)). The work is furthermore supported by the Research Board of Ghent University (BOF) and BELSPO in the frame of IAP/7/05. The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by Ghent University, FWO and the Flemish Government department EWI. We also want to acknowledge L. Vanduyfhuys, S.M.J. Rogge, S. De Waele, M. Marsman, J. Sun and T. Bučko for their valuable input and discussions.

Author contributions

All authors contributed to exchanging ideas, were involved in the discussion of the results and in writing the manuscript. The overall coordination of the research was done by V.V.S. The DFT simulations were performed by J.W. and K.L. The RPA + SE calculations were done by K.L. guided by G.K.

Additional information

Supplementary Information accompanies this paper at <https://doi.org/10.1038/s41467-018-07298-4>.

Competing interests: The authors declare no competing interests.

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Supplementary Information

Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks

Wieme et al.

Supplementary Note 1. DFT calculations

An overview of and the references to the different methodologies used in this work are given in Supplementary Tables 1, 2 and 3. An overview of previously published energy differences between the large-pore (lp) and narrow-pore (np) phase of MIL-53(Al) is given in Supplementary Table 4.

<i>Name</i>	<i>Abbreviation</i>	<i>Reference(s)</i>	<i>Type</i>
Perdew-Burke-Ernzerhof	PBE	[1, 2]	GGA
Perdew-Burke-Ernzerhof revised for solids	PBEsol	[3, 4]	GGA
van der Waals density functional 2	vdW-DF2	[5-8]	GGA
Strongly Constrained and Appropriately Normed	SCAN	[9, 10]	meta-GGA
Strongly Constrained and Appropriately Normed with revised Vydrov-Van Voorhis van der Waals correlation	SCAN+rVV10	[9-13]	meta-GGA
Minnesota '06 (local)	M06-L	[14]	meta-GGA
Becke three-parameter Lee-Yang-Parr	B3LYP	[15-18]	hybrid
Heyd-Scuseria-Ernzerhof	HSE06	[19-21]	hybrid

Supplementary Table 1. Different exchange-correlation functionals used in this work.

<i>Name</i>	<i>Abbreviation</i>	<i>Reference(s)</i>
Grimme D3 dispersion with Becke-Johnson damping	D3(BJ)	[22, 23]
Grimme D3 dispersion with Becke-Johnson damping and Axilrod-Teller-Muto three-body potential	D3(BJ) ^{ATM}	[22-24]
Grimme D2 dispersion	D2	[25]
Tkatchenko-Scheffler method	TS	[26]
Many-body dispersion energy method (MBD@rsSCS)	MBD	[27-30]
Many-body dispersion energy method with a fractionally ionic approach to polarizability (MBD@rsSCS/FI)	MBD/FI	[31]

Supplementary Table 2. Different dispersion schemes used in this work.

<i>Name</i>	<i>XC functional</i>	<i>Dispersion scheme</i>
PBE	PBE	-
PBE+D3(BJ) ^(ATM)	PBE	D3(BJ) ^(ATM)
PBE+TS	PBE	TS
PBEsol+D3(BJ) ^(ATM)	PBEsol	D3(BJ) ^(ATM)
PBE+D2	PBE	D2
PBE+MBD	PBE	MBD
PBE+MBD/FI	PBE	MBD/FI
SCAN	SCAN	-
SCAN+rVV10	SCAN+rVV10	-
vdW-DF2	vdW-DF2	-
M06-L	M06-L	-
B3LYP+D3(BJ) ^(ATM)	B3LYP	D3(BJ) ^(ATM)
HSE06+D3(BJ) ^(ATM)	HSE06	D3(BJ) ^(ATM)

Supplementary Table 3. Overview of DFT methods used in this work.

<i>Reference</i>	<i>XC functional</i>	<i>Dispersion scheme</i>	<i>Code</i>	$\Delta E_{\text{lp-np}}$ (kJ·mol ⁻¹)
Walker <i>et al.</i> (2010) [32]	vdW-DF	-	SIESTA	72
Walker <i>et al.</i> (2010) [32]	PBE	D2	CRYSTAL09	39
Walker <i>et al.</i> (2010) [32]	B3LYP	D2	CRYSTAL09	42
Walker <i>et al.</i> (2010) [32]	B3LYP	D2*	CRYSTAL09	34
Nanthamathee <i>et al.</i> (2015) [33]	PBE	D3 ^{ATM}	CP2K	16
Ling and Slater (2015) [34]	HSE06	D3 ^{ATM}	CP2K	14
Coudert <i>et al.</i> (2014) [35]	B3LYP	D2	CRYSTAL09	37
Wang <i>et al.</i> (2016) [36]	PBE	-	VASP	-60

Supplementary Table 4. Overview of published lp-np energy differences per unit cell of MIL-53(Al).

Supplementary Note 2. Available experimental structural data for MIL-53(Al)

There is very limited high-precision low-temperature experimental data available on the shape of the potential energy surface of MIL-53(Al). Moreover, most structural data on flexible MOFs such as MIL-53(Al) is fitted to powder X-ray diffraction experiments (in contrast to single-crystal X-ray diffraction) under certain approximations, which can also influence, for instance, the reported lattice parameters. Therefore, one of the major reasons to start from a high-level technique such as RPA - which has been extensively benchmarked to high-precision experiments for various other systems - is to generate accurate benchmark data.

<i>Experiment</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
Liu <i>et al.</i> (2008) [37] Neutron Powder Diffraction (77 K)	19.121	6.607	6.871	90.0	90.0	95.5	864
Liu <i>et al.</i> (2008) [37] Neutron Powder Diffraction (295 K)	19.098	6.609	7.055	90.0	90.0	95.1	887
Yot <i>et al.</i> (2014) [38] X-ray Powder Diffraction (298 K)	19.056	6.559	7.160	90.0	90.0	94.7	897
Nevjestić <i>et al.</i> (2016) [39] Synchrotron X-ray Powder Diffraction (298 K) (V-doped)	19.015	6.575	7.620	90.0	90.0	95.3	949

Supplementary Table 5. Overview of experimental lattice parameters for the np phase of MIL-53(Al) available in literature.

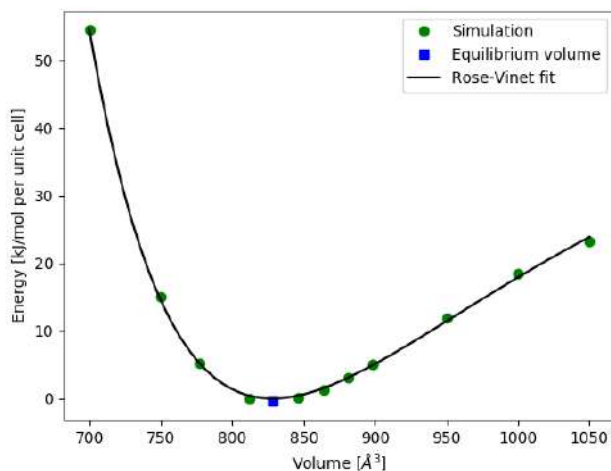
<i>Experiment</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
Liu <i>et al.</i> (2008) [37] Neutron Powder Diffraction (77 K)	16.91	6.624	12.67	90.0	90.0	90.0	1419
Liu <i>et al.</i> (2008) [37] Neutron Powder Diffraction (295 K)	16.84	6.635	12.80	90.0	90.0	90.0	1430
Liu <i>et al.</i> (2008) [37] Neutron Powder Diffraction (295 K)	16.761	6.638	12.839	90.0	90.0	90.0	1429
Yot <i>et al.</i> (2014) [38] X-ray Powder Diffraction (298 K)	16.732	6.630	12.836	90.0	90.0	90.0	1424
Nanthamathee <i>et al.</i> (2015) [33] Synchrotron X-ray Powder Diffraction (150 K)	16.797	6.630	12.747	90.0	90.0	90.0	1420
Nanthamathee <i>et al.</i> (2015) [33] Synchrotron X-ray Powder Diffraction (300 K)	16.758	6.629	12.794	90.0	90.0	90.0	1421
Nevjestič <i>et al.</i> (2017) [40] Synchrotron X-ray Powder Diffraction (455 K) (V-doped)	16.661	6.634	12.961	90.0	90.0	90.0	1432
Loiseau <i>et al.</i> (2004) [41] Laboratory Powder X-ray Diffraction (550 K)	16.675	6.609	12.813	90.0	90.0	90.0	1412

Supplementary Table 6. Overview of experimental lattice parameters for the lp phase of MIL-53(Al) available in literature.

Supplementary Note 3. Sensitivity of DFT relative stability with respect to structural data

An in-depth investigation was performed of the sensitivity of the reported lp-np energy differences of MIL-53(Al) on the specific choice of the geometry, cell shape and equilibrium volume.

The equilibrium volume for all methodologies was systematically determined by fitting a Rose-Vinet equation of state to a local energy profile as a function of the volume.[42, 43] An example of such a fit is given for the np phase in Supplementary Figure 1.



Supplementary Figure 1. An example of a local energy profile as a function of the volume obtained at the PBE+MBD level for the np phase of MIL-53(Al).

The resulting volumes are given in the main manuscript and listed in Supplementary Table 7 together with the experimentally determined values by Liu et al. [37] at 77 K. As we constructed an energy profile as a function of volume with RPA+SE, we can also extract the equilibrium volume predicted by this technique. The resulting values are also listed in Supplementary Table 7.

	V_{np} (Å ³)	V_{lp} (Å ³)	ΔE_{lp-np}^{el} (kJ·mol ⁻¹) (relaxed at the corresponding level of theory)	$\Delta E_{lp-np}^{el,*}$ (kJ·mol ⁻¹) (relaxed at PBE+D3(BJ) level of theory at fixed volumes of 864 Å ³ and 1427 Å ³)	$\Delta E_{lp-np}^{el,*}$ (kJ·mol ⁻¹) (relaxed at the corresponding level of theory but at fixed volumes of 864 Å ³ and 1427 Å ³)
Experiment at 77 K [37]	864	1419*	-	-	-
RPA+SE	860	1455	7.4	7.7 ± 3.5	7.7 ± 3.5**
PBE+D2	808	1457	15.7	12.8	12.7
PBE+D3(BJ)	843	1426	26.6	26.1	26.1
PBE+D3(BJ) ^{ATM}	874	1448	5.8	6.2	6.2
HSE06+D3(BJ)	825	lp unstable	lp unstable	42.3	42.7
HSE06+D3(BJ) ^{ATM}	850	1389	22.3	22.4	22.7
B3LYP+D3(BJ)	789	lp unstable	lp unstable	58.9	58.2
B3LYP+D3(BJ) ^{ATM}	806	1405	43.8	39.0	38.2
PBE+TS	793	lp unstable	lp unstable	74.2	74.3
PBE+MBD	828	1425	25.8	24.5	24.3
PBE+MBD/FI	851	1439	16.4	16.4	16.3
SCAN+rVV10	803	1384	31.2	28.3	28.0
vdW-DF2	869	1456	34.8	35.5	34.9
M06-L	829	lp unstable	lp unstable	36.6	38.4

Supplementary Table 7. The equilibrium volumes for the np and lp phase of MIL-53(Al), and their relative stability for several levels of theory. ΔE_{lp-np}^{el} is the energy difference at the equilibrium volumes and geometries of both phases relaxed with the corresponding method (or PBE+D3(BJ) for RPA+SE). $\Delta E_{lp-np}^{el,*}$ is the energy difference at fixed volumes (864 Å³ (np) and 1427 Å³ (lp)) with/without relaxation at the corresponding level of theory.

*The sample was going towards the np phase on a longer time scale than the measurement. [37]

**The RPA+SE structures were obtained by optimizing at the PBE+D3(BJ) level.

As the theoretical volumes were obtained at 0 K, it is advised to compare with the low-temperature results of Liu *et al.* For the np phase, a measurement at 77 K yielded a volume of 864 Å³. For the porous lp phase, it is difficult to compare with low-temperature data as experimentally this phase is not stable at these temperatures. Liu *et al.* measured a lp phase, which was metastable (the sample was going towards the np phase on a longer time scale than the measurement) resulting in a volume of 1419 Å³. Note also that – at higher temperatures – the experimentally measured values vary for the lp phase from 1412 Å³ to 1432 Å³, and for the np phase from 887 Å³ to 949 Å³ (Supplementary Note 2).

Our RPA+SE volume for the dense phase is in very good agreement (860 Å³ vs. 864 Å³) with the measurement of Liu *et al.* In contrast, most applied DFT methods underestimate the volume, but the agreement improves for schemes including long-range many-body dispersion interactions. Comparison with experimental values for the lp phase should be performed with caution, given previous remarks. We notice that our RPA+SE reference predicts a higher equilibrium volume for the lp phase (1455 Å³ vs 1419 Å³), while the DFT methods (not all methods predict a metastable lp phase) give values between 1384 Å³ and 1457 Å³ and the agreement again improves when including many-body dispersion.

In general there is some spread in the equilibrium volumes obtained with the various DFT methods and dispersion schemes. It is now important to probe the sensitivity of the energy difference between the lp and np pore phase in terms of these observed differences in equilibrium volumes and by extension to the structural data. To this end, three data sets have been generated, which allow to assess the influence of the cell structure on the relative stability of the lp and the np phase:

- (a) The electronic energy difference between the lp and np phase relaxed with the corresponding DFT method. These values were already included in the main manuscript (Table 2).
- (b) The energy difference between the lp and np phase relaxed with the PBE+D3(BJ) method at fixed volumes (864 Å³ and 1427 Å³). These values were already included in the main manuscript (Table 2).
- (c) The energy difference between the lp and np phase relaxed with the corresponding DFT method but at fixed volume (864 Å³ and 1427 Å³). Here, the cell shape and positions were relaxed.

The results are taken up in Supplementary Table 7 (columns 4, 5 and 6). The results in (a) are obtained with different equilibrium volumes, i.e. the volumes optimized at the specific level of theory (given in columns 2 and 3), whereas the results in (b) and (c) use fixed volumes which are representative for the np and lp phase. As will follow from the results discussed below, the precise choice of the equilibrium volume does not influence our results strongly and any reasonable value for the lp phase would give to a large extent the same results due to the flat potential energy surface around the phase equilibria of these flexible materials.

A comparison of the results between cases (b) and (c) indicates that the influence of the specific unit cell shape and positions on the energy difference is limited at fixed volume (the deviation is smaller than 2 kJ·mol⁻¹ for every method). Our single-point fixed volume approach thus enables a good estimate of the order of magnitude of the relative stability, and is ideal to quickly test the performance

of a functional and dispersion scheme in comparison to our high-level result. The unit cells at the fixed volumes are given in Supplementary Tables 8 and 9 (below).

The results of case (a) are only slightly more sensitive to the specific choice of the functional, which can be traced back to the difference in equilibrium volumes compared to the chosen fixed volumes of 864 Å³ and 1427 Å³. However, we remark that even in this case, the difference between (a) and (b) is always lower than 6 kJ·mol⁻¹ and for most methods even lower than 2 kJ·mol⁻¹. Unfortunately, for some functionals, such as HSE06+D3(BJ), B3LYP+D3(BJ), PBE+TS and M06-L, no stable large pore phase can be obtained, which makes a comparison of the relative energy differences impossible using only data set (a).

The results above indicate that there is only a limited influence of the structure on the relative energy difference between the lp and np phase.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>α</i> (°)	<i>β</i> (°)	<i>γ</i> (°)
PBE+D2	19.253	6.667	6.760	90.0	90.0	95.4
PBE+D3(BJ)	19.246	6.661	6.765	90.0	90.0	95.0
HSE06+D3(BJ)	19.068	6.608	6.897	90.0	90.0	94.7
B3LYP+D3(BJ)	19.147	6.629	6.831	90.0	90.0	94.8
PBE+TS	19.250	6.672	6.752	90.0	90.0	95.1
PBE+MBD	19.205	6.641	6.799	90.1	90.0	94.9
PBE+MBD/FI	19.232	6.651	6.781	90.0	90.0	95.1
SCAN+rVV10	19.025	6.600	6.914	90.0	90.0	95.7
vdW-DF2	19.411	6.719	6.650	90.0	90.0	95.0
M06-L	18.935	6.593	6.967	90.0	90.0	96.6

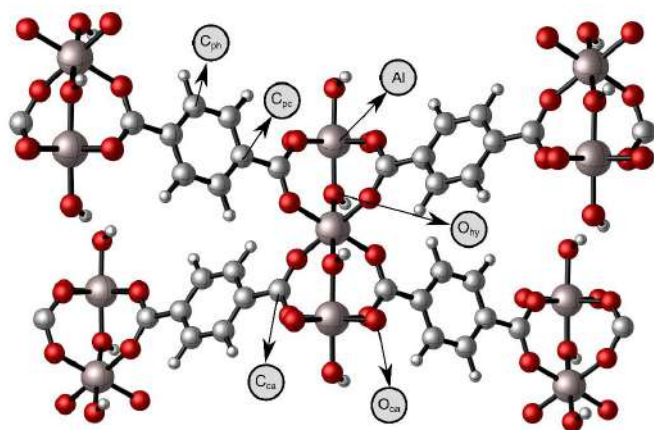
Supplementary Table 8. A comparison of unit cell parameters between different methods in the optimized structure of the np phase of MIL-53(Al) (at 864 Å³).

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
PBE+D2	17.128	6.672	12.493	90.0	90.0	91.0
PBE+D3(BJ)	17.079	6.663	12.545	90.0	90.0	90.8
HSE06+D3(BJ)	16.550	6.625	13.019	90.0	90.0	90.4
B3LYP+D3(BJ)	16.710	6.631	12.883	90.0	90.0	90.6
PBE+TS	17.108	6.665	12.521	90.0	90.0	90.8
PBE+MBD	16.963	6.649	12.657	90.0	90.0	90.7
PBE+MBD/FI	17.054	6.657	12.574	90.0	90.0	90.8
SCAN+rVV10	16.431	6.622	13.120	90.0	90.0	90.7
vdW-DF2	17.548	6.735	12.080	90.0	90.0	91.0
M06-L	16.373	6.639	13.134	90.0	90.0	91.0

Supplementary Table 9. A comparison of unit cell parameters between different methods in the optimized structure of the lp phase of MIL-53(Al) (at 1427 Å³).

As many-body dispersion interactions seem to have an influence on the equilibrium volume, we also investigated the influence of these effects on the internal coordinates of the crystal structure. Different dispersion schemes with/without many-body effects on top of PBE (TS, MBD, MBD/FI, D3(BJ)), and two other functionals (HSE06+D3(BJ) and vdW-DF2) are compared in Supplementary Tables 10 - 15. In these tables, some important internal coordinates (bond lengths, bend angles, dihedral angles) and unit cell parameters are reported for various methods (obtained at fixed volumes of the np and lp phase). The definition of the atom types is displayed in Supplementary Figure 2.

It can be seen that the difference between PBE and the other two functionals is generally larger than the effects of the dispersion schemes on the geometry. This is in contrast with the big dependence of the relative stability on the dispersion method. Especially interesting is the comparison between the PBE+TS (pairwise) and PBE+MBD (many-body effects) level for which the influence of many-body effects on the geometry can directly be probed. The results indicate that many-body effects do not have much influence on the geometry of the structure, which can also be seen in the reported unit cell parameters (see also Supplementary Tables 8 and 9). This analysis also suggests that the ATM corrections will not have a large influence on the unit cell shape and/or internal coordinates, as claimed previously in the literature.[24]



Supplementary Figure 2. Definition of the atom types in MIL-53(Al) used to indicate the internal coordinates.

Bond length (Å)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
Al-O _{ca}	1.92±0.01	1.91±0.01	1.92±0.01	1.92±0.01	1.90±0.01	1.94±0.01
Al-O _{hy}	1.86±0.00	1.85±0.00	1.86±0.00	1.86±0.00	1.84±0.00	1.88±0.00
O _{ca} -C _{ca}	1.27±0.00	1.27±0.00	1.27±0.00	1.27±0.00	1.26±0.00	1.28±0.00
C _{ca} -C _{pc}	1.49±0.00	1.49±0.00	1.49±0.00	1.49±0.00	1.49±0.00	1.50±0.00
C _{pc} -C _{ph}	1.40±0.00	1.40±0.00	1.40±0.00	1.40±0.00	1.39±0.00	1.41±0.00
C _{ph} -C _{ph}	1.39±0.00	1.39±0.00	1.39±0.00	1.39±0.00	1.38±0.00	1.39±0.00

Supplementary Table 10. A comparison of different bond lengths between different methods in the optimized structure of the np phase of MIL-53(Al) (at 864 Å³). The definition of atom types is given in Supplementary Figure 2.

Bond length (Å)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
Al-O _{ca}	1.92±0.01	1.91±0.01	1.92±0.01	1.92±0.01	1.90±0.01	1.94±0.01
Al-O _{hy}	1.86±0.00	1.85±0.00	1.86±0.00	1.86±0.00	1.84±0.00	1.87±0.00
O _{ca} -C _{ca}	1.27±0.00	1.27±0.00	1.27±0.00	1.27±0.00	1.26±0.00	1.28±0.00
C _{ca} -C _{pc}	1.49±0.00	1.49±0.00	1.49±0.00	1.49±0.00	1.49±0.00	1.50±0.00
C _{pc} -C _{ph}	1.40±0.00	1.40±0.00	1.40±0.00	1.40±0.00	1.39±0.00	1.41±0.00
C _{ph} -C _{ph}	1.39±0.00	1.39±0.00	1.39±0.00	1.39±0.00	1.38±0.00	1.39±0.00

Supplementary Table 11. A comparison of different bond lengths between different methods in the optimized structure of the lp phase of MIL-53(Al) (at 1427 Å³). The definition of atom types is given in Supplementary Figure 2.

Bend angle (°)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
O _{ca} -Al-O _{ca}	120.0±42.5	120.0±42.5	120.0±42.5	120.0±42.5	120.0±42.5	120.0±42.5
O _{ca} -C _{ca} -O _{ca}	124.6±0.0	124.5±0.0	124.5±0.0	124.6±0.0	124.5±0.0	124.1±0.0
Al-O _{hy} -Al	127.0±0.0	127.1±0.0	126.9±0.0	127.0±0.0	127.3±0.0	127.0±0.0
O _{hy} -Al-O _{hy}	179.9±0.0	179.9±0.0	180.0±0.0	180.0±0.0	180.0±0.0	180.0±0.0
C _{ph} -C _{pc} -C _{ph}	119.8±0.0	119.8±0.0	119.7±0.0	119.8±0.0	120.0±0.0	119.5±0.0

Supplementary Table 12. A comparison of different bend angles between different methods in the optimized structure of the np phase of MIL-53(Al) (at 864 Å³). The definition of atom types is given in Supplementary Figure 2.

Bend angle (°)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
O _{ca} -Al-O _{ca}	119.6±41.9	119.7±42.0	119.7±42.0	119.7±42.0	119.8±42.1	119.9±42.3
O _{ca} -C _{ca} -O _{ca}	125.5±0.1	125.5±0.1	125.5±0.1	125.5±0.1	125.5±0.1	125.0±0.0
Al-O _{hy} -Al	127.2±0.0	127.4±0.0	127.4±0.0	127.4±0.0	128.1±0.0	128.0±0.0
O _{hy} -Al-O _{hy}	177.8±0.0	178.4±0.0	178.3±0.0	178.3±0.0	178.7±0.0	179.5±0.0
C _{ph} -C _{pc} -C _{ph}	119.8±0.1	119.8±0.1	119.7±0.1	119.8±0.1	119.9±0.1	129.5.±0.0

Supplementary Table 13. A comparison of different bend angles between different methods in the optimized structure of the lp phase of MIL-53(Al) (at 1427 Å³). The definition of atom types is given in Supplementary Figure 2.

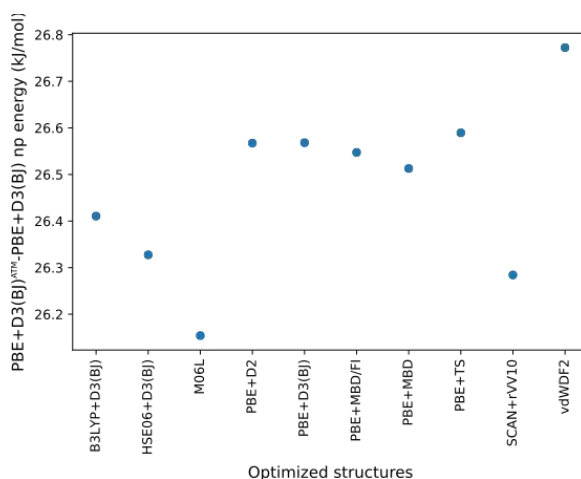
Dihedral angle (°)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
C _{ph} -C _{pc} -C _{ca} -O _{ca}	88.8±86.5	89.0±86.4	89.0±86.4	89.1±86.3	89.6±86.1	88.2±86.7
Al-O _{ca} -C _{ca} -C _{pc}	140.2±14.4	140.5±14.3	140.3±14.7	140.2±14.5	140.7±13.9	139.2±14.3
Al-O _{ca} -C _{ca} -O _{ca}	36.4±14.4	36.0±14.4	36.5±14.8	36.5±14.5	36.3±13.9	36.9±14.3

Supplementary Table 14. A comparison of different dihedral angles between different methods in the optimized structure of the np phase of MIL-53(Al) (at 864 Å³). The definition of atom types is given in Supplementary Figure 2.

Dihedral angle (°)	PBE+TS	PBE+MBD	PBE+MBD/FI	PBE+D3(BJ)	HSE06+D3(BJ)	vdW-DF2
C _{ph} -C _{pc} -C _{ca} -O _{ca}	90.0±86.1	90.0±87.5	90.0±87.6	90.0±86.9	90.0±86.6	90.0±88.5
Al-O _{ca} -C _{ca} -C _{pc}	169.1±8.3	169.8±7.9	169.2±8.8	169.0±9.1	171.7±7.6	165.8±8.0
Al-O _{ca} -C _{ca} -O _{ca}	10.9±8.3	10.2±7.9	10.8±8.8	11.0±9.1	8.5±7.8	14.0±8.0

Supplementary Table 15. A comparison of different dihedral angles between different methods in the optimized structure of the lp phase of MIL-53(Al) (at 1427 Å³). The definition of atom types is given in Supplementary Figure 2.

We also performed single-point calculations on different structures of the dense np phase - which is dispersion dominated - using PBE+D3(BJ) and PBE+D3(BJ)^{ATM}. The different structures are the ones reported in Supplementary Table 8. The energy differences displayed in Supplementary Figure 3 are thus a measure of the ATM corrections for various optimized geometries. The results show that the relative energies or the correction obtained by using the three-body ATM terms is rather insensitive to the specific structure (differences smaller than 1 kJ·mol⁻¹ for the absolute np phase energy). This gives further evidence that small corrections to the unit cell will not influence our findings.



Supplementary Figure 3. Absolute energy difference between PBE+D3(BJ)^{ATM} and PBE+D3(BJ) (or thus the ATM corrections) for different geometries of MIL-53(Al) (at a fixed volume of 864 Å³) obtained with different levels of theory.

Summarizing, this analysis shows that many-body dispersion effects have a smaller impact on the geometries than the choice of the particular exchange-correlation (XC) functional. Furthermore, the observed small changes in the structure due to many-body dispersion effects induce only very small energy differences.

Supplementary Note 4. Sensitivity of DFT relative stability on the coupling between the exchange-correlation functional and the dispersion scheme

To systematically investigate the impact of both the XC functional and the dispersion method, we included other functionals with various dispersion schemes encompassing both pair-wise and many-body dispersion schemes. Supplementary Table 16 lists the electronic energy difference between the lp and np phase of MIL-53(Al) with different methods at fixed geometries obtained with the PBE-D3(BJ) level of theory (Supplementary Tables 8 and 9). The values reported in the main article are indicated in bold.

	XC	XC+D3(BJ)	XC+D3(BJ) ^{ATM}	XC+TS	XC+MBD
PBE	-118.5	26.1	6.2	74.2	24.5
TPSS	-141.6	43.3	23.5	/	/
SCAN	-43.6	33.7 [44]	13.8	/	48.5 ($\beta=1.09$) 36.0 ($\beta=1.16$) 25.3 ($\beta=1.23$) [45]
HSE06	-111.7	42.3 [24]	22.4	75.3 [46]	28.0 [47]
PBE0	-110.8	37.7	17.9	76.2 [48]	28.9
B3LYP	-145.1	58.9	39.0	/	/

Supplementary Table 16. The electronic energy difference between the lp and np phase of MIL-53(Al) with different methods. It is the energy difference at fixed structures (np: 864 Å³, lp: 1427 Å³) relaxed with PBE+D3(BJ). The bold numbers are also indicated in the main manuscript (Table 2). The references to the coupling parameters between the XC functional and dispersion scheme that cannot be found in the original D3(BJ), TS and MBD papers are indicated in the table.

Our results for the TS and MBD scheme (columns 5 and 6) show that irrespective of the XC functional or dispersion method, a similar lp-np energy difference is obtained. The only exception is SCAN, which suffers from a sensitive coupling with dispersion schemes.[45] An entirely different situation is obtained when considering D3(BJ) and D3(BJ)^{ATM} dispersion schemes. In that case, changing the XC functional drastically changes the computed phase stability, raising the energy differences by 20 to 30 kJ·mol⁻¹. The different behavior of D3- and TS-based schemes is due to the coupling between the functional and the dispersion method.

A striking observation is that going from PBE (a local GGA) to meta-GGA (TPSS, SCAN) or hybrid functionals (HSE06, PBE0, B3LYP) worsens the agreement with RPA+SE. In Supplementary Table 17, the results are summarized for PBE and PBE0 and show that the difference Δ between the lp-np energy difference according to PBE and PBE0 coupled with a D3 scheme comes to a large extent from the XC energy difference between PBE and PBE0 and not from the dispersion scheme. The disagreement between PBE0+D3(BJ) and RPA+SE may therefore be due to either an unsuitability of the hybrid functional or, more likely, an insufficiently sensitive fitting of the D3 dispersion parameters to the parent functional. Indeed, the difference between PBE and PBE0 for the TS and MBD schemes is more

subtle and is partially due to the XC energy difference and partially due to the dispersion energy difference, resulting in its previously ascribed robustness. While D3(BJ) predicts a difference in dispersion energy between the lp and np phase that is slightly larger for PBE0 than PBE, TS and MBD display the opposite behavior.

	XC	XC+D3(BJ)	XC+D3(BJ) ^{ATM}	XC+TS	XC+MBD
PBE	-118.5	26.1	6.2	74.2	24.5
PBE0	-110.8	37.7	17.9	76.2	28.9
Δ	-7.7	-11.6	-11.7	-2.0	-4.4

Supplementary Table 17. The electronic energy difference between the lp and np phase of MIL-53(Al) with different methods. It is the energy difference at fixed structures (np: 864 Å³, lp: 1427 Å³) relaxed with PBE+D3(BJ). The fourth row (Δ) corresponds to the difference between the second (PBE) and third row (PBE0) and represents the sensitivity of the lp-np energy difference to the XC functional.

Although the TS or MBD schemes provide a much more robust coupling between the XC functional and the dispersion method, their use does not improve the agreement with the RPA+SE value of 7.7 ± 3.5 kJ·mol⁻¹ for this specific system. Possibly, these results indicate that in case of a hybrid porous material there might be a problem when transferring a model fitted to small and medium-size dimers to large unit cells containing many different bond types simultaneously.

Supplementary Note 5. Selection of a proper geometry for the RPA+SE calculations

Because it is currently computationally not feasible to perform structural relaxations of MIL-53(Al) at the RPA level, RPA calculations were performed using DFT-optimized crystal structures. PBE+D3(BJ) was chosen as a suitable method to produce these structures, as it provides a good estimate of both geometric and energetic features. Indeed, the PBE+D3(BJ)^{ATM} lp-np energy difference and equilibrium volumes of both phases are in good agreement with RPA+SE results (Supplementary Table 7). In addition, Supplementary Tables 10-15 show that the internal coordinates describing the atomic geometry are only negligibly dependent on the level of theory used in the optimization. Finally, Supplementary Table 18 proves that different input geometries only marginally affect the RPA+SE lp-np energy difference.

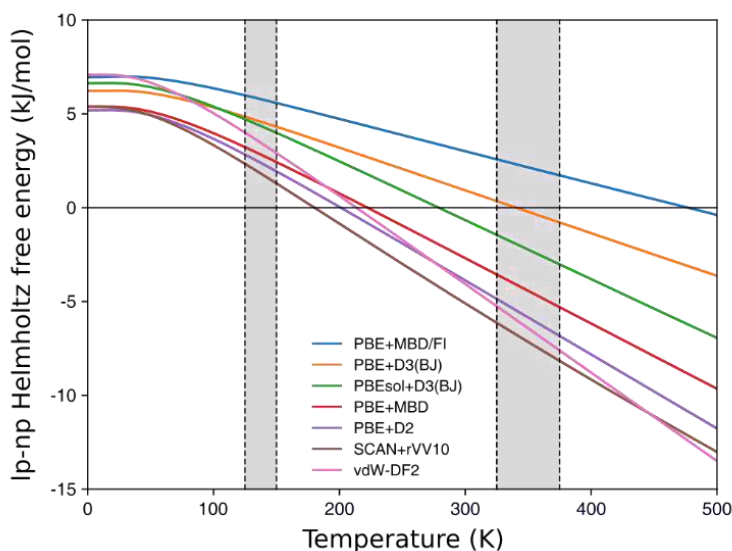
	E_{np} (kJ·mol ⁻¹)	E_{lp} (kJ·mol ⁻¹)	$\Delta E_{lp-np}^{el,*}$ (kJ·mol ⁻¹)
RPA+SE at PBE-D3(BJ) optimized geometries for fixed volumes of 864 Å ³ (np) and 1427 Å ³ (lp)	0	7.7	7.7 ± 3.5
RPA+SE at HSE06-D3(BJ) optimized geometries for fixed volumes of 864 Å ³ (np) and 1427 Å ³ (lp)	60.0	66.2	6.2
RPA+SE at vdW-DF2 optimized geometries for fixed volumes of 864 Å ³ (np) and 1427 Å ³ (lp)	-3.5	6.5	10.0

Supplementary Table 18. The electronic energy difference between the lp and np phase of MIL-53(Al) at the RPA+SE level of theory based on geometries determined with different electronic-structure methods. Absolute energies are expressed relative to the result for RPA+SE on top of the np PBE+D3(BJ) geometry.

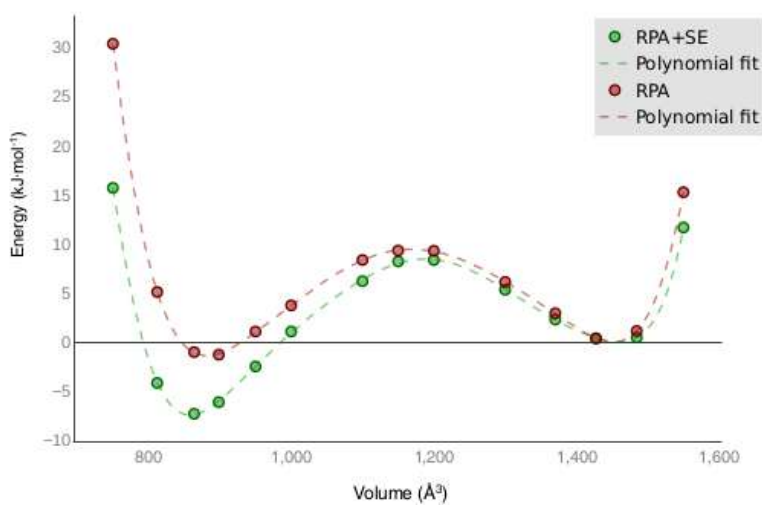
Supplementary Table 18 compares structures relaxed with three different methods (PBE+D3(BJ), HSE06+D3(BJ) and vdW-DF2). These methods were selected to incorporate two different classes of XC functionals (GGA and hybrid functionals) and two types of dispersion approaches (a posteriori corrections and contributions included in the functional itself). In addition, these three functionals yield some of the strongest changes in np cell shape (Supplementary Tables 8 and 9). While absolute RPA+SE energies vary by up to 60 kJ·mol⁻¹, we found the relative stability to remain within the RPA+SE error bar of 3.5 kJ·mol⁻¹ (see Methods section of the main manuscript). This is because small differences in the *b* parameter, which is related to the stiff metal-oxide bonds, yield relatively large differences in absolute RPA+SE energy. However, each of the three considered electronic-structure methods affects these bonds in both the lp and np phase to a similar extent, resulting in an overall negligible difference in lp-np phase stability. Therefore, we can safely assume that our results obtained using PBE+D3(BJ) geometries are only slightly sensitive to the precise level of theory used for the geometries.

Supplementary Note 6. Finite-temperature corrections with DFT

The spread on the finite-temperature corrections in Figure 3 (main article) results from different predicted phonon densities of states, showing that these predictions are also sensitive to the chosen method. As thermal corrections at the RPA+SE level for large systems like MOFs are not possible using the available current computational resources, we cannot benchmark our DFT predictions to a higher-level method, which is why we included all predictions to indicate the sensitivity. However, for this specific system, some of us recently investigated the experimental infrared and Raman spectrum of the np and lp phase of MIL-53(Al) and showed a good agreement with our PBE+D3(BJ) predicted spectrum.[49]



Supplementary Figure 4. Finite-temperature corrections for the lp-np energy difference of MIL-53(Al) with DFT on top of the RPA+SE electronic energy difference.

Supplementary Note 7. RPA(+SE) energy profile as a function of the volume

Supplementary Figure 5. MIL-53(Al) energy profile as a function of the volume with RPA and RPA+SE illustrating the importance of the inclusion of the SE contribution.

Supplementary Note 8. Structures

An overview is provided of the materials considered in this work and their names used in literature in Supplementary Table 19. The optimized geometries for the series of isorecticular MIL-53(Al) materials used to calculate the Helmholtz free energy difference between the np and lp phase as a function of temperature are given in Supplementary Table 20 and are compared to the experimental structures.

<i>Material</i>	<i>Inorganic part</i>	<i>Organic Linker</i>	<i>Chemical Name</i>	<i>Synonyms</i>
MIL-53(Al)	Al(OH) 1D chain	1,4-benzene dicarboxylate (H ₄ C ₈ O ₄ , BDC)	Al(OH)(BDC)	MIL-53(Al)-BDC, Aluminum terephthalate, Basolite A100
MIL-53(Ga)	Ga(OH) 1D chain	1,4-benzene dicarboxylate (H ₄ C ₈ O ₄ , BDC)	Ga(OH)BDC	MIL-53(Ga)-BDC, Gallium terephthalate, IM-19
MIL-53(Al)-FA	Al(OH) 1D chain	fumaric acid (H ₂ C ₄ O ₄ , FA)	Al(OH)(FA)	A520, Aluminum fumarate
DUT-4	Al(OH) 1D chain	2,6-naphthalene dicarboxylate (H ₆ C ₁₂ O ₄ , NDC)	Al(OH)(NDC)	MIL-69, MIL-53(Al)-NDC
DUT-5	Al(OH) 1D chain	4,4'-biphenyl dicarboxylate (H ₈ C ₁₄ O ₄ , BPDC)	Al(OH)(BPDC)	MIL-53(Al)-BPDC

Supplementary Table 19. Overview of considered materials and their names used in literature.

<i>Material</i>	<i>Phase</i>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
MIL-53(Al)	np	19.252	6.655	6.606	90.0	90.0	95.3	843
	np (exp. at 77 K) [37]	19.121	6.607	6.871	90.0	90.0	95.5	864
	lp	17.089	6.662	12.528	90.0	90.0	90.8	1,426
	lp (exp. at 77 K) [37]	16.91	6.624	12.67	90.0	90.0	90.0	1,419
MIL-53(Ga)	np	19.522	6.771	6.387	97.4	92.3	96.3	831
	np (exp. at 413 K) [50]	19.302	6.716	7.158	90.0	90.0	95.1	924
	lp	17.018	6.739	13.166	90.0	90.0	90.4	1,510
	lp (exp. at 623 K) [50]	16.734	6.741	13.282	90.0	90.0	90.0	1,498
MIL-53(Al)-FA	np	15.054	6.720	6.285	107.7	90.0	90.0	606
	np (exp. at 298 K and 410 MPa) [51]	15.120	6.630	7.676	103.4	90.0	90.0	750
	lp	13.449	6.688	10.744	101.61	90.0	90.0	947
	lp (exp. at 298 K) [51]	12.154	7.022	11.846	99.6	90.0	90.0	998
DUT-4	np	23.697	6.639	6.974	90.0	90.0	91.0	1,097
	np (exp. at 298 K with H ₂ O) [41]	24.625	6.560	7.528	90.0	90.0	91.4	1,160
	lp*	19.633	6.683	16.550	90.0	90.0	96.2	2,159
	lp (exp. at 293 K) [52]	18.825	6.787	16.901	90.0	90.0	90.0	2,159
DUT-5	np	27.852	6.643	6.628	98.2	92.5	96.2	1,205
	lp	24.509	6.653	17.044	90.0	90.0	90.2	2,779
	lp (exp. at 293 K) [52]	22.698	6.607	19.240	90.0	90.0	90.0	2,885

Supplementary Table 20. Crystallographic data of a series of isorecticular MIL-53(Al) materials. The equilibrium volume was obtained by fitting the Rose-Vinet equation of state [42] to a local PBE+D3(BJ) energy profile as a function of volume.

*The lp phase of DUT-4 is not a minimum on the potential energy surface as a function of volume at the PBE+D3(BJ) level and was optimized at the experimental volume.

Supplementary References

1. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
2. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **78**, 1396 (1997).
3. Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.* **100**, 136406 (2008).
4. Perdew, J. P. et al. Erratum: Restoring the density-gradient expansion for exchange in solids and surfaces [Phys. Rev. Lett. 100, 136406 (2008)]. *Phys. Rev. Lett.* **102**, 039902 (2009).
5. Dion, M., Rydberg, H., Schröder, E., Langreth, D. C. & Lundqvist, B. I. Van der Waals density functional for general geometries. *Phys. Rev. Lett.* **92**, 246401 (2004).
6. Klimeš, J., Bowler, J. R. & Michaelides, A. Van der Waals density functionals applied to solids. *Phys. Rev. B* **83**, 195131 (2011).
7. Lee, K., Murray, É. D., Kong, L., Lundqvist, B. I. & Langreth, D. C. Higher-accuracy van der Waals density functional. *Phys. Rev. B* **82**, 081101 (2010).
8. Román-Pérez, G. & Soler, J. M. Efficient implementation of a van der Waals density functional: application to double-wall carbon nanotubes. *Phys. Rev. Lett.* **103**, 096102 (2009).
9. Sun, J. et al. Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional. *Nat. Chem.* **8**, 831-836 (2016).
10. Sun, J., Ruzsinszky, A. & Perdew, J. P. Strongly constrained and appropriately normed semilocal density functional. *Phys. Rev. Lett.* **115**, 036402 (2015).
11. Peng, H., Yang, Z.-H., Perdew, J. P. & Sun, J. Versatile van der Waals density functional based on a meta-generalized gradient approximation. *Phys. Rev. X* **6**, 041005 (2016).
12. Sabatini, R., Gorni, T. & de Gironcoli, S. Nonlocal van der Waals density functional made simple and efficient. *Phys. Rev. B* **87**, 041108(R) (2013).
13. Vydrov, O. A. & Van Voorhis, T. Nonlocal van der Waals density functional: the simpler the better. *J. Chem. Phys.* **133**, 244103 (2010).
14. Zhao, Y. & Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **125**, 194101 (2006).
15. Becke, A.D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **38**, 3098-3100 (1988).
16. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993).
17. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789 (1988).
18. Vosko, S. H., Wilk, L. & Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* **58**, 1200-1211 (1980).
19. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207 (2003).
20. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Erratum: "Hybrid functionals based on a screened Coulomb potential" [J. Chem. Phys. 118, 8207 (2003)]. *J. Chem. Phys.* **124**, 219906 (2006).
21. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **125**, 224106 (2006).
22. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **132**, 15104 (2010).
23. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **132**, 1456-1465 (2011).

24. Moellmann, J. & Grimme, S. DFT-D3 study of some molecular crystals. *J. Phys. Chem. C* **118**, 7615-7621 (2014).
25. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787-1799 (2006).
26. Tkatchenko, A. & Scheffler, M. Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.* **102**, 073005 (2009).
27. Ambrosetti, A., Reilly, A. M., DiStasio Jr., R. A. & Tkatchenko, A. Long-range correlation energy calculated from coupled atomic response functions. *J. Chem. Phys.* **140**, 18A508 (2014).
28. Bučko, T., Lebègue, S., Gould, T. & Ángyán, J. G. Many-body dispersion corrections for periodic systems: An efficient reciprocal space implementation. *J. Phys. Condens. Matter.* **28**, 045201 (2016).
29. DiStasio Jr., R. A., Gobre, V. V. & Tkatchenko, A. Many-body van der Waals interactions in molecules and condensed matter. *J. Phys. Condens. Matter* **26**, 213202 (2014).
30. Tkatchenko, A., DiStasio Jr., R. A., Car, R. & Scheffler, M. Accurate and efficient method for many-body van der Waals interactions. *Phys. Rev. Lett.* **108**, 236402 (2012).
31. Gould, T., Lebègue, S., Ángyán, J. G. & Bučko, T. A fractionally ionic approach to polarizability and van der Waals many-body dispersion calculations. *J. Chem. Theory Comput.* **12**, 5920-5930 (2016).
32. Walker, A. M. et al. Flexibility in a metal-organic framework controlled by weak dispersion forces: the bistability of MIL-53(Al). *Angew. Chem. Int. Ed.* **49**, 7501-7503 (2010).
33. Nanthamathee, C., Ling, S., Slater, B. & Attfield, M. P. Contradistinct thermoresponsive behavior of isostructural MIL-53 type metal-organic frameworks by modifying the framework inorganic anion. *Chem. Mater* **27**, 85-95 (2015).
34. Ling, S. & Slater, B. Unusually large band gap changes in breathing metal-organic framework materials. *J. Phys. Chem. C* **119**, 16667-16677 (2015).
35. Coudert, F.-X., Boutin, A. & Fuchs, A. H. A thermodynamic description of the adsorption-induced structural transitions in flexible MIL-53 metal-organic framework. *Mol. Phys.* **112**, 1257-1261 (2014).
36. Wang, M., Zhang, X. & Li, D. How guest molecules stabilize the narrow pore phase of soft porous crystals: structural and mechanical properties of MIL-53(Al)·H₂O. *J. Phys. Chem. C* **120**, 5059-5066 (2016).
37. Liu, Y. et al. Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **130**, 11813-11818 (2008).
38. Yot, P. G. et al. Metal-organic frameworks as potential shock absorbers: the case of the highly flexible MIL-53(Al). *Chem. Commun.* **50**, 9462-9464 (2014).
39. Nevjestić, I. et al. In situ electron paramagnetic resonance and X-ray diffraction monitoring of temperature-induced breathing and related structural transformations in activated V-doped MIL-53(Al). *J. Phys. Chem. C* **120**, 17400-17407 (2016).
40. Nevjestić, I. et al. Sensing the framework state and guest molecules in MIL-53(Al) via the electron paramagnetic resonance spectrum of V^{IV} dopant ions. *Phys. Chem. Chem. Phys.* **19**, 24545-24554 (2017).
41. Loiseau, T. et al. A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. *Chem.-Eur. J.* **10**, 1373-1382 (2004).
42. Vinet, P., Ferrante, J., Rose, J. H. & Smith, J. R. Compressibility of solids. *J. Geophys. Res.* **92**, 9319-9325 (1987).
43. Vanpoucke, D. E. P., Lejaeghere, K., Van Speybroeck, V., Waroquier, M. & Ghysels, A. Mechanical properties from periodic plane wave quantum mechanical codes: the challenge of the flexible nanoporous MIL-47(V) framework. *J. Phys. Chem. C* **119**, 23752-23766 (2015).
44. Brandenburg, J. G., Bates, J. E., Sun, J. & Perdew, J. P. Benchmark tests of a strongly constrained semilocal functional with a long-range dispersion correction. *Phys. Rev. B* **94**, 115144 (2016).

45. Hermann, J. & Tkatchenko, A. Electronic exchange and correlation in van der Waals systems: balancing semilocal and nonlocal energy contributions. *J. Chem. Theory Comput.* **14**, 1361-1369 (2018).
46. Zhang, G.-X., Tkatchenko, A., Paier, J., Appel, H. & Scheffler, M. Van der Waals interactions in ionic and semiconductor solids. *Phys. Rev. Lett.* **107**, 245501 (2011).
47. Maurer, R. J., Ruiz, V. G. & Tkatchenko, A. Many-body dispersion effects in the binding of adsorbates on metal surfaces. *J. Chem. Phys.* **143**, 102808 (2015).
48. Marom, N., Tkatchenko, A., Scheffler, M. & Kronik, L. Describing both dispersion interactions and electronic structure using density functional theory: the case of metal-phthalocyanine dimers. *J. Chem. Theory Comput.* **6**, 81-90 (2010).
49. Hoffman, A. E. J. et al. Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/computational approach. *J. Phys. Chem. C* **122**, 2734-2746 (2018).
50. Chaplais, G. et al. IM-19: a new flexible microporous gallium based-MOF framework with pressure- and temperature-dependent openings. *Phys. Chem. Chem. Phys.* **11**, 5241-5245 (2009).
51. Yot, P. G. et al. Mechanical energy storage performance of an aluminum fumarate metal-organic framework. *Chem. Sci.* **7**, 446-450 (2016).
52. Senkovska, I. et al. New highly porous aluminium based metal-organic frameworks: Al(OH)(NDC) (NDC = 2,6-naphthalene dicarboxylate) and Al(OH)(BPDC) (BPDC = 4,4'-biphenyl dicarboxylate). *Micropor. Mesopor. Mat.* **122**, 93-98 (2009).

Paper VI

On the importance of anharmonicities and nuclear quantum effects in modelling the structural and thermal expansion of MOF-5

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The Journal of Chemical Physics, **2019**, 150, 094503

J. Wieme was one of the counsellors of A. Lemaire's master thesis and had a large contribution in the interpretation of the results.

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On the importance of anharmonicities and nuclear quantum effects in modelling the structural properties and thermal expansion of MOF-5

Cite as: J. Chem. Phys. 150, 094503 (2019); doi: 10.1063/1.5085649

Submitted: 13 December 2018 • Accepted: 6 February 2019 •

Published Online: 4 March 2019



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ABSTRACT

In this article, we investigate the influence of anharmonicities and nuclear quantum effects (NQE) in modelling the structural properties and thermal expansion of the empty MOF-5 metal-organic framework. To introduce NQEs in classical molecular dynamics simulations, two different methodologies are considered, comparing the approximate, but computationally cheap, method of generalised Langevin equation thermostating to the more advanced, computationally demanding path integral molecular dynamics technique. For both methodologies, similar results were obtained for all the properties under investigation. The structural properties of MOF-5, probed by means of radial distribution functions (RDFs), show some distinct differences with respect to a classical description. Besides a broadening of the RDF peaks under the influence of quantum fluctuations, a different temperature dependence is also observed due to a dominant zero-point energy (ZPE) contribution. For the thermal expansion of MOF-5, by contrast, NQEs appear to be only of secondary importance with respect to an adequate modelling of the anharmonicities of the potential energy surface (PES), as demonstrated by the use of two differently parametrised force fields. Despite the small effect in the temperature dependence of the volume of MOF-5, NQEs do however significantly affect the absolute volume of MOF-5, in which the ZPE resulting from the intertwining of NQEs and anharmonicities plays a crucial role. A sufficiently accurate description of the PES is therefore prerequisite when modelling NQEs.

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I. INTRODUCTION

Within the past few decades, the field of atomistic computer simulations has established itself as an important and complementary tool to experimental research in the characterisation of various types of materials. This computational approach does not only provide information about the fundamental molecular features underlying the material's properties but also allows for a large scale screening of potentially interesting materials, where new material designs can be assessed without the burdening

requirement of synthesis that precedes experimental characterisation.¹ For metal-organic frameworks (MOFs),^{2–4} in particular, a screening by means of atomistic simulations is recommended as these crystalline materials are built up out of inorganic building blocks that are connected to one another through organic linkers, giving rise to a virtually unlimited number of possible frameworks that can be constructed out of the vast amount of building blocks.^{5–7} The designer aspect of MOFs along with the versatility in properties of the different MOF structures makes this class of nanoporous materials most attractive for industrial applications,⁸ ranging from

gas storage and gas separation^{9,10} over heterogeneous catalysis¹¹ to shock absorption for the more flexible framework materials.¹²

Computationally, material properties can be obtained from molecular dynamics (MD) simulations as time averaged quantities by integrating the equations of motion throughout time. By relying on the Born-Oppenheimer approximation, as is usually done in MD simulations, one can separate the dynamics of the nuclei from the dynamics of the electronic structure of the system. Depending on the required length of the simulation and the size of the molecular system, the potential energy surface (PES) is then described *ab initio*, typically by means of density functional theory (DFT), or analytically, using force fields. However, irrespective of the description of the PES, a vast majority of the MD simulations treats the atomic nuclei as classical particles, in spite of their quantum mechanical nature. For sufficiently heavy atoms at sufficiently high temperatures, subjected to moderate interatomic interactions, this approximation is expected to be reasonable. Lighter atoms at lower temperatures or atoms subjected to strong interatomic interactions on the contrary cannot be described as classical particles, but have to be treated quantum mechanically as nuclear quantum effects (NQE) such as zero-point energy (ZPE) and tunnelling can induce significant deviations from the classical behaviour. For water, a prototypical case study within the context of NQEs, the importance of NQEs has been demonstrated for ample of aspects,^{13,14} including the occurrence of transient autoprotolysis events in liquid water¹⁵ and a proper description of the heat capacity of both liquid water and ice.¹⁶ Given the large ZPE of about 21 kJ/mol per O–H stretch,¹³ which is in sharp contrast with the classical contribution to the kinetic energy of only 3.7 kJ/mol at 300 K (as predicted by the equipartition law), the importance of NQEs in water is abundantly clear.

Within the context of MOFs, NQEs are hardly ever taken into account, despite the presence of many light framework atoms, such as hydrogen and carbon. Only when studying water molecules confined in the pores of a framework, NQEs have been included to some extent.^{17,18} In this work, the importance of NQEs in the structural and thermal properties of the empty framework of MOF-5¹⁹ is assessed by means of MD simulations. In this way, the NQEs inherent to the MOF itself are investigated rather than the NQEs associated with water present in its pores, using MOF-5 as a prototypical rigid framework (Fig. 1). The structural properties of MOF-5 are probed by means of radial distribution functions (RDFs), which yield information about the interatomic equilibrium distances and the thermal activation of bond stretches of different atom pairs. The thermal property under review is the well-known negative thermal expansion of MOF-5,^{20–25} for which a delicate interplay between the modelling of anharmonicities and NQEs is demonstrated.

For each of these properties, the importance of NQEs is assessed by comparing ordinary, classical MD simulations to MD simulations including NQEs, where the quantum mechanical description of the nuclei is pursued using two different methodologies. The first method is the so-called generalised

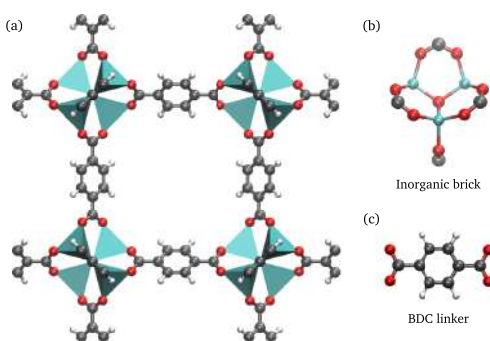


FIG. 1. (a) Conventional unit cell of MOF-5, with the ZnO₄ tetrahedra indicated in light blue. (b) Zn₄O(CO₂)₆ metal oxide cluster. (c) 1,4-benzenedicarboxylate (BDC) linker.

Langevin equation (GLE) quantum thermostat,²⁶ which allows us to include harmonic NQEs at virtually no additional computational cost. The second method that will be considered is the more advanced technique of path integral MD (PIMD),^{27,28} which entails a more rigorous description of both harmonic and anharmonic NQEs, at a sometimes considerable additional computational expense. By combining both methods, the computational cost of PIMD simulations can however be reduced by a factor of about four^{29,30} and therefore, this synergistic approach will also be considered, alongside the GLE quantum thermostat and regular PIMD, as explained in Sec. II.

II. METHODOLOGY: MODELLING NUCLEAR QUANTUM EFFECTS

A. GLE quantum thermostat

A first, but approximate technique to include NQEs in MD simulations is the so-called generalised Langevin equation (GLE) quantum thermostat.²⁶ Just as any other thermostat, the GLE thermostat imposes a sampling of the canonical ensemble instead of the microcanonical ensemble by adapting Hamilton's equations of motion, to allow for an exchange of heat with the system's surroundings

$$\dot{q}(t) = p(t), \quad (1)$$

$$\dot{p}(t) = -\frac{dV(q)}{dq} - \int_{-\infty}^t K(t-\tau)p(\tau)d\tau + \zeta(t), \quad (2)$$

with q the generalised coordinate describing the position of a particle with a unit mass, p the conjugate momentum, $V(q)$ the potential energy, $K(t)$ the memory kernel of the GLE, and $\zeta(t)$ a random Gaussian distributed force. To impose a canonical sampling, the time correlation function $H(t) = \langle \zeta(t)\zeta(0) \rangle$ of the random force $\zeta(t)$ has to be related to the memory kernel $K(t)$ by means of the fluctuation-dissipation theorem^{31,32}

$$H(\omega) = k_B \text{TK}(\omega), \quad (3)$$

with k_B the Boltzmann constant, T the temperature, and $H(\omega)$ and $K(\omega)$ the Fourier transforms of, respectively, $H(t)$ and $K(t)$. However, if one wants to turn the GLE thermostat into a GLE quantum thermostat, which can be used as a tool to introduce NQEs in MD simulations, the constraint imposed by the fluctuation-dissipation theorem has to be relaxed to provide the necessary freedom to include harmonic NQEs. To that end, an effective temperature T^* , given by

$$T^* = \frac{\hbar\omega}{2k_B} \coth\left(\frac{\hbar\omega}{2k_B T}\right), \quad (4)$$

is introduced in order to match the probability distribution ρ of the displacement q of a classical harmonic oscillator with frequency ω and mass m ,

$$\rho(q) \propto \exp\left(-\frac{m\omega^2 q^2}{2k_B T}\right), \quad (5)$$

to the quantum mechanical probability distribution of the displacement (see Sec. S1), which is proportional to

$$\rho(q) \propto \exp\left[-\frac{1}{2}m\omega^2 q^2 \frac{1}{\frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_B T}\right)}\right]. \quad (6)$$

In this way, the classical canonical sampling imposed by the Boltzmann distribution [Eq. (5)] can be transformed into a quantum mechanical sampling that is in accordance with the probability distribution of the quantum harmonic oscillator [Eq. (6)] and as a consequence introduces a sampling of the harmonic NQEs. Therefore, one should picture the GLE quantum thermostat as a thermostat that excites every vibrational mode present in a molecular system to an effective temperature T^* , which is the temperature the mode is supposed to have according to the probability distribution of the quantum harmonic oscillator.

The appropriate canonical sampling is then once again obtained by imposing the fluctuation-dissipation theorem, where the effective, frequency-dependent temperature T^* now takes the role of the physical temperature T so that

$$H(\omega) = k_B T^* K(\omega). \quad (7)$$

However, since the GLE quantum thermostat is a so-called non-equilibrium thermostat that violates the fluctuation-dissipation theorem (i.e., the fluctuation-dissipation theorem for the physical temperature T), one now also needs to explicitly impose the equipartition theorem, as this cannot longer be taken for granted for a non-equilibrium thermostat. In view of an adequate modelling of harmonic NQEs, one therefore also has to satisfy the equipartition theorem for the quantum harmonic oscillator, which requires that

$$\langle p^2 \rangle = m^2 \omega^2 \langle q^2 \rangle = \frac{\hbar m \omega}{2} \coth\left(\frac{\hbar \omega}{2k_B T}\right). \quad (8)$$

The only difference between an ordinary GLE thermostat and the GLE quantum thermostat is hence the way in which the memory kernel $K(t)$ and the random force $\zeta(t)$ are related to one another so that the GLE thermostat allows us

to include harmonic NQEs in MD simulations without almost any additional computational cost. For a more detailed discussion of the GLE quantum thermostat, the reader is referred to Refs. 26, 33, and 34

B. Second order path integral MD

A more rigorous method to model NQEs in MD simulations is given by the path integral MD formalism.³⁵ In this formalism, which can be traced back to Feynman's path integral formulation of quantum mechanics,³⁶ NQEs are evoked by replacing every atom of the molecular structure by a so-called ring polymer that consists of P atom replicas, called beads, that interact with one another via a harmonic nearest-neighbour interaction, as depicted schematically in Fig. 2.

For an N -atom molecular system characterised by the Hamiltonian

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (9)$$

with $\mathbf{p}_i$ and $\mathbf{r}_i$, respectively, the momentum and position of the i th particle and $V(\mathbf{r}_1, \dots, \mathbf{r}_N)$ the potential energy, this more rigorous introduction of NQEs can be readily obtained by means of a Trotter factorisation of the quantum mechanical canonical partition function $Z = \text{Tr}[e^{-\beta \hat{H}}]$, expanding the canonical density matrix $e^{-\beta \hat{H}}$ as follows:

$$e^{-\beta \hat{H}} = \left[e^{-\frac{\beta}{P} \hat{H}} e^{-\frac{\beta}{P} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i}} e^{-\frac{\beta}{P} \hat{H}} \right]^P + \mathcal{O}(P^{-2}), \quad (10)$$

with $\beta = (k_B T)^{-1}$ the inverse temperature and P the number of beads. The resulting expression for the quantum mechanical canonical partition function Z then becomes (see Sec. S2)

$$Z_P = \prod_{k=1}^P \prod_{i=1}^N \int d\mathbf{p}_i^{(k)} \int d\mathbf{r}_i^{(k)} e^{-\beta H_P}, \quad (11)$$

where the Hamiltonian of the N -atom system is replaced by the Hamiltonian of an extended molecular system given by

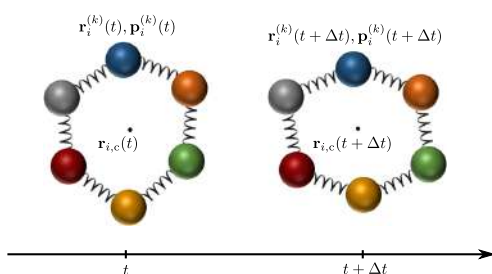


FIG. 2. Schematic representation of the time evolution of a 6 bead ring polymer with centroid $r_{i,c}$.

$$H_P = H_P^0 + V_P, \quad (12)$$

with

$$H_P^0 = \sum_{k=1}^P \sum_{i=1}^N \left[\frac{\mathbf{p}_i^{(k)^2}}{2m_i} + \frac{1}{2} m_i \omega_P^2 \left(\mathbf{r}_i^{(k+1)} - \mathbf{r}_i^{(k)} \right)^2 \right] \quad (13)$$

and

$$V_P = \frac{1}{P} \sum_{k=1}^P V(\mathbf{r}_1^{(k)}, \dots, \mathbf{r}_N^{(k)}), \quad (14)$$

with $\mathbf{r}_i^{(k)}$ and $\mathbf{p}_i^{(k)}$, respectively, the position and momentum of the k th bead of the i th particle, $\omega_P = \frac{\sqrt{P}}{\beta\hbar}$ the angular frequency of the harmonic interaction between the neighbouring beads of the ring polymer, and $\mathbf{r}_i^{(P+1)} = \mathbf{r}_i^{(1)}$.

The higher the number of beads P , the smaller the error in the Trotter factorisation of Eq. (10), yielding quantum mechanically exact results in the limit of an infinite number of beads. PIMD is therefore not only more accurate than the GLE quantum thermostat, as it takes both harmonic and anharmonic NQEs into account, but it also allows us to systematically increase the accuracy with which NQEs are modelled by increasing the number of beads, a desirable feature that is lacking for the GLE quantum thermostat.

The major downside of PIMD when compared to the GLE quantum thermostat is the considerable computational overhead that is induced by substituting every atom in the system by multiple bead replicas. Given the efficiency of the GLE quantum thermostat in modelling harmonic NQEs, it is however possible to develop a hybrid PI + GLE scheme,^{29,30} combining PIMD with a GLE quantum thermostat in order to reduce the number of beads required to converge PIMD simulations. In the so-called PIGLET thermostatting scheme,³⁰ the potential and kinetic energy of the system are enforced to match the harmonic quantum limit by subjecting the path centroid, defined as

$$\mathbf{r}_{i,c} = \frac{1}{P} \sum_{k=1}^P \mathbf{r}_i^{(k)}, \quad (15)$$

to classical thermostatting, while the individual beads are subjected to a GLE quantum thermostat. As a consequence, the required number of beads to converge the energy is reduced by a factor of about four since the GLE quantum thermostat already takes care of the harmonic NQEs so that higher bead multiples are only necessary to converge the remaining anharmonic NQEs.¹³

Besides PIGLET thermostatting, there also exist other cost reducing techniques for PIMD,³⁷ such as multiple time stepping (MTS),³⁸ ring polymer contraction (RPC),^{28,39} and perturbed path integrals (PPI).^{40,41} In the MTS algorithm, an algorithm first devised for classical MD, a more efficient force evaluation is obtained by separating the slowly varying long-range interactions from the rapidly varying short-range interactions. Given their different characteristic time scales, the long-range interactions only need to be evaluated at fixed time multiples of the short-range interactions, which are

calculated at every time step. A similar splitting of the interaction is used in RPC, where the long-range part of the potential is evaluated on a contracted ring polymer containing fewer than P beads. In the limit of contraction to a single bead, the classical long-range force evaluation is retrieved. A different approach is used in PPI, where the theory of Feynman path integrals is combined with quantum mechanical perturbation theory to reduce the required number of beads by means of an *a posteriori* correction to the canonical partition function [Eq. (11)].

Finally, the convergence of PIMD simulations can also be accelerated by so-called high-order PI schemes, which rely on a more accurate decomposition of the canonical density matrix than the second-order Trotter factorisation [Eq. (10)]. A more accurate decomposition scheme such as the Suzuki-Chin (SC) scheme^{42,43} then reduces the error to $\mathcal{O}(P^{-4})$, which also reduces the required number of beads to reach convergence. The force evaluation in SC PIMD is, however, more expensive than in Trotter PIMD,⁴⁴ as the equivalent of Eq. (14) not only depends on the physical potential energy, but also on the derivative of the physical potential energy. Nonetheless, SC PIMD becomes very advantageous at low temperatures or when a high accuracy is required. Therefore, this technique is used to validate our results, as outlined in Sec. IV.

III. COMPUTATIONAL DETAILS

As already mentioned in the Introduction, the importance of NQEs in MOF-5 will be assessed within this work by comparing ordinary, classical MD simulations to MD simulations including NQEs, using either a GLE quantum thermostat or PIMD. Given the rather large conventional unit cell of MOF-5, containing 424 atoms, an *ab initio* description of the PES is to be viewed as computationally too expensive, especially in combination with PIMD, so that all MD simulations within this work are performed using an in-house developed force field, generated from *ab initio* data using the in-house developed software package QuickFF.^{45,46} In view of recent publications exemplifying a delicate interplay between a correct description of anharmonic force field contributions and NQEs,^{14,47-49} the bond and bend contributions in the force field of MOF-5 are parametrised both by harmonic potentials, resulting in a "harmonic" force field, and by higher order polynomials, resulting in an "anharmonic" force field (see Sec. S3). For both types of force fields, the simulation results are discussed in Sec. IV.

All MD simulations are furthermore conducted in the NPT ensemble at a pressure of 1 bar, using a cut-off radius of 15 Å for the long-range interactions. For the classical and GLE quantum thermostatting MD simulations, the in-house MD code Yaff⁵⁰ is used in combination with LAMMPS,⁵¹ which allows us to speed up the evaluation of the non-covalent force field contributions. The PIMD simulations on the other hand are performed with the iPI software package,^{52,53} delegating the force evaluation to Yaff.

In the classical MD simulations, temperature and pressure are, respectively, controlled by a three bead Nosé-Hoover

chain (NHC) thermostat^{54–56} and a Martyna-Tuckerman-Tobias-Klein (MTTK) barostat.^{57,58} For the GLE quantum thermostatted MD simulations, a Langevin barostat is employed, whereas the PIMD simulations use white noise Langevin²⁷ or PIGLET thermostating³⁰ in combination with a Bussi-Zykova-Parrinello barostat.⁵² The relaxation times of the different thermostats and barostats are set to, respectively, 0.1 ps and 1 ps.⁵⁹ For all simulations, except for the ordinary PIMD simulations using a white noise Langevin thermostat, an MD integration step of 0.5 fs is used. The ordinary PIMD simulations require a smaller integration step of 0.25 fs due to the presence of artificial high-frequency modes introduced by the harmonic nearest neighbour coupling.²⁸ The total simulation time of all PIMD simulations is 1.25 ns, whereas the classical and GLE quantum thermostatted simulations have a total simulation time of 3 ns. The equilibration time is set to 150 ps.

Finally, to fix the number of replicas in the PIMD simulations, the convergence of the volume was tested as function of the number of beads (Fig. S1), reaching convergence at, respectively, 8 beads for PIGLET thermostatted PIMD simulations and 32 beads for ordinary PIMD simulations.

IV. RESULTS AND DISCUSSION

A. Structural properties: RDFs

To evaluate the influence of NQEs upon the structural properties of MOF-5, a series of radial distribution functions (RDFs) is constructed, focussing on two different atom pairs. On the one hand, we consider C–H pairs of atoms, as the C–H bonds in MOF-5 have the highest characteristic frequency, i.e., about 3195 cm^{−1}, as obtained from a normal mode analysis performed with TAMkin.⁶⁰ On the other hand, we also consider Zn–O pairs of atoms, as the Zn–O bond in MOF-5 is characterised by a much lower characteristic frequency of about 450 cm^{−1} and the low-frequency modes involving ZnO₄ tetrahedra are believed to contribute to the negative thermal expansion of MOF-5.²⁰ Based on their characteristic frequency, these bonds can also be attributed a so-called characteristic temperature or Debye temperature

$$\Theta_D = \frac{\hbar\omega}{k_B}, \quad (16)$$

which can be used as a measure to quantify the importance of NQEs, as it represents the temperature at which the quantum mechanical energy quantum $\hbar\omega$ equals the thermal energy quantum $k_B T$ and NQEs are only expected to be of importance for temperatures $T \ll \Theta_D$. For the C–H and Zn–O bonds in MOF-5, the characteristic temperatures are, respectively, given by 4600 K and 650 K.

For both types of atom pairs, the RDFs are shown in Fig. 3, comparing classical MD simulations to MD simulations including NQEs at different temperatures, using the anharmonic force field of MOF-5. The first peak of each RDF is always located at the equilibrium bond distance of the atom pair in MOF-5. The atom pairs contributing to the other RDF peaks are indicated on Fig. S2. For the C–H pairs of atoms,

the equilibrium bond length is observed to increase by an amount of about 0.02 Å when including NQEs (see Table S2 and Fig. S6), shifting the first RDF peak towards slightly higher equilibrium distances. This shift is also present for the more distant RDF peaks, indicating that the molecular structure as a whole is affected by the presence of NQEs. Furthermore, the RDF peaks are also observed to be much broader when modelled quantum mechanically instead of classically, yielding widths that are more than twice as large (see Fig. S3). In addition, the quantum mechanical widths appear to be more or less temperature independent so that, in contrast to the classical description, the C–H stretch is not yet thermally active at temperatures below 500 K. Quantum mechanically, the behaviour of the C–H stretch is therefore dominated by the ZPE it possesses, as it is significantly larger than the thermal energy up to temperatures as high as $\Theta_D/2 = 2300$ K (within a harmonic approximation).

For the Zn–O pairs of atoms, the differences between the RDFs with and without NQEs are less pronounced, but nevertheless still present. Given the much lower characteristic temperature of the Zn–O stretch in comparison with the C–H stretch, the ZPE associated with the Zn–O bond only dominates the thermal energy up to a temperature of about 300 K. Contrary to the C–H pairs of atoms, the first RDF peak of the Zn–O pairs of atoms shows no appreciable shift when including NQEs (see Table S3 and Fig. S6), as it is comprised of two overlapping RDF peaks corresponding to the Zn–O₁ and Zn–O₂ bonds [see Fig. 4(a)], limiting the peak's resolution. If the probability distribution of the Zn–O₁ bond is however isolated, as done in Fig. 4(b), one does observe a minor shift in the equilibrium bond length, just as for the C–H atom pairs. The different RDF peaks are furthermore also observed to broaden under the influence of NQEs, albeit by less than half their classical width (see Fig. S4).

When comparing the RDFs obtained using different methods to model NQEs, as shown for GLE quantum thermostatted MD simulations and PIGLET thermostatted PIMD simulations in the right column of Fig. 3, the different methods are found to agree well with one another. For the Zn–O pairs of atoms, there is almost no observable difference between the RDFs, whereas for the C–H pairs of atoms only minor differences are present, which are limited to the first RDF peak. The GLE quantum thermostat therefore performs remarkably well in comparison with PIMD, given its approximate nature and low computational cost. In order to benchmark the accuracy of the PIGLET thermostatted PIMD simulations, a 16 bead SC PIMD simulation was performed at 300 K⁴⁴ confirming the validity of the results obtained with PIGLET thermostating, as shown in Fig. S5.

Performing the above mentioned simulations with a harmonic force field of MOF-5 instead of an anharmonic force field leads to similar results (see Sec. S5). The inclusion of anharmonic contributions in the force field mainly causes the RDF peaks to shift towards larger interatomic distances, as the equilibrium bond lengths are larger for anharmonic potentials with the same force constant, as illustrated by Fig. 5. When including NQEs, this effect becomes even more pronounced for the bonds with a high characteristic frequency.

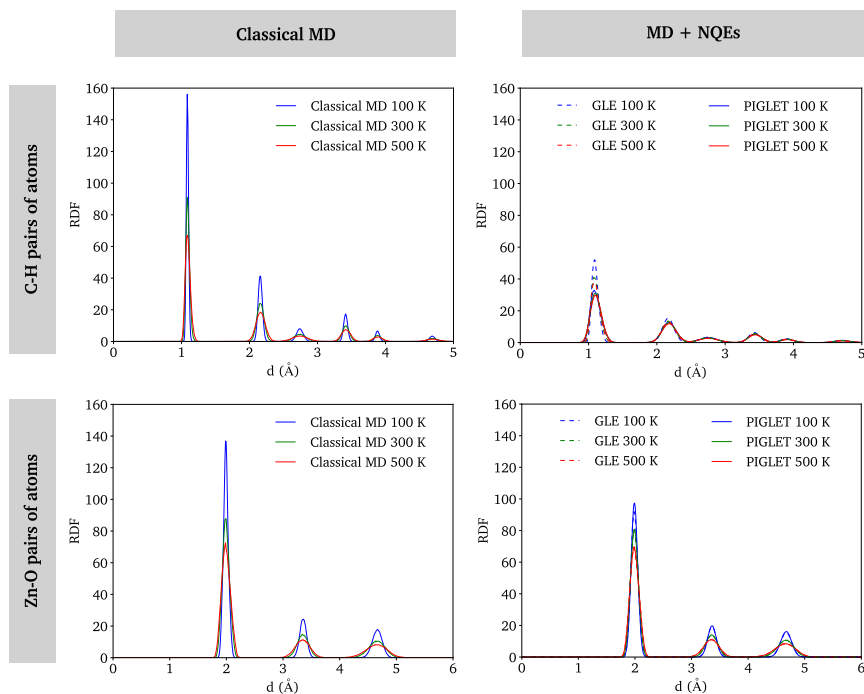


FIG. 3. RDFs of C—H pairs of atoms (top row) and Zn—O pairs of atoms (bottom row) of MOF-5 as obtained using classical MD simulations (left column) and MD simulations including NQEs (right column) at different temperatures, using the anharmonic force field of MOF-5.

For the Zn—O RDFs, there is no additional shift due to NQEs, as a consequence of the low characteristic temperature of the Zn—O stretch (Table S3). For the C—H RDFs, by contrast, the difference in peak positions is about 0.02 Å for the first peak at 100 K, a value that further increases both with the peak number and the temperature, reaching a value of 0.06 Å for the sixth peak at 500 K (Table S2), a value that is two times larger than in classical simulations. This correlated effect between the inclusion of anharmonicities in the bond description and an adequate modelling of NQEs can be inferred from the quantum mechanical description of an anharmonic potential such as the well-known Morse potential. In comparison with a harmonic potential, the anharmonic potential systematically yields a larger equilibrium bond distance, even at the lowest vibrational energy level, where the bond only possesses a ZPE (Fig. 5). As higher vibrational energy levels of the anharmonic potential are occupied, the equilibrium bond distance increases up to a point where the occupation of additional vibrational energy levels no longer affects the equilibrium bond distance, explaining the observed

temperature dependence of the RDF peak shifts. The more distinct differences for the C—H RDFs can be related to the higher characteristic frequency of the C—H bond, resulting in a larger ZPE and a larger separation between the vibrational energy levels. The higher the peak number, the larger the peak shift due to the accumulated effect of increased equilibrium bond lengths for the intermediate atoms. This coupling between the description of anharmonicities and NQEs will also prove to be important in an accurate description of the negative thermal expansion of MOF-5, as explained in Sec. IV B.

Apart from RDFs, the structural properties of MOF-5 can also be characterised by other means such as probability distributions of internal coordinates including (dihedral) angles, X-ray diffraction (XRD) patterns, or pore volume sizes. An example of an interesting internal coordinate is the $C_1-C_2-C_2$ angle [Fig. 4(d)], which can be viewed as a measure for the transverse translational motion of the benzene ring, an important motion in the negative thermal expansion of MOF-5.²⁰ Just as for atomic bonds, the probability distribution of the

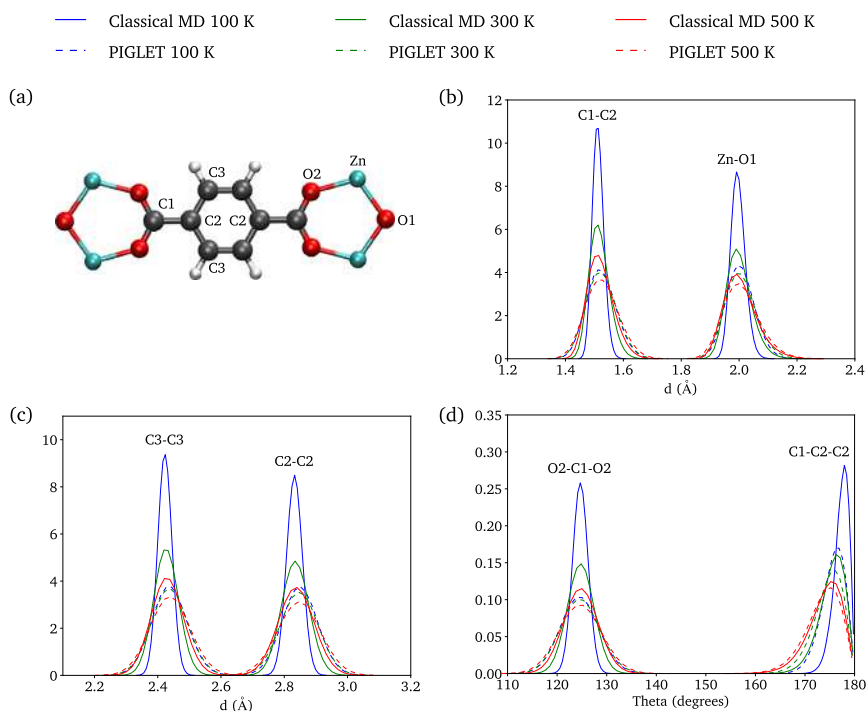


FIG. 4. (a) Labeling convention of the atoms in MOF-5. (b) Probability distribution of C₁–C₂ and Zn–O₁ distances. (c) Probability distribution of C₂–C₂ and C₃–C₃ distances. (d) Probability distribution of O₂–C₁–O₂ and C₁–C₂–C₂ angles. Solid lines indicate classical MD results, whereas dotted lines indicate PIGLET thermostatted PIMD results.

angle is observed to have a different mean value and to become noticeably broader when including NQEs, especially at lower temperatures. The XRD pattern by contrast shows no appreciable differences (Fig. S7), as its resolution is less adequate to identify smaller structural changes. Similarly, also the pore

volume of MOF-5 is observed to change only marginally when including NQEs.

B. Thermal expansion

The second property of MOF-5 for which the importance of NQEs is examined is the negative thermal expansion of MOF-5.^{20–25} Quantitatively, the thermal expansion can be characterised by the volumetric thermal expansion coefficient α_V , defined as the relative change in volume with respect to temperature at constant pressure, that is,

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial \ln V}{\partial T} \right)_P. \quad (17)$$

Within first order, the volumetric thermal expansion coefficient α_V is then obtained as the slope of a linear fit to the logarithm of the volume as a function of temperature. For periodic framework materials such as MOF-5, one can also define a lattice thermal expansion coefficient α_a , which is related

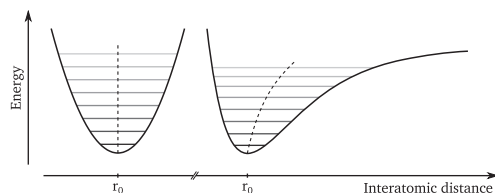


FIG. 5. Schematic representation of the energy levels of a harmonic potential (left) and an anharmonic Morse potential (right). The expectation value of the position is represented by the dashed black line.

to the volumetric thermal expansion coefficient by $\alpha_V = 3\alpha_a$, assuming an isotropic thermal expansion.

In Fig. 6, the temperature dependence of the volume of MOF-5 is shown for (PI)MD simulations performed with both the harmonic and anharmonic force fields, for which the corresponding lattice thermal expansion coefficients are listed in Table I. As all the thermal expansion coefficients calculated with the anharmonic force field lie within the experimental range, including the value derived from classical MD simulations, NQEs appear to be only of secondary importance in modelling the thermal expansion of MOF-5. A proper description of the anharmonicities of the underlying PES is observed to be far more important, as evidenced by the simulation results obtained with the harmonic force field of MOF-5. Also in the harmonic case, NQEs only yield small corrections to the classically obtained results, which does however partly correct for the overestimation of the lattice thermal expansion coefficient in comparison with experimental values (see Table I and Fig. S11). As a consequence, more accurate MD simulations accounting for NQEs are only useful if the PES is modelled sufficiently accurately, as the most decisive contribution to the thermal expansion stems from an adequate modelling of the anharmonicities, reducing the thermal expansion coefficient by about 20%–30% for MOF-5.

The absolute volume on the other hand is significantly affected by the presence of NQEs in an anharmonic description of the atomic bonds, yielding differences of the order of $150 \text{ \AA}^3$ with respect to the classically predicted volume, an effect which is completely absent within a harmonic description of the atomic bonds (Fig. 6). To explain this interplay between NQEs and anharmonicities, the equilibrium volume at 0 K is determined by means of a series of fixed volume geometry optimisations, as shown in Fig. 7. NQEs are then only accounted for within the harmonic limit, yielding a ZPE contribution of $\sum_k \frac{\hbar\omega_k}{2}$, with ω_k the normal mode

TABLE I. Lattice thermal expansion coefficient of MOF-5. (PI)MD simulations performed with the harmonic force field of MOF-5 are indicated by "harm. FF," whereas the anharmonic force field simulations are indicated by "anh. FF."

	α_a (10^{-6} K^{-1})
Classical MD (harm. FF)	−21.5
GLE (harm. FF)	−19.1
PIGLET PIMD (harm. FF)	−19.5
PIMD (harm. FF)	−19.9
Classical MD (anh. FF)	−14.2
GLE (anh. FF)	−15.3
PIGLET PIMD (anh. FF)	−16.0
PIMD (anh. FF)	−16.4
Literature ^{21,61}	[−13.3, −5.3]
Experimental (Ref. 24)	[−16, −10]
Experimental (Ref. 20)	−13.1(1)

frequencies as determined with TAMkin. The resulting equilibrium volumes, with and without NQEs, are indicated in Fig. 6 and are observed to agree well with the extrapolated (PI)MD simulation data so that the explanation for the difference in volumes is to be found within the phenomenon of ZPE.

In the harmonic limit, the ZPE only depends on the normal mode frequencies of the structure so that it is instructive to determine how those frequencies depend on the volume of the structure. For a harmonic potential, the normal mode frequencies as given by the second order positional derivative of the potential are volume independent, yielding a constant ZPE contribution as a function of volume (see Sec. S6). An anharmonic potential by contrast has a second order positional derivative that depends on the position, due to the presence of higher order polynomial contributions to the potential, and is hence characterised by a set of volume dependent normal mode frequencies. As a consequence,

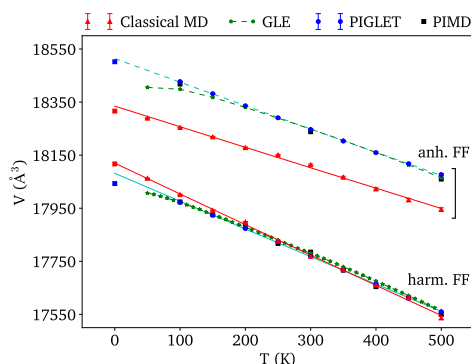


FIG. 6. Volume of MOF-5 as a function of temperature as obtained from (PI)MD simulations using the harmonic ("harm. FF," bottom curves) and anharmonic ("anh. FF," top curves) force field of MOF-5. The data points at 0 K were obtained from geometry optimisations with Yaff.

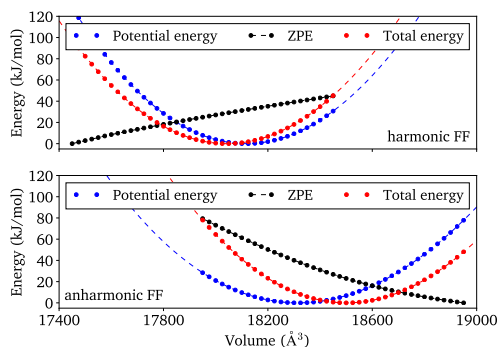


FIG. 7. Potential energy, ZPE, and the sum of both energies as a function of the volume of MOF-5, obtained using Yaff geometry optimisations with the harmonic (top figure) and anharmonic (bottom figure) force fields of MOF-5.

also the ZPE becomes volume dependent, which translates into a temperature dependence within the context of thermal expansion. With decreasing volumes, the normal mode frequencies of MOF-5 are observed to increase up to 30 cm^{-1} (Fig. S8), resulting in an increase of the corresponding ZPE contributions. As the total increase in ZPE is about one order of magnitude larger than the corresponding increase in thermal energy (i.e., 41.2 kJ/mol versus 4.0 kJ/mol), the difference in volume due to the presence of NQEs is perceived within a wide temperature range. Only at very high temperatures, classical and quantum mechanical volumes can be observed to converge to one another (Fig. S10).

The volume dependence of the ZPE of MOF-5 in the harmonic force field (Fig. 7) is to be attributed to other energy contributions in the force field that have an anharmonic character, such as the non-covalent electrostatic and van der Waals contributions. With decreasing volume, or equivalently increasing temperature, the normal mode frequencies are now observed to decrease (Fig. S8) so that also the ZPE decreases with temperature and the thermal energy becomes the dominant energy contribution. The difference in volume due to the presence of NQEs is therefore only noticeable in a relatively small low temperature range, in contrast with the anharmonic case.

To conclude, we also evaluate the different methodologies used to model NQEs in the thermal expansion of MOF-5. Just as for the RDFs, the GLE quantum thermostat performs well when compared to the more demanding PIMD simulations, yielding similar absolute volumes and a matching volumetric temperature dependence. Only at the lowest temperatures, below 100 K , the GLE quantum thermostat predicts a deviating behaviour from the PIMD results, as for the GLE thermostat the volume is observed to saturate. Given the approximate nature of the GLE quantum thermostat, modelling only harmonic NQEs, this saturation of the crystal volume can be understood as an artefact of the constant harmonic ZPE, which causes the bond length fluctuations to become constant and thus saturates the crystal volume.

V. CONCLUSIONS

In this article, we examined the influence of anharmonicities and NQEs upon an accurate modelling of the structural and thermal properties of MOF-5. The structural properties, probed by means of RDFs, were shown to be significantly affected by the presence of NQEs. Under the influence of quantum fluctuations, the RDF peaks tend to broaden and show furthermore a small shift towards larger interatomic distances, due to a coupling between NQEs and the anharmonicities of the PES. Also for the temperature dependence of the RDFs and hence, the structure itself, a different picture emerges. At lower temperatures, the ZPE becomes the most dominant energy contribution and as a consequence, reduces the importance of the thermal energy. For the highest characteristic frequencies in MOF-5, this effect is perceivable up to very high temperatures, making the C–H bond virtually

temperature independent below 500 K . For the negative thermal expansion of MOF-5, by contrast, the inclusion of NQEs appears to be only of secondary importance with respect to a proper modelling of the anharmonicities of the PES, as it yields only small corrections to the thermal expansion coefficient. The interplay between NQEs and anharmonicities does however affect the absolute volume, as volume dependent characteristic frequencies lead to a volume dependent ZPE, resulting in a different equilibrium volume. A sufficiently accurate description of the PES is therefore prerequisite when modelling NQEs.

A comparison of different methodologies capable of modelling NQEs furthermore showed an excellent agreement between the approximate technique of GLE thermostatting and the more rigorous framework of PIMD, at least for the structural properties and the negative thermal expansion of MOF-5. Therefore, the inclusion of NQEs in MD simulations of MOF-5 can be achieved most efficiently by means of a GLE thermostat, which produces almost no computational overhead.

SUPPLEMENTARY MATERIAL

In the [supplementary material](#), a more elaborate discussion of the GLE quantum thermostat and PIMD can be found, as well as additional information concerning the RDFs and thermal expansion of MOF-5. Also the convergence of the PIMD simulations and the force field parametrisation are addressed, providing a force field parameter input file for MOF-5.

ACKNOWLEDGMENTS

This work was supported by the Fund for Scientific Research Flanders (FWO), the Research Board of Ghent University, and the European Union's Horizon 2020 research and innovation programme [consolidator ERC Grant Agreement No. 647755-DYNPOR (2015–2020)]. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation–Flanders (FWO) and the Flemish Government–department EWI. We would also like to thank Michele Ceriotti (COSMO, EPFL) for his valuable input and his help in improving this manuscript.

REFERENCES

- ¹S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, "The high-throughput highway to computational materials design," *Nat. Mater.* **12**, 191–201 (2013).
- ²H. Furukawa, K. E. Cordova, M. O'Keeffe, and O. M. Yaghi, "The chemistry and applications of metal-organic frameworks," *Science* **341**, 1230444 (2013).
- ³S. Kitagawa, "Future porous materials," *Acc. Chem. Res.* **50**, 514–516 (2017).
- ⁴G. Maurin, C. Serre, A. Cooper, and G. Férey, "The new age of MOFs and of their porous-related solids," *Chem. Soc. Rev.* **46**, 3104–3107 (2017).
- ⁵M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, and O. M. Yaghi, "Modular chemistry: Secondary building units as a basis for the

design of highly porous and robust metal-organic carboxylate frameworks," *Acc. Chem. Res.* **34**, 319–330 (2001).

⁶C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, and R. Q. Snurr, "Large-scale screening of hypothetical metal-organic frameworks," *Nat. Chem.* **4**, 83 (2011).

⁷P. Z. Moghadam, A. Li, S. B. Wiggins, A. Tao, A. G. P. Maloney, P. A. Wood, S. C. Ward, and D. Fairen-Jimenez, "Development of a Cambridge structural database subset: A collection of metal-organic frameworks for past, present, and future," *Chem. Mater.* **29**, 2618–2625 (2017).

⁸P. Silva, S. M. F. Vilela, J. P. C. Tomé, and F. A. Almeida Paz, "Multi-functional metal-organic frameworks: From academia to industrial applications," *Chem. Soc. Rev.* **44**, 6774–6803 (2015).

⁹J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi, and J. R. Long, "Methane storage in flexible metal-organic frameworks with intrinsic thermal management," *Nature* **527**, 357–361 (2015).

¹⁰E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren, and L. Brammer, "Solvent-switchable continuous-breathing behaviour in a diamondoid metal-organic framework and its influence on CO₂ versus CH₄ selectivity," *Nat. Chem.* **9**, 882–889 (2017).

¹¹S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clot, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, and J. Gascon, "Metal-organic and covalent organic frameworks as single-site catalysts," *Chem. Soc. Rev.* **46**, 3134–3184 (2017).

¹²L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, and V. Van Speybroeck, "Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals," *Nat. Commun.* **9**, 204 (2018).

¹³M. Ceriotti, W. Fang, P. G. Kusalik, R. H. McKenzie, A. Michaelides, M. A. Morales, and T. E. Markland, "Nuclear quantum effects in water and aqueous systems: Experiment, theory, and current challenges," *Chem. Rev.* **116**, 7529–7550 (2016).

¹⁴S. Habershon, T. E. Markland, and D. E. Manolopoulos, "Competing quantum effects in the dynamics of a flexible water model," *J. Chem. Phys.* **131**, 024501 (2009).

¹⁵M. Ceriotti, J. Cuny, M. Parrinello, and D. E. Manolopoulos, "Nuclear quantum effects and hydrogen bond fluctuations in water," *Proc. Natl. Acad. Sci. U.S.A.* **110**, 15591–15596 (2013).

¹⁶C. Vega, M. M. Conde, C. McBride, J. L. F. Abascal, E. G. Noya, R. Ramirez, and L. M. Sesé, "Heat capacity of water: A signature of nuclear quantum effects," *J. Chem. Phys.* **132**, 046101 (2010).

¹⁷F. Paesani, "Water in metal-organic frameworks: Structure and diffusion of H₂O in MIL-53(Cr) from quantum simulations," *Mol. Simul.* **38**, 631–641 (2012).

¹⁸D. D. Borges, R. Semino, S. Devautour-Vinot, H. Jobic, F. Paesani, and G. Maurin, "Computational exploration of the water concentration dependence of the proton transport in the porous UiO-66(Zr)-(CO₂H)₂ metal-organic framework," *Chem. Mater.* **29**, 1569–1576 (2017).

¹⁹H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, "Design and synthesis of an exceptionally stable and highly porous metal-organic framework," *Nature* **402**, 276–279 (1999).

²⁰N. Lock, Y. Wu, M. Christensen, L. J. Cameron, V. K. Peterson, A. J. Bridgeman, C. J. Kepert, and B. B. Iversen, "Elucidating negative thermal expansion in MOF-5," *J. Phys. Chem. C* **114**, 16181–16186 (2010).

²¹D. Dubbeldam, K. Walton, D. Ellis, and R. Snurr, "Exceptional negative thermal expansion in isoreticular metal-organic frameworks," *Angew. Chem.* **119**, 4580–4583 (2007).

²²S. S. Han and W. A. Goddard, "Metal-organic frameworks provide large negative thermal expansion behavior," *J. Phys. Chem. C* **111**, 15185–15191 (2007).

²³J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, and O. M. Yaghi, "Gas adsorption sites in a large-pore metal-organic framework," *Science* **309**, 1350–1354 (2005).

²⁴W. Zhou, H. Wu, T. Yildirim, J. R. Simpson, and A. R. H. Walker, "Origin of the exceptional negative thermal expansion in metal-organic framework-5 Zn₄O(1,4-benzenedicarboxylate)₃," *Phys. Rev. B* **78**, 054114 (2008).

²⁵L. H. N. Rimmer, M. T. Dove, A. L. Goodwin, and D. C. Palmer, "Acoustic phonons and negative thermal expansion in MOF-5," *Phys. Chem. Chem. Phys.* **16**, 21144–21152 (2014).

²⁶M. Ceriotti, G. Bussi, and M. Parrinello, "Colored-noise thermostats à la carte," *J. Chem. Theory Comput.* **6**, 1170–1180 (2010).

²⁷M. Ceriotti, M. Parrinello, T. E. Markland, and D. E. Manolopoulos, "Efficient stochastic thermostating of path integral molecular dynamics," *J. Chem. Phys.* **133**, 124104 (2010).

²⁸S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, "Ring-polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space," *Annu. Rev. Phys. Chem.* **64**, 387–413 (2013).

²⁹M. Ceriotti, D. E. Manolopoulos, and M. Parrinello, "Accelerating the convergence of path integral dynamics with a generalized Langevin equation," *J. Chem. Phys.* **134**, 084104 (2011).

³⁰M. Ceriotti and D. E. Manolopoulos, "Efficient first-principles calculation of the quantum kinetic energy and momentum distribution of nuclei," *Phys. Rev. Lett.* **109**, 100604 (2012).

³¹R. Zwanzig, "Memory effects in irreversible thermodynamics," *Phys. Rev.* **124**, 983–992 (1961).

³²R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, 2001).

³³M. Ceriotti, G. Bussi, and M. Parrinello, "Langevin equation with colored noise for constant-temperature molecular dynamics simulations," *Phys. Rev. Lett.* **102**, 020601 (2009).

³⁴M. Ceriotti, G. Bussi, and M. Parrinello, "Nuclear quantum effects in solids using a colored-noise thermostat," *Phys. Rev. Lett.* **103**, 030603 (2009).

³⁵M. E. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (OUP, Oxford, 2010).

³⁶R. P. Feynman, "Space-time approach to non-relativistic quantum mechanics," *Rev. Mod. Phys.* **20**, 367–387 (1948).

³⁷T. E. Markland and M. Ceriotti, "Nuclear quantum effects enter the mainstream," *Nat. Rev. Chem.* **2**, 0109 (2018).

³⁸V. Kapil, J. VandeVondele, and M. Ceriotti, "Accurate molecular dynamics and nuclear quantum effects at low cost by multiple steps in real and imaginary time: Using density functional theory to accelerate wavefunction methods," *J. Chem. Phys.* **144**, 054111 (2016).

³⁹T. E. Markland and D. E. Manolopoulos, "An efficient ring polymer contraction scheme for imaginary time path integral simulations," *J. Chem. Phys.* **129**, 024105 (2008).

⁴⁰I. Poltavsky and A. Tkatchenko, "Modeling quantum nuclei with perturbed path integral molecular dynamics," *Chem. Sci.* **7**, 1368–1372 (2016).

⁴¹I. Poltavsky, R. A. DiStasio, Jr., and A. Tkatchenko, "Perturbed path integrals in imaginary time: Efficiently modeling nuclear quantum effects in molecules and materials," *J. Chem. Phys.* **148**, 102325 (2018).

⁴²M. Suzuki, "Hybrid exponential product formulas for unbounded operators with possible applications to Monte Carlo simulations," *Phys. Lett. A* **201**, 425–428 (1995).

⁴³S. A. Chin, "Symplectic integrators from composite operator factorizations," *Phys. Lett. A* **226**, 344–348 (1997).

⁴⁴V. Kapil, J. Behler, and M. Ceriotti, "High order path integrals made easy," *J. Chem. Phys.* **145**, 234103 (2016).

⁴⁵L. Vanduyfhuys, S. Vandenbrande, T. Verstraelen, R. Schmid, M. Waroquier, and V. Van Speybroeck, "QuickFF: A program for a quick and easy derivation of force fields for metal-organic frameworks from *ab initio* input," *J. Comput. Chem.* **36**, 1015–1027 (2015).

⁴⁶L. Vanduyfhuys, S. Vandenbrande, J. Wieme, M. Waroquier, T. Verstraelen, and V. Van Speybroeck, "Extension of the QuickFF force field protocol

for an improved accuracy of structural, vibrational, mechanical and thermal properties of metal-organic frameworks," *J. Comput. Chem.* **39**, 999–1011 (2018).

⁴⁷T. E. Markland and B. J. Berne, "Unraveling quantum mechanical effects in water using isotopic fractionation," *Proc. Natl. Acad. Sci. U. S. A.* **109**, 7988–7991 (2012).

⁴⁸M. Rossi, P. Gasparotto, and M. Ceriotti, "Anharmonic and quantum fluctuations in molecular crystals: A first-principles study of the stability of paracetamol," *Phys. Rev. Lett.* **117**, 115702 (2016).

⁴⁹H.-Y. Ko, R. A. DiStasio, B. Santra, and R. Car, "Thermal expansion in dispersion-bound molecular crystals," *Phys. Rev. Mater.* **2**, 055603 (2018).

⁵⁰T. Verstraelen, L. Vanduyfhuys, and S. Vandenbrande, Yaff, yet another force field, 2011, <http://molmod.ugent.be/software/>.

⁵¹S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *J. Comput. Phys.* **117**, 1–19 (1995).

⁵²M. Ceriotti, J. More, and D. E. Manolopoulos, "i-PI: A Python interface for *ab initio* path integral molecular dynamics simulations," *Comput. Phys. Commun.* **185**, 1019–1026 (2014).

⁵³V. Kapil, M. Rossi, O. Marsalek, R. Petraglia, Y. Litman, T. Spura, B. Cheng, A. Cuzzocrea, R. H. Meißner, D. M. Wilkins, P. Juda, S. P. Bienvenue, W. Fang, J. Kessler, I. Poltavsky, S. Vandenbrande, J. Wieme, C. Corminboeuf, T. D. Kühne, D. E. Manolopoulos, T. E. Markland, J. O. Richardson, A. Tkatchenko, G. A. Tribello, V. Van Speybroeck, and M. Ceriotti, "i-PI 2.0: A

universal force engine for advanced molecular simulations," *Comput. Phys. Commun.* **236**, 214–223 (2018).

⁵⁴S. Nosé, "A molecular dynamics method for simulations in the canonical ensemble," *Mol. Phys.* **52**, 255–268 (1984).

⁵⁵W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions," *Phys. Rev. A* **31**, 1695–1697 (1985).

⁵⁶G. J. Martyna, M. L. Klein, and M. Tuckerman, "Nosé-Hoover chains: The canonical ensemble via continuous dynamics," *J. Chem. Phys.* **97**, 2635–2643 (1992).

⁵⁷G. J. Martyna, D. J. Tobias, and M. L. Klein, "Constant pressure molecular dynamics algorithms," *J. Chem. Phys.* **101**, 4177–4189 (1994).

⁵⁸G. J. Martyna, M. E. Tuckerman, D. J. Tobias, and M. L. Klein, "Explicit reversible integrators for extended systems dynamics," *Mol. Phys.* **87**, 1117–1157 (1996).

⁵⁹S. M. J. Rogge, L. Vanduyfhuys, A. Ghysels, M. Waroquier, T. Verstraelen, G. Maurin, and V. Van Speybroeck, "A comparison of barostats for the mechanical characterization of metal-organic frameworks," *J. Chem. Theory Comput.* **11**, 5583–5597 (2015).

⁶⁰A. Ghysels, T. Verstraelen, K. Hemelsoet, M. Waroquier, and V. Van Speybroeck, "TAMkin: A versatile package for vibrational analysis and chemical kinetics," *J. Chem. Inf. Model.* **50**, 1736–1750 (2010).

⁶¹J. K. Bristow, D. Tiana, and A. Walsh, "Transferable force field for metal-organic frameworks from first-principles: BTW-FF," *J. Chem. Theory Comput.* **10**, 4644–4652 (2014).

Paper VII

The impact of lattice vibrations on the macroscopic breathing behavior of MIL-53(Al)

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Zeitschrift für Kristallographie - Crystalline Materials, **2019**, 234, 529-545

J. Wieme performed DFT simulations, and had a large contribution in the interpretation of the results as well as the preparation of the manuscript.

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The impact of lattice vibrations on the macroscopic breathing behavior of MIL-53(Al)

<https://doi.org/10.1515/zkri-2018-2154>

Received November 30, 2018; accepted January 28, 2019; published online February 14, 2019

Abstract: The mechanism inducing the breathing in flexible metal-organic frameworks, such as MIL-53(Al), is still not fully understood. Herein, the influence of lattice vibrations on the breathing transition in MIL-53(Al) is investigated to gain insight in this phenomenon. Through solid-state density-functional theory calculations, the volume-dependent IR spectrum is computed together with the volume-frequency relations of all vibrational modes. Furthermore, important thermodynamic properties such as the Helmholtz free energy, the specific heat capacity, the bulk modulus, and the volumetric thermal expansion coefficient are derived via these volume-frequency relations using the quasi-harmonic approximation. The simulations expose a general volume-dependency of the vibrations with wavenumbers above 300 cm^{-1} due to their localized nature. In contrast, a diverse set of volume-frequency relations are observed for vibrations in the terahertz region ($<300\text{ cm}^{-1}$) containing the vibrations exhibiting collective behavior. Some terahertz vibrations display large frequency differences over the computed volume range, induced by either repulsion or strain effects, potentially triggering the phase transformation. Finally, the impact of the lattice vibrations on the thermodynamic properties is investigated. This reveals that the closed pore to large pore phase transformation in MIL-53(Al) is mainly facilitated by terahertz vibrations inducing rotations of the organic linker, while the large pore to closed pore phase transformation relies on two framework-specific soft modes.

Keywords: density-functional theory; metal-organic frameworks; phase transformation; thermodynamic properties; vibrational spectroscopy.

Introduction

Present-day challenges such as global warming and energy supply have revealed a dire need for newly designed functional materials. Metal-organic frameworks (MOFs), also called porous coordination polymers, are a class of nanoporous materials potentially able to offer solutions to these challenges [1, 2]. MOFs are hybrid materials containing metal complexes connected with organic linkers. The intrinsic organic-inorganic nature of these crystalline frameworks has led to the construction of many thousands of MOFs [3] and even more hypothetical ones [4] with different dimensionalities. This variety is the key ingredient in finding suitable materials for energy-related applications [5], such as gas separation [6], chemical sensing [7], and heterogeneous catalysis [8].

The interplay of organic and inorganic moieties allows some MOFs to exhibit a high degree of structural flexibility without losing their crystallinity, so-called soft porous crystals [9–12]. A specific type of framework flexibility, called breathing, causes a large change in unit cell volume through the transformation from a large pore (LP) phase to a closed pore (CP) phase. This breathing behavior is of high industrial relevance due to its potential use in, for example, shock absorbers [13], drug delivery devices [14], and temperature-sensitive [15] and CO_2 sensors [16]. The prototype of a breathing MOF is the well-studied MIL-53(Al), consisting of 1D aluminum-oxide chains linked by benzenedicarboxylate (BDC) linkers [17]. Under the influence of external stimuli such as a mechanical pressure [13], temperature [18], and the adsorption and desorption of guest molecules [19], MIL-53(Al) can undergo a transition between a LP phase and a CP phase (see Figure 1).

Given the importance of the breathing behavior, the elucidation of the underlying mechanism in MIL-53(Al) has been the subject of research lately. Thermodynamic considerations have unraveled the macroscopic conditions governing breathing [12, 20]. At the microscopic level, it has been suggested that lattice vibrations trigger the observed flexibility, as the structural dynamics in MOFs strongly depends on their terahertz vibrations [21–24]. Liu et al. suggested that twisting motions of the phenyl rings induce the transformation from the CP to the LP phase at

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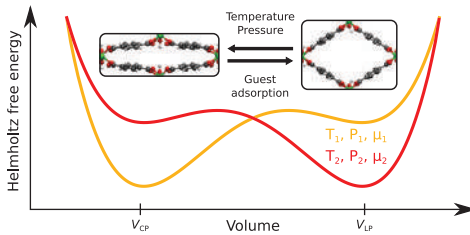


Fig. 1: Illustration of hypothetical Helmholtz free energy profiles of MIL-53(Al) as a function of the volume. The minima indicate the existence of a (meta)stable CP and LP phase, which are visually represented. A transition between both phases can occur under the influence of temperature, pressure, and/or the adsorption of guest molecules. For example, by increasing the temperature, MIL-53(Al) can undergo a transition from the CP phase to the LP phase [18].

high temperatures, since such twists are less restricted in the LP phase [18]. Furthermore, it has been shown that the CP phase is the most stable structure at low temperatures due to dispersion stabilization effects and that the larger vibrational entropy in the LP phase causes the CP-to-LP transition at high temperatures [15, 25]. We have recently proposed additional terahertz vibrations as driving forces for the breathing phenomenon [24]. Although our work provided a detailed picture of the vibrational fingerprints in both the CP and the LP phase separately, it remains an open question how the typical vibrations change in terms of the volume and which vibrations dominate the phase transformation.

Besides governing the structural dynamics of a material, lattice vibrations also contribute to the thermodynamic potential. This thermodynamic potential defines the (meta)stable states of the system and their relative stability (see Figure 1 for an illustration). Some of the present authors showed that the thermodynamic potential yields insight into the macroscopic conditions that affect breathing [12]. However, the impact of individual vibrations on the total thermodynamic potential has not been studied so far. Nevertheless, this would result in a better view on the circumstances giving rise to the breathing phenomenon.

Lattice vibrations can be studied by spectroscopic techniques, such as infrared (IR) and Raman spectroscopy, and inelastic neutron scattering, which enable to experimentally describe (part of) the material's vibrational fingerprints. However, under realistic experimental conditions, MIL-53(Al) shows no (meta)stable structures with a unit cell volume between those of the CP and LP phases in the absence of guests, which makes it impossible to track the evolution of lattice vibrations during the transition by means of such experimental techniques.

From a theoretical point of view, it is possible to perform simulations at intermediate volumes, which facilitates the connection of equivalent modes.

This work will fill the aforementioned gaps and provide a detailed understanding of the lattice vibrations of MIL-53(Al) and its influence on the thermodynamic properties of the material. For that purpose, the vibrational modes and their corresponding frequencies have been computed at several unit cell volumes via solid-state density-functional theory (DFT) calculations. This allowed us to determine the evolution of the IR spectrum of MIL-53(Al) as a function of the volume and to construct volume-frequency relations for each mode separately. In this way, the vibrational fingerprints in the CP and the LP phases of MIL-53(Al) could be linked unequivocally. The focus will be on the terahertz vibrations and their impact on the breathing transition. Furthermore, the quasi-harmonic approximation (QHA) [26, 27] has been applied, which enabled us to construct the Helmholtz free energy profile as a function of the volume at different temperatures. Finally, various mechanical and thermal thermodynamic properties such as the specific heat capacity, the bulk modulus, and the volumetric thermal expansion coefficient were derived from this profile and their dependence on specific terahertz vibrations is highlighted.

The remainder of this article is organized as follows. First, the computational settings of our calculations will be reported and the procedure used to construct the volume-frequency relations of the vibrational modes will be rationalized. Afterwards, the evolution of the normal mode vibrations as a function of the volume will be discussed. In the end, the influence of important terahertz vibrations on the thermodynamic properties of MIL-53(Al) will be examined.

Computational

Periodic simulations are performed with VASP [28] at the PBE-D3(BJ) level of theory [29–31] using a projector-augmented plane-wave basis set [32, 33] with a plane-wave cutoff of 600 eV. A $2 \times 6 \times 6$ Monkhorst-Pack k-mesh [34] is employed for structures with a unit cell volume smaller than $1200 \text{ \AA}^3$, while a $2 \times 6 \times 2$ Monkhorst-Pack k-mesh is used for larger unit cell volumes [35]. The self-consistent field (SCF) cycle of an electronic structure calculation is terminated when the energy difference is lower than 10^{-8} eV. To construct the volume-frequency relations of MIL-53(Al), Hessians, i.e. the second-order derivatives of the energy with respect to the atomic coordinates, are determined at 26 unit cell volumes encompassing the

CP phase, the LP phase, and the transition region. Prior to each Hessian calculation, a fixed volume geometry optimization is performed, in which both the ions and cell shape are allowed to relax. The geometry optimizations are assumed to be converged when the energy difference between two subsequent steps decreases below 10^{-7} eV. The Hessians are calculated according to a finite difference scheme where the ions are displaced separately along the three directions with ± 0.01 Å. The vibrational modes are finally obtained by performing a normal mode analysis on the calculated Hessian with TAMkin [36].

To follow the evolution of the vibrational modes as a function of the volume, two different approaches are used. First, the IR spectrum of MIL-53(Al) is calculated at different volumes. Thereto, additional calculations of the Born effective charges are required at each unit cell volume, for which the density-functional perturbation theory method implemented in VASP is used [37, 38] similar to our previous study [24]. In addition to the volume-dependent IR spectrum, an alternative approach is used to investigate the volume dependence of vibrational modes. Based on a procedure applied by Erba et al. [26, 39], an explicit volume-frequency relation of each vibrational mode is constructed by evaluating the scalar products of this mode at a certain unit cell volume with all eigenmodes at the next unit cell volume. The vibrational mode is subsequently linked with the eigenmode yielding the highest scalar product (see Supporting Information Section S1). These volume-frequency relations can be constructed for all vibrational modes enabling the study of IR inactive vibrations.

After calculation of the electronic energies and the vibrational frequencies at distinct unit cell volumes, the thermodynamic and mechanical properties can be evaluated. The central quantity is the Helmholtz free energy F , which is the sum of the electronic energy E_{el} and a vibrational contribution F_{vib} ,

$$F(V, T) = E_{el}(V) + F_{vib}(V, T) \quad (1)$$

$$F_{vib}(V, T) = \frac{1}{2} \sum_{i=1}^N \hbar \omega_i(V) + k_B T \ln \left(1 - e^{-\frac{\hbar \omega_i(V)}{k_B T}} \right) \quad (2)$$

Here, $\hbar$ and k_B represent the Planck and Boltzmann constant, respectively. $\omega_i(V)$ is the volume-frequency relation of mode i multiplied by 2π . At temperature $T = 0$ K, F_{vib} still contributes to the Helmholtz free energy via the zero-point energy (ZPE),

$$\text{ZPE} = \frac{1}{2} \sum_{i=1}^N \hbar \omega_i(V) \quad (3)$$

Also the vibrational free energy can be subdivided in two contributions, i.e. an energetic part E_{vib} and an entropic part $-TS$,

$$F_{vib}(V, T) = E_{vib}(V, T) - TS(V, T) \quad (4)$$

$$E_{vib}(V, T) = \sum_{i=1}^N \hbar \omega_i(V) \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega_i(V)}{k_B T}} - 1} \right) \quad (5)$$

From the Helmholtz free energy as a function of the volume, the bulk modulus K can be calculated by taking its second-order derivative with respect to the volume multiplied by the volume,

$$K(V, T) = V \frac{\partial^2 F(V, T)}{\partial V^2} \quad (6)$$

Furthermore, the volumetric thermal expansion coefficients α_v of the (meta)stable phases of MIL-53(Al) can be computed from the Helmholtz free energy profile. First, the equilibrium volumes of these phases need to be identified as the minima of the Helmholtz free energy profile for different temperatures. Subsequently, α_v is calculated by taking the derivative of the equilibrium volume with respect to temperature,

$$\alpha_v(T) = \frac{1}{V(T)} \frac{\partial V(T)}{\partial T} \quad (7)$$

Finally, also the heat capacity at constant volume C_v and constant pressure C_p can be obtained starting from the volume-frequency relations and previously derived properties,

$$C_v(V, T) = \sum_{i=1}^N \frac{(\hbar \omega_i(V))^2}{k_B T^2} \frac{e^{\frac{\hbar \omega_i(V)}{k_B T}}}{(e^{\frac{\hbar \omega_i(V)}{k_B T}} - 1)^2} \quad (8)$$

$$C_p(T) = C_v(T) + \alpha_v^2(T) K(T) V(T) T \quad (9)$$

Discussion

Following the procedures explained in Section “Computational”, the volume dependence of the vibrational fingerprints in MIL-53(Al) can be investigated. First, the volume dependence of the IR spectrum is examined. Several vibrational modes, showing large spectral changes over the calculated volume range, are discussed. Afterwards,

the volume-frequency relations of the terahertz vibrations within MIL-53(Al) and their possible role in the breathing mechanism are discussed. Once a clear picture of the lattice vibrations is obtained, some thermodynamic properties of MIL-53(Al), calculated within the QHA, are presented. Those results are compared with experimental and computational reference data and possible deviations are addressed, focusing on the influence of specific terahertz vibrations.

Lattice vibrations

In this subsection, the evolution of various vibrational frequencies is tracked as a function of the volume based on two techniques described in the computational details (see Section “Computational”). In the first approach, the IR spectrum is computed at different unit cell volumes, which only shows the changes of frequencies for IR active vibrations. The focus will be on the fingerprint vibrations that have been reported as ideal identifiers to detect the breathing transition [24, 40, 41]. Moreover, volume-frequency relations are constructed which allow to investigate all vibrational modes, including IR inactive ones. The volume-frequency relations will be used to detect terahertz vibrations with deviating behavior, as these are potential triggers for the breathing transition.

IR spectra

Experimentally, only the IR spectra of the (meta)stable CP and LP phases have been measured as an *in situ* measurement of the IR spectrum during the phase transformation is not yet possible. These experimental reports describe several IR active vibrations that distinguish the CP phase from the LP phase [24, 40, 41]. It is observed that the vibrational frequencies of most of these vibrations increase after transition from the CP to the LP phase and thus cost more energy. In our theoretical approach, it is possible to predict the volume-dependency of these IR fingerprints. The calculated IR spectrum of MIL-53(Al) as a function of the volume is represented in Figure 2a. The fingerprint vibrations are labeled in correspondence with our earlier work [24] (Labels from A to I, further explained in the caption of Figure 2). To facilitate the recognition of specific trends, the volume-frequency and volume-IR-intensity relations of these specific modes are represented in Figure 2b and c, respectively.

Starting with the IR intensities as a function of the volume (Figure 2c), no clear trend can be observed.

Moreover, the intensity difference between the vibrational modes in the CP and the LP phases is small, except for mode A1 (symmetric stretching of aluminum-oxide backbone), which doubles in intensity when going from the CP toward the LP phase.

A more interesting behavior is observed for the volume-frequency relations. The vibrational frequencies of the majority of the fingerprint vibrations follow a certain trend as a function of the volume. Three regimes can be distinguished (see Figure 2). In the first regime, at low unit cell volumes, the frequency strongly decreases as a function of the volume. A second regime starts around the volume where the CP phase is stable ($843 \text{ \AA}^3$ from electronic structure calculations). From this point onwards, the vibrational frequencies of most normal modes steadily increase until the volume region of the stable LP phase is encountered ($1426 \text{ \AA}^3$ from electronic structure calculations). Finally, the frequency drops again in the third regime at high unit cell volumes. The strong decrease in frequency as a function of the volume in regimes 1 and 3 can be explained by the weakening of covalent interactions. This can be illustrated by looking at the example of the aluminum-oxide bond (Figure 3a–c). At very low and high volumes, the bond distance strongly increases as a function of the volume indicating a decrease in the strength of the covalent bond. At the same time, the frequencies of all stretching vibrations of the aluminum-oxide bond decrease (the corresponding frequency region is highlighted by a gray background in Figure 2a). Within regime 2 the strength of the covalent interactions remains more or less unaltered as the bond distances remain almost constant. Nevertheless, an increase in the vibrational frequency is observed as a function of the volume. This is a result of dispersion interactions, which are important in MIL-53(Al) [15] (see Supporting Information Section S2).

Some modes differ from the general volume-frequency trend, for example the wagging mode of the CH-bonds (mode B in Figure 2), the antisymmetric stretching mode of the carboxyl group (mode I in Figure 2), and the bend and stretch modes of the hydroxyl group around 970 cm^{-1} (D in Figure 2) and 3750 cm^{-1} (Figure 3e), respectively. Limiting the discussion to the last two examples, it is observed that the hydroxyl bend vibration shows a decreasing frequency for increasing volumes at small unit cell volumes and afterwards the frequency increases, but instead of going down again it keeps on increasing. The hydroxyl stretch vibration shows the opposite behavior: at small volumes, the frequency increases upon increasing volume, but it starts decreasing at larger volumes. Those modes are extremely localized, which makes them only dependent on the geometry of the hydroxyl group.

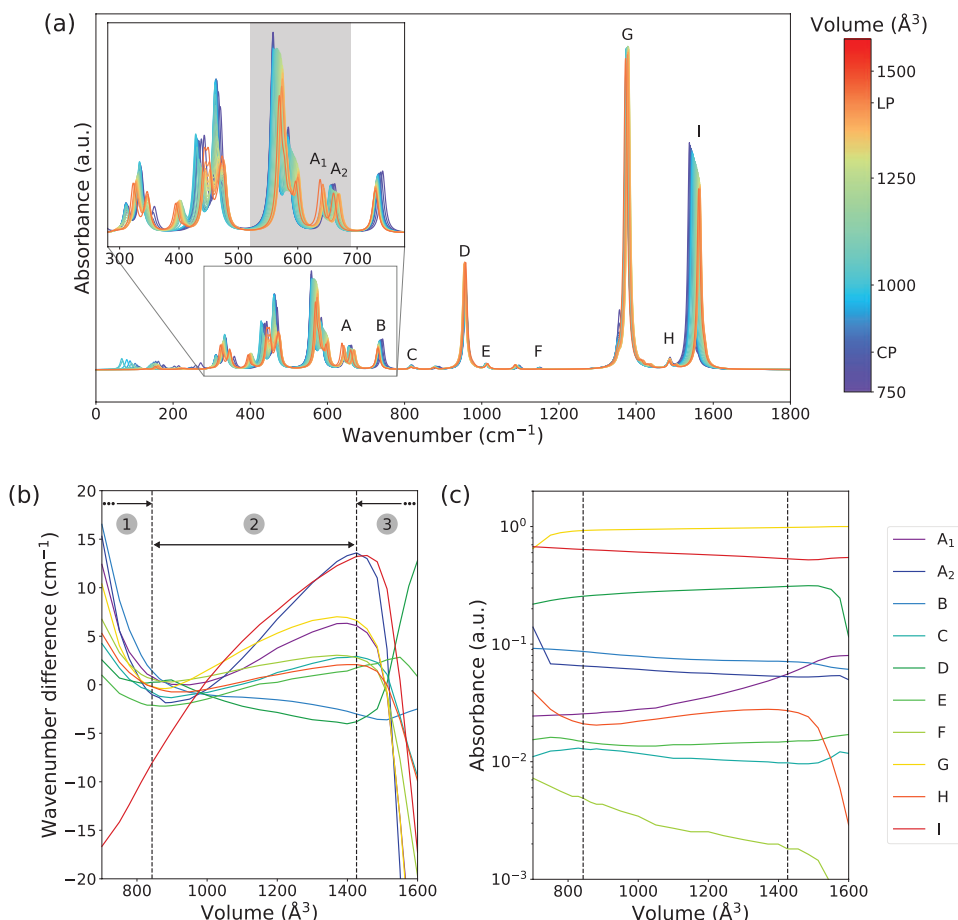


Fig. 2: (a) Theoretical IR spectra of MIL-53 (Al) at different unit cell volumes within the wavenumber range 0–1800 cm^{-1} . The inset zooms in upon the range 280–780 cm^{-1} . The region of the aluminum-oxide stretch vibrations is highlighted with a gray background. Fingerprint vibrations, identified in earlier reports [24, 40, 41], are indicated with a capital letter and follow the same labeling as in Ref. [24]. (A1) Symmetric stretching of the aluminum-oxide backbone. (A2) Antisymmetric stretching of the aluminum-oxide backbone. (B) Out-of-plane wagging of hydrogen atoms on the aromatic ring. (C) Bending of the carboxyl group and within the aromatic ring. (D) Rocking of hydroxyl group. (E) Bending within the aromatic ring. (F) Stretching between the aromatic ring and the carboxyl group. (G) Symmetric stretching of the carboxyl group. (H) Stretching between the aromatic ring and the carboxyl group. (I) Antisymmetric stretching of the carboxyl group. (b) Volume-frequency relations of the IR fingerprint vibrations. The wavenumbers are shifted by their average value over the computed volume range. Dotted lines indicate the equilibrium volumes of the CP and LP phases obtained from electronic structure calculations. The volume ranges of the three different volume-frequency regimes are indicated. (c) Volume-IR-intensity relations of the IR fingerprint vibrations. Dotted lines indicate the equilibrium volumes of the CP and LP phases obtained from electronic structure calculations.

Looking at the volume-frequency relations of the hydroxyl stretch vibrations and the bond length of the hydroxyl group as a function of the volume (Figure 3e and f, respectively), there exists indeed a clear correlation between the

bond length and the vibrational frequency of the hydroxyl group.

For wavenumbers between 300 and 500 cm^{-1} , the IR spectrum as a function of the volume shows more abrupt

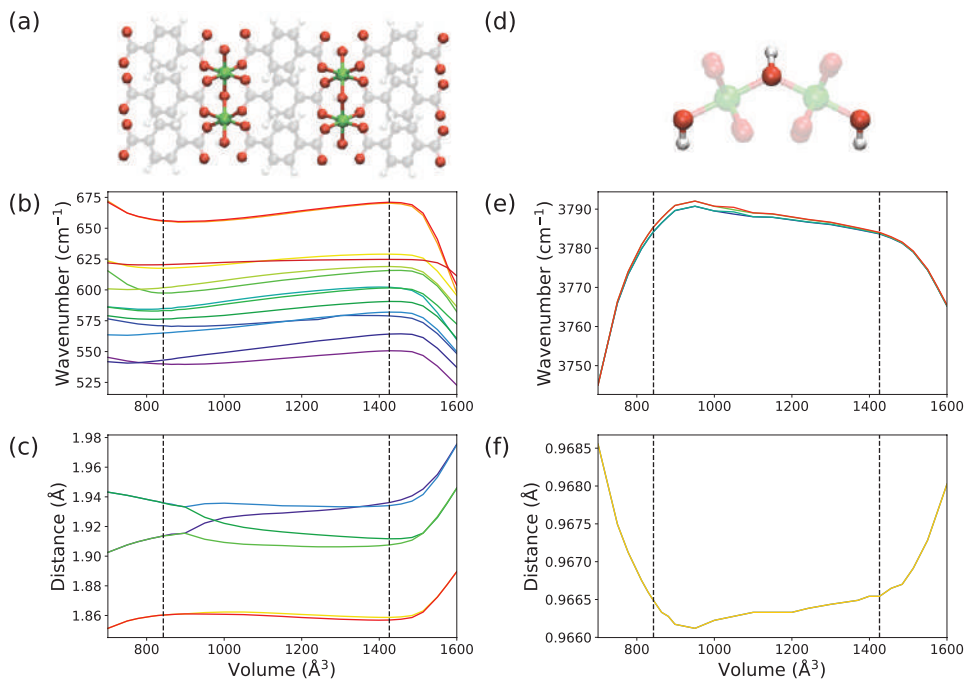


Fig. 3: (a) Visualization of the aluminum-oxide bonds. (b) Volume-frequency relations of all vibrational modes describing stretches of aluminum-oxide bonds. (c) Length of the aluminum-oxide bonds as a function of the volume. (d) Visualization of the hydroxyl bond. (e) Volume-frequency relations of all hydroxyl stretch vibrations. (f) Length of the hydroxyl bond. Dotted lines indicate the equilibrium volumes of the CP and LP phases obtained from electronic structure calculations.

changes. This is caused by a change in IR activity of specific modes, rather than deviations from the general volume-frequency trend (see Supporting Information Section S3). In our previous work [24], it was argued that some of the changes in IR activity originate from rocking of the hydroxyl group, which is present at large volumes, but suppressed at small volumes. This claim is confirmed in our simulations.

Terahertz vibrations

The terahertz region ($<300 \text{ cm}^{-1}$) is especially interesting for soft porous crystals as it contains the modes which influence the dynamics of the framework most profoundly. In this frequency region, the IR spectrum of MIL-53(Al) contains only a few IR active modes, so we have to restrict our discussion to the volume-frequency relations to obtain a complete view of the vibrational spectrum (Figure 4). It is clear that the behavior of low-frequency modes differs

from the behavior of high-frequency modes as it concerns mainly collective vibrations. Here, the modes showing the most interesting volume-frequency curves are highlighted. First of all, the vibrations describing linker rotations (indicated in blue in Figure 4) and trampoline-like motions (red curves in Figure 4) are discussed. Similar terahertz vibrations were recently reported around the same frequencies in MIL-140A, a Zr-based MOF with BDC linkers [42]. We find in our study that such modes display a large increase in frequency for decreasing unit cell volume, as these vibrations are heavily constrained at small unit cell volumes. Among the vibrations exhibiting linker rotations, two types can be distinguished, which do also appear in the MIL-140A framework [42]. Namely, those where opposite linkers rotate in the same direction and those where opposite linkers rotate in the opposite direction. The former are heavily constrained in dense structures yielding high vibrational frequencies, while the latter are less restricted in small unit cells. This causes a splitting of their volume-frequency relations

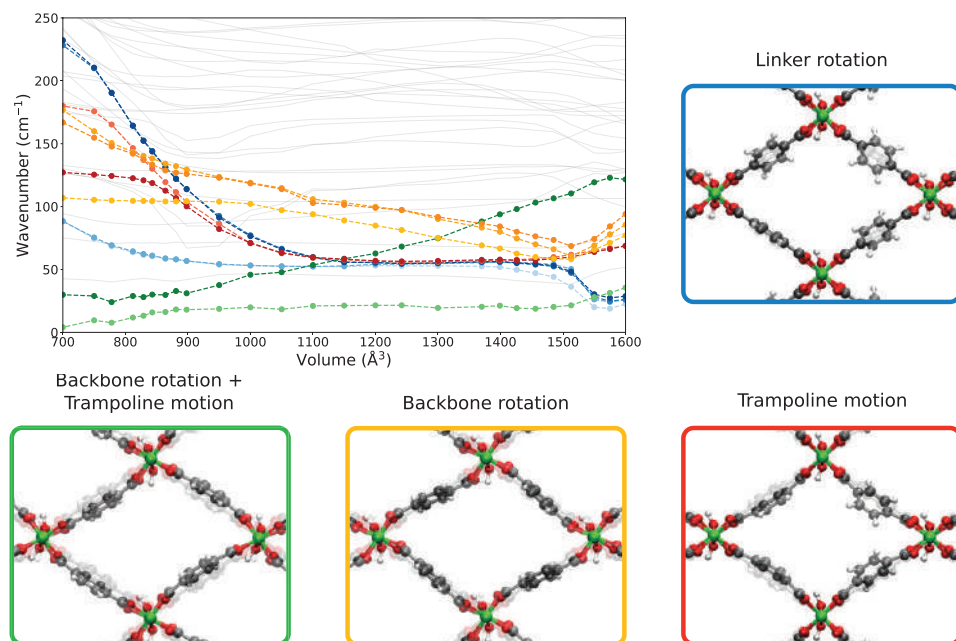


Fig. 4: Volume-frequency relations of the terahertz vibrations in MIL-53(Al). The collective vibrations with the most significant frequency differences over the computed volume range are highlighted and visually represented. Blue curves: vibrations inducing linker rotations. Green curves: soft modes combining translations and rotations of the aluminum-oxide backbone and the linkers. Yellow curves: vibrations inducing rotations of the aluminum-oxide backbone. Red curves: trampoline-like vibrations.

around 1200 $\text{\AA}^3$. It has to be noted that, according to our simulations, the vibrational frequencies of all linker rotation modes show a sudden decrease when increasing the volume above 1520 $\text{\AA}^3$. This decrease in frequency is induced by a decrease in the dihedral angles of the Al-O-C-O units, illustrated in Figure 5. For large volumes this dihedral angle approaches zero, which lowers the energy barrier for linker rotations and thus its corresponding vibrational frequency. This sudden decrease in frequency results in a large increase of the vibrational entropy (see Section “Thermodynamic properties”) which may trigger the CP-to-LP phase transformation.

Furthermore, there are three modes showing rotations of the metal-oxide backbone (yellow curves in Figure 4). This rotation is also constrained at small volumes, hence the increase in frequency upon lowering the volume, but the frequency also increases at large volumes. This probably results from linkers which become overstretched when the backbone rotates at large volumes. Finally, two modes have a completely different volume-frequency relation, showing a continuous increase in frequency upon

increasing volume (green curves in Figure 4). Both modes consist of a combination of linker and metal-oxide chain movements. The mode that has the lowest frequency over the entire volume range can be described by a rotation of the metal-oxide backbones, which induces a trampoline-like motion of the linkers (see green box in Figure 4 for a visualization). The other mode shows a translation of the metal-oxide backbones, inducing a rotation of the linkers (see Supporting Information Section S4 for a visualization). The volume-frequency relations of these two modes are strongly coupled with the volume-dependency of the diagonal elements of the Lagrangian strain tensor η [43] (see Figure 6). The latter can be obtained by taking matrix products of the cell matrices at a reference unit cell volume, $\mathbf{h}_0$, and a deformed unit cell volume, $\mathbf{h}(V)$:

$$\eta(V) = \frac{1}{2} (\mathbf{h}_0^{-T} \mathbf{h}^T(V) \mathbf{h}(V) \mathbf{h}_0^{-1} - \mathbf{1}) \quad (10)$$

The vibrational frequency as a function of the volume of the mode exhibiting rotations of the aluminum-oxide

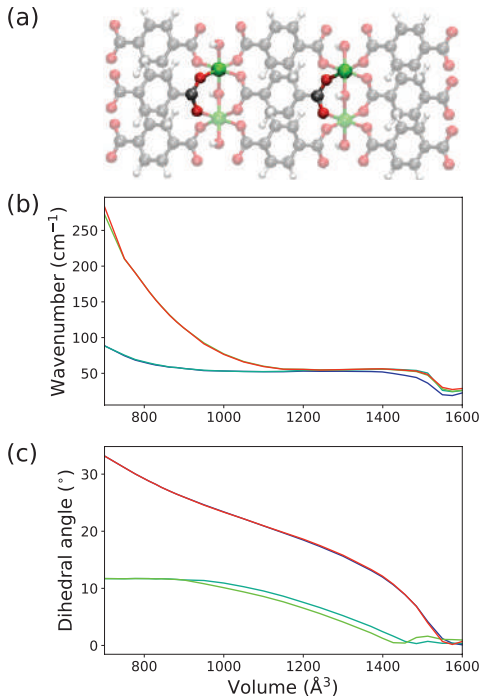


Fig. 5: (a) Visualization of the Al-O-C-O dihedral. (b) Volume-frequency relations of the terahertz vibrations exhibiting rotations of the linkers. (c) Different Al-O-C-O dihedrals.

chain is strongly linearly correlated with the strain along this chain, η_{xx} , as a function of the volume. Moreover, a linear relation is observed between the volume-dependency of the vibrational frequency of the mode characterized by translations of the aluminum-oxide backbone and the strain along the pore diagonals, η_{yy} and η_{zz} , as a function of the volume. This correspondence indicates that the particular volume-frequency relations of these two terahertz vibrations originate from the strain developed within the framework. As such, this procedure allows us to reveal the relevant vibrational modes that are most affected by the breathing-induced strain in the material, a macroscopic property, through the strain tensor. As both modes become very soft at small volumes, they are very important for the dynamics in the CP phase of MIL-53(Al). The vibration inducing rotations of the aluminum-oxide backbone, for example, can trigger the transition from a closed pore phase to a very closed pore phase as reported in MIL-53(Sc) [44]. In the remainder, we will refer to these two modes as soft modes.

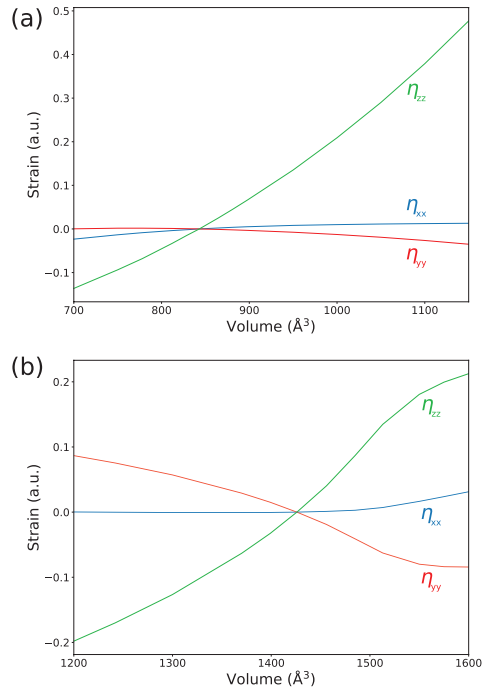


Fig. 6: The strain within MIL-53(Al) along the three Cartesian directions as a function of the volume for structures with the CP phase (843 Å³) as reference volume (a) and the LP phase (1426 Å³) as reference volume (b). The volume-dependency of the strain along the aluminum-oxide chain, η_{xx} , is small and proportional to the volume-frequency relation of the soft mode exhibiting rotations of the metal-oxide backbone. The volume-dependency of the strains along the pore diagonals, η_{yy} and η_{zz} , is large and proportional to the volume-frequency relation of the soft mode exhibiting translations of the metal-oxide backbone.

Thermodynamic properties

Up to this point, the direct influence of vibrational modes on the lattice dynamics was investigated. However, normal mode vibrations also contribute to the thermodynamic potential, which in its turn can teach us more about the macroscopic conditions that govern breathing [12]. In this section, this thermodynamic potential will be examined by looking at several mechanical and thermal thermodynamic properties of MIL-53(Al), which can be approximated from the vibrational frequencies at different unit cell volumes obtained by our calculations. First of all, the Helmholtz free energy profile will be constructed and afterwards some derived properties will be determined.

As vibrational modes at different unit cell volumes were successfully matched in the previous section, it becomes possible to assess the influence of specific modes to the thermodynamic quantities.

Helmholtz free energy profile

Starting from the analytic expressions for the volume-frequency relations, obtained after fitting a ninth-order Taylor expansion to the data points, the Helmholtz free energy profile as a function of the volume can be constructed at different temperatures (Figure 7a). Those results are compared with the electronic energy profile without vibrational contributions such as the zero-point energy (ZPE) (black curve).

Within the considered temperature window, we recognize two minima in the Helmholtz free energy profile corresponding to the presence of the (meta)stable CP and LP phases. At 1 K, the equilibrium volumes of the CP and the LP phases are located around 860 and 1461 Å³, respectively. Using another degree for the fitted polynomials can shift these values by 5 Å³, introducing an uncertainty on the predicted values. Note that, even at 1 K, the Helmholtz free energy profile differs substantially from the electronic energy profile. The main effect of the ZPE is a shift of the equilibrium volumes of both the CP and LP phases by about 20 Å³. The value for the CP phase volume corresponds well with the experimental value measured by Liu et al. [18] at 77 K, while the LP phase volume is slightly overestimated in our simulations. The free energy difference between the (meta)stable phases is nearly unaffected by the ZPE and has a value of 26 kJ · mol⁻¹ at 1 K. This free

energy difference falls in the range of the results obtained by other computational studies [15, 25, 45].

By looking at the temperature response of the Helmholtz free energy profile, a slight increase in equilibrium volumes is observed for both the CP and the LP phases for temperatures above 50 K. More pronounced is the decrease of the free energy difference for increasing temperatures. It reaches values of 19 and 14 kJ · mol⁻¹ at 300 and 500 K, respectively. This behavior is expected as the LP phase is entropically favored over the CP phase [15, 18, 25]. However, even for temperatures as high as 500 K, the LP phase has not become the most stable phase, while the experimental CP-to-LP transition temperature is found around 350 K [18]. This deviation with the experimental observations is caused by an exaggerated stability of the CP phase due to the applied computational methodology [15]. The PBE-D3(BJ) level of theory, used in this work, overestimates the dispersion interactions, which results in an unphysical stabilization of the CP phase. This point was extensively studied in a recent contribution by some of the presenting authors [15]. When the random-phase approximation is applied, a higher level of theory for a more accurate description of correlation effects, the electronic energy difference between the CP and the LP phase reduces to about 7 kJ · mol⁻¹ [15]. Given the excessive computational cost and the current computational resources, a vibrational analysis using the latter approach is not feasible. Nevertheless, starting from the energy difference at the RPA level of theory and considering the vibrational frequencies as predicted in this work using PBE-D3(BJ), the CP and LP phases become equally stable around 300 K (see Supporting Information Section S5), which is more in line with experimental observations [18]. Furthermore,

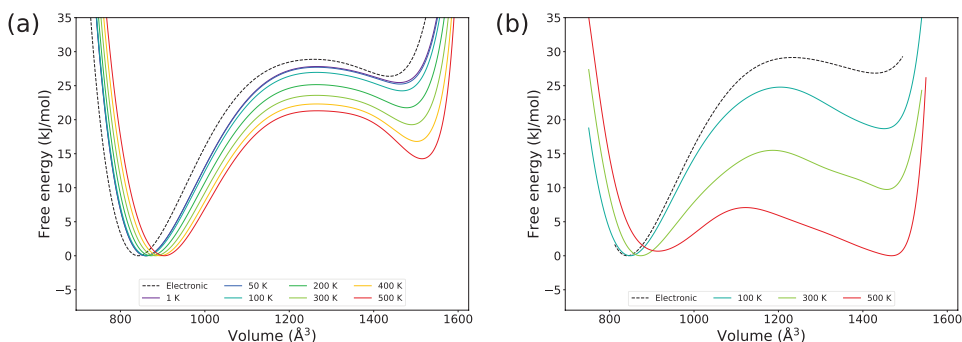


Fig. 7: Helmholtz free energy as a function of the volume at different temperatures (solid lines) and the electronic energy as a function of the volume (black dashed line) using the QHA (a) (this work) and dynamic methods (b) (Figure reproduced from Ref. [45] with permission of the American Chemical Society).

comparison of the lattice vibrations at the PBE-D3(BJ) level of theory with a hybrid functional did not yield significant changes (see Supporting Information Section S5). Finally, in our earlier study a good agreement was found between the experimental IR and Raman spectra and the computational spectra at the PBE-D3(BJ) level of theory [24]. This hints at a reliable prediction of the lattice dynamics at the current level of theory. To conclude this paragraph, it is worth mentioning that the Helmholtz free energy profile in Figure 7a is constructed via the QHA, which still neglects certain anharmonic effects. By including these effects via dynamical methods, which are computationally more expensive, an increased entropic stabilization of the LP phase is observed [45] (see Figure 7b). Although, it has to be noted that the results obtained from these ab initio molecular dynamics simulations are prone to large sampling uncertainties.

Energetic and entropic contributions

The specific temperature dependence of the Helmholtz free energy profile can be more thoroughly understood when considering the contributions of the electronic energy, the vibrational energy and the entropy to the free energy. The free energy difference between the LP and the CP phases of these contributions and the total free energy difference as a function of temperature are presented in Figure 8. At low temperatures, the total free

energy difference between the LP and the CP phases is mainly the result of the difference in electronic energy. Furthermore, this plot illustrates that the difference in the vibrational energy between the LP and the CP phases is limited over the complete temperature range, whereas the difference in entropic contribution decreases significantly, canceling out the increase in the electronic energy difference. As temperature alters the equilibrium LP and CP volumes, also the electronic energy difference between these two phases will change even though the electronic energy in itself is temperature independent at a fixed volume. The steady decrease in the difference of the entropic contribution originates from the activation of the vibrations inducing linker rotations, which have very low frequencies at large unit cell volumes. As a consequence, the entropic stabilization of the LP phase is mainly the result of this type of vibrations, as already suggested by Liu et al. [18].

Contributions from vibrational modes

Up to this point, we could identify the vibrations exhibiting linker rotations as important contributors to the Helmholtz free energy profile, but they are not the only ones shaping the free energy landscape. This becomes clear when analyzing the vibrational free energy profile of each mode separately (Figure 9). At 1 K, the vibrational free energy is restricted to the ZPE. Several terahertz modes undergo a large frequency change as a function of the volume and, therefore, they yield ZPE differences over the calculated volume range as large as $1.2 \text{ kJ} \cdot \text{mol}^{-1}$. Nonetheless, their impact on the total free energy profile remains small as also multiple localized vibrations give rise to a substantial ZPE difference. At 300 K, the picture looks completely different. Now, the vibrational free energy differences are dominated by the terahertz vibrations. First in line are the vibrations exposing linker rotations (blue curves) which generate free energy differences of at least $4 \text{ kJ} \cdot \text{mol}^{-1}$, favoring open pore structures. However, these modes are counteracted by the soft modes (green curves), showing combined collective behavior of the linkers and the metal-oxide backbones. The magnitude of the free energy difference produced by these two vibrations are of comparable size to the free energy difference of the vibrations exhibiting linker rotations. As such, it can be expected that these modes are of crucial importance in the LP-to-CP phase transition at low temperatures and that they partially hinder the transition from the CP to the LP phase at elevated temperatures. Other modes worth mentioning are those inducing trampoline-like motions of the linkers (red curves) and metal-oxide backbone rotations

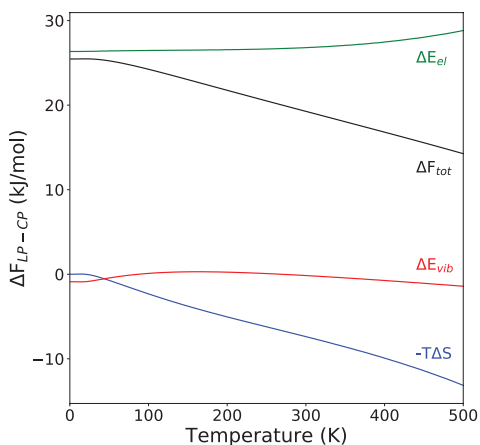


Fig. 8: Total free energy difference between the LP and CP phases as a function of temperature, ΔF_{tot} (black curve), and its three contributions: entropy $-T\Delta S$ (blue), vibrational energy ΔE_{vib} (red), and electronic energy ΔE_{el} (green).

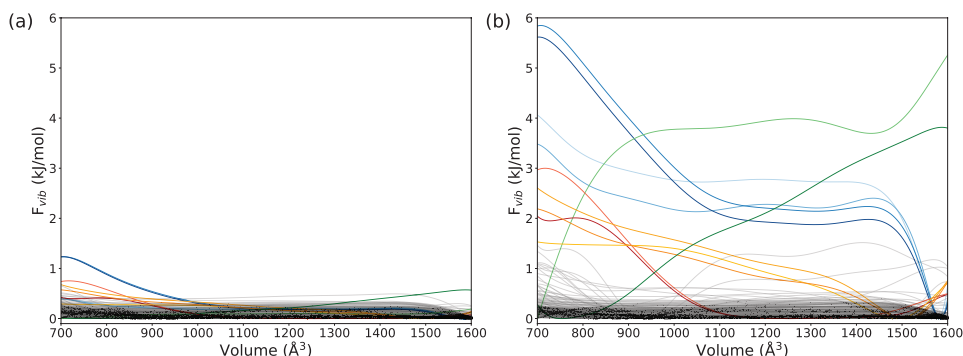


Fig. 9: Contributions of the different vibrational modes to the Helmholtz free energy at 1 K (a) and 300 K (b). The terahertz vibrations discussed in Section “Terahertz vibrations” are highlighted with the same colors as in Figure 4.

(yellow curves). These modes attribute considerably to the stabilization of the LP phase at high temperatures.

Derived properties

Besides the Helmholtz free energy profile, knowledge of the vibrational modes allows to predict other thermodynamic properties, such as the specific heat capacity, the bulk modulus, and the volumetric thermal expansion coefficient. The temperature dependence of these properties will be investigated in this subsection for both the CP and the LP phases. For a discussion of the pressure-versus-volume ($P(V)$) equation of state, we refer to the Supporting Information Section S6. As the bulk modulus and the volumetric thermal expansion coefficient are derived from the Helmholtz free energy profile, uncertainties on the latter due to fitting may accumulate. Therefore, the predicted values, obtained by fitting the Rose-Vinet equation of state [46] to the Helmholtz free energy profiles around the equilibrium volumes, will be presented together with an uncertainty region determined by the fitting of different orders of Taylor expansions to the volume-frequency relations.

Specific heat capacity

The specific heat capacity is a measure for the ability of a material to store heat. A large specific heat capacity will allow the material to absorb more heat and, as a consequence, increase its resistance against undesired thermal effects. The specific heat capacity at constant pressure for both the CP and LP phases are shown in Figure 10a in the temperature range 0–500 K. The curves of the

(meta)stable phases coincide almost over the complete temperature range, except for very low temperatures. In that region, the CP phase has a somewhat lower value as the heat capacity is dominated by the lowest vibrational frequency. The specific heat capacity increases monotonically with temperature from $0 \text{ J g}^{-1} \text{ K}^{-1}$ at 0 K towards $1.4 \text{ J g}^{-1} \text{ K}^{-1}$ at 500 K. These values remain unaffected by applying different fitting polynomials. Our predictions overestimate the experimental value obtained by Kloutse et al. only by $0.1 \text{ J g}^{-1} \text{ K}^{-1}$ [47].

Bulk modulus

The bulk modulus provides information on the resistance to isotropically compress a material. Therefore, this property is relevant in the study of the highly flexible MIL-53(Al) material. The bulk modulus is proportional to the second-order derivative of the Helmholtz free energy with respect to the volume. As a consequence, possible noise on the free energy due to fitting can yield large uncertainties in the predicted value of the bulk modulus. This is clearly visible in Figure 10b, where the predicted values, using different orders of polynomials, are represented by shaded areas. From the Rose-Vinet fit a value of 3.8 GPa is expected for the CP phase at 0 K, which reduces to 3.4 GPa at 300 K. This falls in the range of the results obtained by force field MD simulations at 300 K, which yield values between 3.3 and 3.7 GPa [49]. However, the bulk modulus at 0 K deviates substantially from the RPA result of 2.6 GPa [15]. In the latter, the ZPE was not taken into account, but our simulations suggest a decrease in bulk modulus when ZPE is included. The bulk modulus from the Rose-Vinet fit to the LP phase ranges from 2.1 GPa at 0 K to 8.4 GPa at 500 K. At 300 K, a value of 4.2 GPa

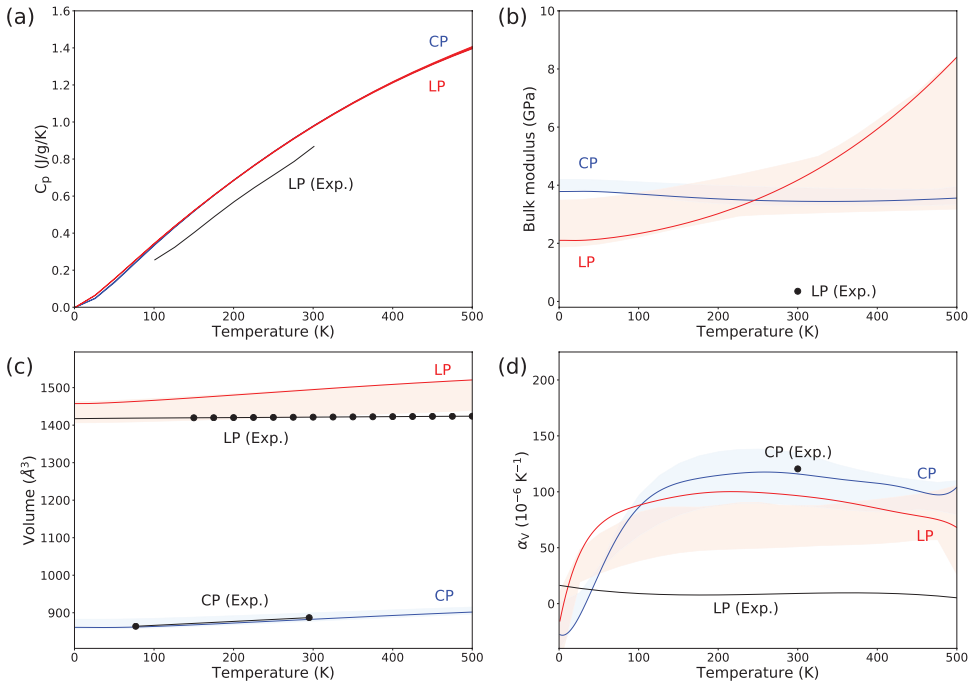


Fig. 10: Thermodynamic properties of the CP (blue) and LP (red) phases as a function of temperature. The blue and red solid lines represent the results from a Rose-Vinet fit [46] (except for the specific heat capacity). The shaded area represents the uncertainty due to the used fitting polynomial. (a) Specific heat capacity at constant pressure. (b) Bulk modulus. (c) Equilibrium volume. (d) Volumetric thermal expansion coefficient. All calculated properties are compared with experimental reference data from Refs. [13, 18, 47, 48].

is predicted, which overestimates the experimentally obtained result of 0.35 GPa by one order of magnitude [13] and also force field MD simulations give lower values [49]. In our simulations, the bulk modulus at 300 K is higher for the LP phase than for the CP phase, which is counterintuitive. The strong increase in the LP phase bulk modulus for increasing temperatures is a consequence of a too large volumetric thermal expansion (see next subsection). This shifts the equilibrium volume to regions where the electronic energy profile has a strong curvature.

Volumetric thermal expansion

A last thermodynamic property of MIL-53(Al) that can be obtained within the QHA is the volumetric thermal expansion coefficient. In order to derive this quantity for the CP and the LP phases, the equilibrium volumes have to be determined from the Helmholtz free energy profile within the temperature range of interest (Figure 10c). For the

equilibrium volume of the CP phase, we observe an excellent agreement with the experimental result [18], while the one of the LP phase [48] is consistently overestimated by our calculations.

The volumetric thermal expansion coefficient is proportional to the derivative of the equilibrium volume with respect to temperature. In Figure 10d, this thermodynamic quantity is presented. A large spread on the predicted value is noticed. Nonetheless, it can be concluded that the thermal expansion of the CP phase is lower than the one of the LP phase below 100 K, while the opposite holds for higher temperatures. Based on our simulations, we expect small negative thermal expansion (NTE) below 40 K for the CP phase, which turns into positive thermal expansion (PTE) at higher temperatures. This is also supported by the mode Grüneisen parameters, which often form an indication for NTE or PTE behavior [50] (see Supporting Information Section S7). The magnitude of the experimentally measured volumetric thermal expansion coefficient

of the CP phase at 300 K is $120 \cdot 10^{-6} \text{ K}^{-1}$, which is obtained by considering the equilibrium volumes at only two different temperatures [18]. Ab initio MD simulations (AIMD) predict values of the order $180 \cdot 10^{-6} \text{ K}^{-1}$ [45]. In contrast, the thermal expansion coefficient of the LP phase overestimates the experimental result by one order of magnitude [48]. AIMD simulations give also a lower value for this property. The predicted value for the thermal expansion

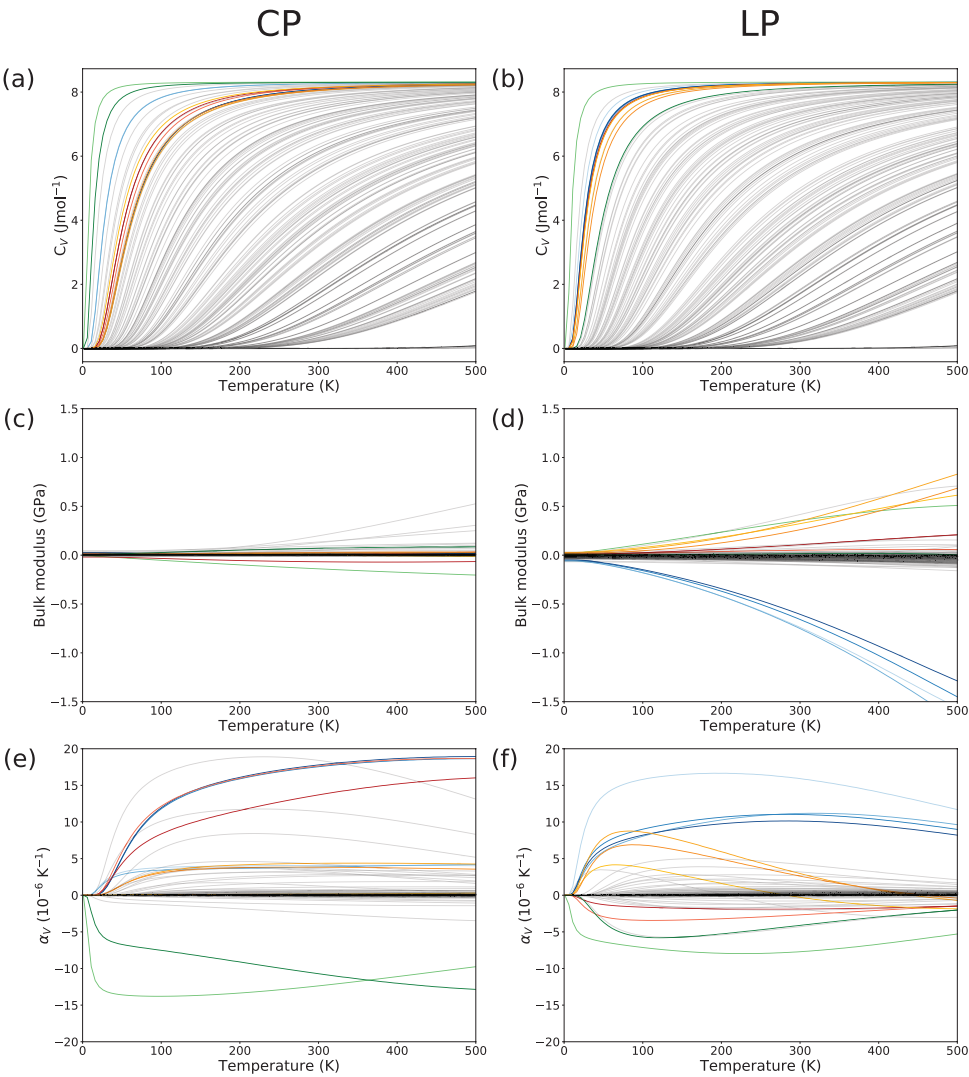


Fig. 11: Contribution of the lattice vibrations to the thermodynamic properties of the CP and LP phases as a function of temperature. The terahertz vibrations discussed in Section “Terahertz vibrations” are highlighted in the same color as in Figure 4. Heat capacity at constant volume of the CP phase (a) and the LP phase (b). Bulk modulus of the CP phase (c) and the LP phase (d). Volumetric thermal expansion coefficient of the CP phase (e) and the LP phase (f).

coefficient in the LP phase is heavily influenced by the linker rotation vibrational frequencies (see Section “Influence of lattice vibrations on thermodynamic properties”). Their entropic contribution to the Helmholtz free energy profile is peaked around 1570 Å³, which can induce a relatively large shift in equilibrium volume at elevated temperatures.

Influence of lattice vibrations on thermodynamic properties

In previous paragraphs, we have argued that the thermodynamic properties are mainly affected by terahertz vibrations. As we have derived analytical expressions for the vibrational frequencies as a function of the volume, it becomes possible to determine the influence of each lattice vibration on the thermodynamic properties (see Supporting Information Section S8). In Figure 11, the vibrational contributions to the specific heat capacity at constant volume, the bulk modulus, and the volumetric expansion coefficient of the CP and LP phases are presented. Starting with the heat capacity at constant volume, we observe only minor differences between both phases. As the LP phase consists of more vibrations with very-low frequencies, it has a slightly larger total heat capacity at low temperatures, but once the contribution from these modes to the heat capacity is saturated, the total heat capacities of both phases have equal magnitudes.

The lattice vibrations have a more pronounced effect on the bulk modulus and the volumetric thermal expansion. The bulk modulus of the CP phase depends mainly on the contributions from the soft modes (green curves) and a few other low-frequency vibrations, although their magnitudes remain small below 500 K. For the LP phase structure, we observe a large negative contribution to the bulk modulus from the vibrations exhibiting linker rotations (blue curves) on the one hand and a large positive contribution from the vibrations describing rotations of the aluminum-oxide backbone (yellow) and one of the soft modes (green). The magnitudes of these contributions increase with temperature reaching values of −0.7 GPa and 0.4 GPa, respectively. The large negative bulk modulus of the vibrations inducing linker rotations has a considerable impact on the total bulk modulus. Nevertheless, the latter increases for increasing temperatures. This is a result of the curvature of the electronic contribution to the Helmholtz free energy profile, which increases for increasing equilibrium temperatures, as the equilibrium volume alters.

Finally, we discuss the mode contributions to the volumetric thermal expansion. For the CP phase, we notice

that the two soft modes (green) give a large negative contributions to the volumetric thermal expansion coefficient giving rise to NTE even at very low temperatures. At higher temperatures, there are more vibrational modes with a positive contribution to α_v , for example the vibrations inducing linker rotations (blue) and trampoline motions (red), yielding PTE. Also for the LP phase, the soft modes tend to lower the value of α_v , but they are counteracted by both the vibrations showing rotations of the linker (blue) and the metal-oxide backbone (yellow). Especially the modes with linker rotations have a large impact on the PTE behavior over the complete temperature range. We assume that an overestimation of the contribution of these low-frequency vibrations are the main cause of the too large α_v of the LP phase and, hence, the too large increase in equilibrium volume leading to an overestimation of the bulk modulus.

It is clear that terahertz vibrations have a considerable effect on the prediction of thermodynamic properties. Therefore, it is essential to simulate the vibrational frequencies of terahertz modes accurately, as small changes in the frequencies or their derivatives with respect to the volume can substantially affect the predicted thermodynamic properties. Although, even with high computational standards, a correct prediction of low-frequency vibrations remains hard when the potential energy surface is flat and/or anharmonicities are present [51, 52].

Conclusion

This work investigated the influence of lattice vibrations on the breathing transition and thermodynamic properties of MIL-53(Al). For that purpose, volume-frequency relations were determined for each normal mode. It was shown that most high-frequency vibrations (>300 cm^{−1}) in MIL-53(Al) follow a general volume-frequency trend. At high and low unit cell volumes the vibrational frequency decreases for increasing unit cell volumes due to weakening of the covalent bonds, while for intermediate volumes the opposite behavior is observed, which is an effect of dispersion forces. As a result, most vibrational frequencies show a counterintuitive increase when the material undergoes a transition from the CP phase to the LP phase.

Furthermore, the low-frequency vibrations in the terahertz region were examined. It has become clear that only a few modes will influence the dynamics of the phase transformation. On the one hand, a large decrease in vibrational frequencies for increasing unit cell volumes

was observed for those modes showing rotations of the organic linker thereby triggering the CP-to-LP phase transformation at high temperatures. On the other hand, two soft modes were predicted showing the opposite volume-frequency trend, which originates from an internal strain induced by the volume change. These soft modes stabilize the CP phase structure at low temperatures and trigger the LP-to-CP phase transformation. In addition, several other modes with an interesting volume-frequency behavior were discovered such as those exhibiting trampoline-like motion of the linker, which may also play an important role in the breathing process.

Analytical expressions could be fitted to the volume-frequency relations, which allowed to derive several thermodynamic properties as a function of the volume and temperature such as the Helmholtz free energy profile, the specific heat capacity, the bulk modulus, and the volumetric thermal expansion. The results were in fair agreement with literature data, especially for the CP phase. However, the predicted bulk modulus and the volumetric thermal expansion coefficient of the LP phase were overestimated. We claimed that the too high values of the mentioned properties resulted from the contribution of the low-frequency vibrations exhibiting rotations of the organic linkers. In general, terahertz vibrations were found to influence the thermodynamic properties significantly. Subsequently, small errors in the predicted frequencies can cause large deviations in the thermodynamic properties, indicating the urge of highly accurate DFT calculations including a high degree of anharmonicities.

Acknowledgement: This work is supported by the Fund for Scientific Research Flanders (FWO), the Research Board of the Ghent University (BOF), and BELSPO in the frame of IAP/7/05. Other funds are provided by the European Union's Horizon 2020 research and innovation programme [consolidator ERC Grant Agreement No.647755 - DYNPOR (2015–2020)]. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation – Flanders (FWO) and the Flemish Government – department EWI.

References

- [1] H.-C. Zhou, S. Kitagawa, Metal–organic frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415.
- [2] G. Maurin, C. Serre, A. Cooper, G. Férey, The new age of MOFs and of their porous-related solids. *Chem. Soc. Rev.* **2017**, *46*, 1104.
- [3] P. Z. Moghadam, A. Li, S. B. Wiggins, A. Tao, A. G. Maloney, P. A. Wood, S. C. Ward, D. Fairen-Jimenez, Development of a Cambridge structural database subset: a collection of metal–organic frameworks for past, present, and future. *Chem. Mater.* **2017**, *29*, 2618.
- [4] C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, R. Q. Snurr, Large-scale screening of hypothetical metal–organic frameworks. *Nature Chem.* **2012**, *4*, 83.
- [5] Y. Cui, B. Li, H. He, W. Zhou, B. Chen, G. Qian, Metal–organic frameworks as platforms for functional materials. *Acc. Chem. Res.* **2016**, *49*, 483.
- [6] Q. Yang, D. Liu, C. Zhong, J.-R. Li, Development of computational methodologies for metal–organic frameworks and their application in gas separations. *Chem. Rev.* **2013**, *113*, 8261.
- [7] F.-Y. Yi, D. Chen, M.-K. Wu, L. Han, H.-L. Jiang, Chemical sensors based on metal–organic frameworks. *ChemPlusChem.* **2016**, *81*, 675.
- [8] S. M. J. Rogge, A. Bavykina, J. Hajek, H. García, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, Metal–organic and covalent organic frameworks as single-site catalysts. *Chem. Soc. Rev.* **2017**, *46*, 3134.
- [9] S. Horike, S. Shimomura, S. Kitagawa, Soft porous crystals. *Nature Chem.* **2009**, *1*, 695.
- [10] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, Flexible metal–organic frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062.
- [11] F.-X. Coudert, Responsive metal–organic frameworks and framework materials: under pressure, taking the heat, in the spotlight, with friends. *Chem. Mater.* **2015**, *27*, 1905.
- [12] L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, V. Van Speybroeck, Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals. *Nature Commun.* **2018**, *9*, 204.
- [13] P. G. Yot, Z. Boudene, J. Macia, D. Granier, L. Vanduyfhuys, T. Verstraeten, V. Van Speybroeck, T. Devic, C. Serre, G. Férey, N. Stock, G. Maurin, Metal–organic frameworks as potential shock absorbers: the case of the highly flexible MIL-53(Al). *Chem. Commun.* **2014**, *50*, 9462.
- [14] P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, Flexible porous metal–organic frameworks for a controlled drug delivery. *J. Am. Chem. Soc.* **2008**, *130*, 6774.
- [15] J. Wieme, K. Lejaeghere, G. Kresse, V. Van Speybroeck, Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal–organic frameworks. *Nature Commun.* **2018**, *9*, 4899.
- [16] P. Freund, L. Mielewczyk, M. Rauche, I. Senkovska, S. Ehrling, E. Brunner, S. Kaskel, MIL-53(Al)/carbon films for CO₂-sensing at high pressure. *ACS Sustain. Chem. Eng.* DOI: 10.1021/acssuschemeng.8b05368.
- [17] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. *Chem. Eur. J.* **2004**, *10*, 1373.
- [18] Y. Liu, J.-H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann, C. M. Brown, Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **2008**, *130*, 11813.

- [19] A. Boutin, M.-A. Springuel-Huet, A. Nossou, A. Gédéon, T. Loiseau, C. Volkringer, G. Férey, F.-X. Coudert, A. H. Fuchs, Breathing transitions in MIL-53(Al) metal–organic framework upon xenon adsorption. *Angew. Chem. Int. Ed.* **2009**, *48*, 8314.
- [20] F.-X. Coudert, A. Boutin, A. H. Fuchs, A. V. Neimark, Adsorption deformation and structural transitions in metal–organic frameworks: from the unit cell to the crystal. *J. Phys. Chem. Lett.* **2013**, *4*, 3198.
- [21] M. R. Ryder, B. Civalleri, T. D. Bennett, S. Henke, S. Rudić, G. Cinque, F. Fernandez-Alonso, J.-C. Tan, Identifying the role of terahertz vibrations in metal–organic frameworks: from gate-opening phenomenon to shear-driven structural destabilization. *Phys. Rev. Lett.* **2014**, *113*, 215502.
- [22] M. R. Ryder, B. Civalleri, G. Cinque, J.-C. Tan, Discovering connections between terahertz vibrations and elasticity underpinning the collective dynamics of the HKUST-1 metal–organic framework. *CrystEngComm*. **2016**, *18*, 4303.
- [23] A. Krylov, A. Vtyurin, P. Petkov, I. Senkovska, M. Maliuta, V. Bon, T. Heine, S. Kaskel, E. Silyusareva, Raman spectroscopy studies of the terahertz vibrational modes of a DUT-8(Ni) metal–organic framework. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32099.
- [24] A. E. J. Hoffman, L. Vanduyfhuys, I. Nevjestic, J. Wieme, S. M. J. Rogge, H. Depauw, P. Van Der Voort, H. Vrielinck, V. Van Speybroeck, Elucidating the vibrational fingerprint of the flexible metal–organic framework MIL-53(Al) using a combined experimental/computational approach. *J. Phys. Chem. C* **2018**, *122*, 2734.
- [25] A. M. Walker, B. Civalleri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Román-Pérez, J. M. Soler, J. D. Gale, Flexibility in a metal–organic framework material controlled by weak dispersion forces: the bistability of MIL-53(Al). *Angew. Chem. Int. Ed.* **2010**, *49*, 7501.
- [26] A. Erba, On combining temperature and pressure effects on structural properties of crystals with standard ab initio techniques. *J. Chem. Phys.* **2014**, *141*, 124115.
- [27] E. Cockayne, Thermodynamics of the flexible metal–organic framework material MIL-53(Cr) from first-principles. *J. Phys. Chem. C* **2017**, *121*, 4312.
- [28] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.
- [29] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [30] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- [31] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456.
- [32] P. E. Blöchl, Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.
- [33] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.
- [34] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188.
- [35] D. E. P. Vanpoucke, K. Lejaeghere, V. Van Speybroeck, M. Waroquier, A. Ghysels, Mechanical properties from periodic plane wave quantum mechanical codes: The challenge of the flexible nanoporous MIL-47(V) framework. *J. Phys. Chem. C* **2015**, *119*, 23752.
- [36] A. Ghysels, T. Verstraelen, K. Hemelsoet, M. Waroquier, V. Van Speybroeck, TAMkin: a versatile package for vibrational analysis and chemical kinetics. *J. Chem. Inf. Model.* **2010**, *50*, 1736.
- [37] S. Baroni, S. De Gironcoli, A. Dal Corso, P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **2001**, *73*, 515.
- [38] X. Wu, D. Vanderbilt, D. R. Hamann, Systematic treatment of displacements, strains, and electric fields in density-functional perturbation theory. *Phys. Rev. B* **2005**, *72*, 035105.
- [39] A. Erba, M. Shahrokhi, R. Moradian, R. Dovesi, On how differently the quasi-harmonic approximation works for two isostructural crystals: thermal properties of periclase and lime. *J. Chem. Phys.* **2015**, *142*, 044114.
- [40] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, An explanation for the very large breathing effect of a metal–organic framework during CO₂ adsorption. *Adv. Mater.* **2007**, *19*, 2246.
- [41] J. Salazar, G. Weber, J. Simon, I. Bezverkhyy, J. Bellat, Characterization of adsorbed water in MIL-53(Al) by FTIR spectroscopy and ab-initio calculations. *J. Chem. Phys.* **2015**, *142*, 124702.
- [42] M. R. Ryder, B. Van de Voorde, B. Civalleri, T. D. Bennett, S. Mukhopadhyay, G. Cinque, F. Fernandez-Alonso, D. De Vos, S. Rudić, J.-C. Tan, Detecting molecular rotational dynamics complementing the low-frequency terahertz vibrations in a zirconium-based metal–organic framework. *Phys. Rev. Lett.* **2017**, *118*, 255502.
- [43] S. M. J. Rogge, M. Waroquier, V. Van Speybroeck, Reliably modeling the mechanical stability of rigid and flexible metal–organic frameworks. *Acc. Chem. Res.* **2017**, *51*, 138.
- [44] J. P. S. Mowat, V. R. Seymour, J. M. Griffin, S. P. Thompson, A. M. Z. Slawin, D. Fairen-Jimenez, T. Düren, S. E. Ashbrook, P. A. Wright, A novel structural form of MIL-53 observed for the scandium analogue and its response to temperature variation and CO₂ adsorption. *Dalton Trans.* **2012**, *41*, 3937.
- [45] R. Demuyne, S. M. J. Rogge, L. Vanduyfhuys, J. Wieme, M. Waroquier, V. Van Speybroeck, Efficient construction of free energy profiles of breathing metal–organic frameworks using advanced molecular dynamics simulations. *J. Chem. Theory Comput.* **2017**, *13*, 5861.
- [46] P. Vinet, J. Ferrante, J. H. Rose, J. R. Smith, Compressibility of solids. *J. Geophys. Res.* **1987**, *92*, 9319.
- [47] F. A. Kloutse, R. Zacharia, D. Cossement, R. Chahine, Specific heat capacities of MOF-5, Cu-BTC, Fe-BTC, MOF-177 and MIL-53(Al) over wide temperature ranges: measurements and application of empirical group contribution method. *Microporous Mesoporous Mater.* **2015**, *217*, 1.
- [48] C. Nanthamathée, S. Ling, B. Slater, M. P. Attfield, Contradistinct thermoresponsive behavior of isostructural MIL-53 type metal–organic frameworks by modifying the framework inorganic anion. *Chem. Mater.* **2014**, *27*, 85.
- [49] S. M. J. Rogge, L. Vanduyfhuys, A. Ghysels, M. Waroquier, T. Verstraelen, G. Maurin, V. Van Speybroeck, A comparison of

- barostats for the mechanical characterization of metal–organic frameworks. *J. Chem. Theory Comput.* **2015**, *11*, 5583.
- [50] L. Wang, C. Wang, Y. Sun, K. Shi, S. Deng, H. Lu, Large negative thermal expansion provided by metal-organic framework MOF-5: a first-principles study. *Mater. Chem. Phys.* **2016**, *175*, 138.
- [51] V. Barone, M. Biczysko, J. Bloino, Fully anharmonic IR and Raman spectra of medium-size molecular systems: accuracy and interpretation. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1759.
- [52] M. T. Ruggiero, J. A. Zeidler, A. Erba, Intermolecular anharmonicity in molecular crystals: interplay between experimental low-frequency dynamics and quantum quasi-harmonic simulations of solid purine. *Chem. Commun.* **2017**, *53*, 3781.

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/zkri-2018-2154>).

Paper VIII

Modeling the structural and thermal properties of loaded metal-organic frameworks. An interplay of quantum and anharmonic fluctuations

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Journal of Chemical Theory and Computation, **2019**, 15, 3237-3249

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J. Wieme performed the simulations on MOF-5, and had a large contribution in the interpretation of the results as well as the preparation of the manuscript.

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Modeling the Structural and Thermal Properties of Loaded Metal–Organic Frameworks. An Interplay of Quantum and Anharmonic Fluctuations

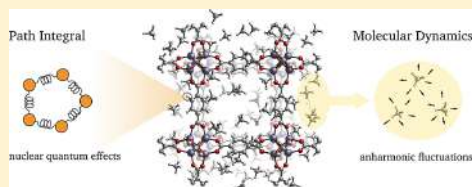
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Supporting Information

ABSTRACT: Metal–organic frameworks show both fundamental interest and great promise for applications in adsorption-based technologies, such as the separation and storage of gases. The flexibility and complexity of the molecular scaffold pose a considerable challenge to atomistic modeling, especially when also considering the presence of guest molecules. We investigate the role played by quantum and anharmonic fluctuations in the archetypical case of MOF-5, comparing the material at various levels of methane loading. Accurate path integral simulations of such effects are made affordable by the introduction of an accelerated simulation scheme and the use of an optimized force field based on first-principles reference calculations. We find that the level of statistical treatment that is required for predictive modeling depends significantly on the property of interest. The thermal properties of the lattice are generally well described by a quantum harmonic treatment, with the adsorbate behaving in a classical but strongly anharmonic manner. The heat capacity of the loaded framework—which plays an important role in the characterization of the framework and in determining its stability to thermal fluctuations during adsorption/desorption cycles—requires, however, a full quantum and anharmonic treatment, either by path integral methods or by a simple but approximate scheme. We also present molecular-level insight into the nanoscopic interactions contributing to the material's properties and suggest design principles to optimize them.



1. INTRODUCTION

Tailor-made porous materials¹ like metal–organic frameworks (MOFs)² are at the core of emerging technologies due to their exceptional physical and chemical properties, such as a high tunable porosity and an associated large gas storage capacity. Therefore, they have been proposed for applications such as adsorbed natural gas (ANG) storage in vehicles,^{3,4} adsorption-driven heat pumps,^{5,6} and carbon capture and sequestration (CCS).^{7,8} While a lot of work still needs to be done to optimize the crucial adsorption and storage properties of these porous materials,⁹ studies on other critical requirements such as heat management are gaining interest.¹⁰ For instance, the heat capacity, i.e., the amount of energy required to increase the material's temperature, is a fundamental thermodynamic property of interest in these applications which involve large thermal fluctuations, as adsorption and desorption processes imply the release or consumption of energy. Moreover, the heat capacity of the MOF affects the energy penalty to regenerate the adsorbent in, for example, CCS.¹¹ To date, however, information on the heat capacity is lacking for most MOFs,^{12,13} and the influence of adsorbed guest molecules on

the heat capacity has not yet been investigated, in contrast to other thermal properties such as the thermal expansion behavior and the thermal conductivity.^{14,15}

Within this context, an efficient and accurate simulation protocol to tackle the structural and thermal properties of MOFs including all the relevant physical effects could facilitate a better understanding of the structure–property relations and suggest design principles for materials with improved properties. Due to the importance of finite-temperature effects, anharmonicity, and nuclear quantum effects (NQEs), the modeling of the thermophysics of MOFs is generally not a trivial exercise. The first two effects have already been the subject of many investigations and were included in our protocol to characterize the thermodynamics of MOFs.^{16,17} Furthermore, very recently, some of the present authors highlighted the necessity of an accurate theoretical framework for the design of thermoresponsive MOFs.¹⁸ However, the impact of NQEs has so far received far less attention within the

Received: December 23, 2018

Published: April 19, 2019



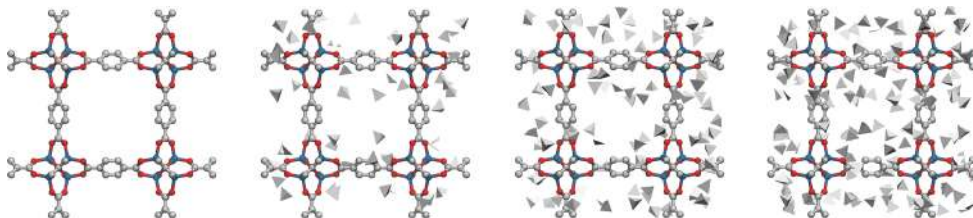


Figure 1. Structure of MOF-5 with a gas loading x of 0, 50, 100, and 150 molecules of methane (left to right) in the conventional unit cell ($8(\text{Zn}_4\text{O}(\text{CO}_2)_6) \cdot x\text{CH}_4$). The oxygen, carbon, and zinc atoms are shown in red, silver, and blue, respectively. For the sake of aesthetics, the hydrogen atoms are not included. The methane molecules are represented by silver tetrahedra.

MOF community, despite the many light atoms contained in the crystal structure and present inside the pores.^{19–21}

In this regard, path integral molecular dynamics (PIMD)²² provides an ideal reference framework for the evaluation of thermodynamic averages, as it seamlessly captures both NQEs and the anharmonic motion of nuclei. The statistics of distinguishable quantum particles can be obtained through the equivalence between the thermodynamics of a quantum system and a classical ring polymer containing P replicas of the system.²³ In the limit of large P values, NQEs can then be systematically accounted for. The major downside of this technique is the associated high computational cost, i.e., P times the corresponding cost of a classical molecular dynamics (MD) simulation. However, several methodological advances^{24–29} that enable a reduction of the computational cost have made it a mainstream technique for material modeling.³⁰

An additional difficulty arises from the fact that most experiments and practical applications are performed in isothermal–isobaric conditions, while the vast majority of atomistic simulations are performed with a fixed unit cell, corresponding to isochoric conditions. As most solid materials have a very small compressibility, the difference between the two ensembles is often negligible. For MOFs on the contrary—particularly when loaded with a gas—the behavior in isobaric and isochoric conditions can be very different. Some of us emphasized the importance of taking into account the variations of the cell shape to simulate properties of flexible MOFs.¹⁶ While algorithms for performing path integral simulations at constant pressure conditions exist,^{31,32} an accurate evaluation of the thermophysical properties requires a very large number of replicas to reach convergence. In this Article, we introduce a method, based on a recently developed implementation of high-order path integral factorizations,²⁶ to greatly accelerate the convergence of these simulations.

This method, in combination with a first-principles-based force field,^{17,33,34} makes it possible to characterize the structural and thermophysical properties of complex molecular systems such as guest-loaded MOFs. We investigate the archetypical case of the well-known MOF-5^{35,36} in the presence and absence of methane in its pores (see Figure 1). Evaluating and understanding the impact of methane adsorption on the properties of MOFs is especially important as they have been proposed as potential adsorbents for natural gas storage applications.^{3,4,9} We demonstrate the crucial role of a complete statistical-mechanical treatment of the quantum and anharmonic fluctuations in MOFs for a correct description of the structural properties and the heat capacity of guest-loaded MOFs. By meticulously disentangling anharmonic and

nuclear quantum effects for both the lattice and the guest molecules, we are able to propose an efficient empirical calculation scheme which may be used to screen MOFs for beneficial thermal properties on a larger scale.

2. METHODOLOGY

2.1. Materials. The materials that are considered in this theoretical work are pristine and methane-loaded MOF-5 scaffolds.³⁵ This framework consists of $\text{Zn}_4\text{O}(\text{CO}_2)_6$ inorganic nodes connected through 1,4-benzenedicarboxylate (bdc) linkers. The unit cell is cubic and contains eight inorganic nodes, as shown in Figure 1. We consider three different loadings x of 50, 100, and 150 methane molecules in the conventional unit cell ($8(\text{Zn}_4\text{O}(\text{CO}_2)_6) \cdot x\text{CH}_4$), which encompass both the low- and high-adsorption regime.^{3,37} At 100 bar and room temperature, for example, approximately 120 methane molecules are present per conventional unit cell, as experimentally measured by Mason et al.³ (see SI Figure S2). Our force field underestimates the high-pressure saturation loading at various temperatures (see SI Figure S3), which is a property that is extremely sensitive to the underlying potential energy surface.³⁸ It is also important to note that experimentally the chemical potential is controlled and not the number of guest molecules and that the experimental loading is highly dependent on the temperature. For computational convenience, we performed all our molecular dynamics simulations at a fixed number of particles. The purpose of comparing multiple loadings is only to provide qualitative insight into the interplay between temperature, framework, and guest molecules rather than to compare directly with experiment.

2.2. First-Principles-Derived Force Fields. The molecular simulations are performed using newly developed force fields for MOF-5 and methane. They are constructed with QuickFF,^{33,34} a software package developed to derive force fields for MOFs in an easy yet accurate way based on information obtained from first-principles input data. Isolated cluster models were used to generate the required first-principles input data, which includes the equilibrium geometry and Hessian together with the atomic charges. Within the QuickFF protocol, the quantum mechanical potential energy surface (PES) is approximated by a sum of analytical functions of the nuclear coordinates that describe the covalent and noncovalent interactions. The covalent interactions, which mimic the chemical bonds between the atoms, are approximated by different terms as a function of the internal coordinates (bonds, bends, out-of-plane distances, and dihedrals). The noncovalent interactions are composed of

electrostatic and van der Waals interactions. The guest–host interactions between MOF-5 and methane only include noncovalent terms. A detailed discussion of the force field energy expression and derivation is provided in the Supporting Information (see SI Section S4).

2.3. Thermodynamic Ensembles. In order to study the classical and quantum isobaric heat capacity of the guest-loaded MOF scaffold, the classical and quantum isothermal–isobaric thermodynamic ensembles—as defined in ref 16—are respectively used. For a system with N particles, subject to an external mechanical stress $\sigma = \mathcal{P}\mathbf{I} + \sigma_a$, with $\mathcal{P}$ the hydrostatic pressure and σ_a the deviatoric stress, the classical ($\square = \text{cl}$) and quantum ($\square = \text{qn}$) isothermal–isobaric ensembles at temperature $k_B T = \beta^{-1}$ and fixed normalized cell tensor $\mathbf{h}_0$ are described by the partition functions

$$\Delta_{\square}(N, \mathcal{P}(\mathbf{h}_0), T) \propto \int dV e^{-\beta \mathcal{P}V} Z_{\square}(N, \mathcal{V}(\mathbf{h}_0), T) \quad (1)$$

where $Z_{\square}(N, \mathcal{V}(\mathbf{h}_0), T)$ are the corresponding canonical partition functions at volume $\mathcal{V}$, normalized cell tensor $\mathbf{h}_0$, and temperature T . Similarly, the flexible $N\mathcal{P}(\sigma_a = \mathbf{0})T$ partition functions, which allow the cell shape to change, are defined by the partition functions:³⁹

$$\Delta_{\square}(N, \mathcal{P}(\sigma_a = \mathbf{0}), T) \propto \int dV e^{-\beta \mathcal{P}V} \int d\mathbf{h}_0 \delta(\det(\mathbf{h}_0) - 1) Z_{\square}(N, \mathcal{V}(\mathbf{h}_0), T) \quad (2)$$

The classical ensembles are sampled by classical molecular dynamics, whereas the quantum ensembles are sampled using path integral molecular dynamics.²² The latter maps the quantum partition function of a system onto that of a classical ring polymer Hamiltonian made of P replicas of the system.²³ Formally, exact results can be obtained in the limit of $P \rightarrow \infty$. Unfortunately, the requisite value of P to calculate structural properties rises rapidly with decreasing temperature, and for properties such as heat capacity⁴⁰ the increase in P is even greater. This makes the standard scheme prohibitively expensive.

2.4. Accelerated Simulation Scheme. To remedy this problem, we present an accelerated scheme based on a constant pressure integrator for the high-order path integral method.²⁴ The quantum statistics of distinguishable particles arises from the noncommutative nature of the potential and kinetic energy operators. In standard (second-order) path integral schemes, an approximate factorization of the high-temperature Boltzmann operator is introduced, that leads to an error that decreases as $O(1/P^2)$. High-order techniques use an alternative splitting of the Boltzmann operator,^{41,42} leading to an alternative ring polymer Hamiltonian with a faster, $O(1/P^4)$ convergence to the exact quantum limit. This makes it possible to reduce the number of replicas and hence the computational cost.²⁴ While many high-order schemes exist,^{29,41} here we focus on the specific case⁴³ of a fourth-order Suzuki–Chin (SC) splitting,^{42,44} which yields a so-called SC Hamiltonian $H_P^{\text{SC}}(\mathbf{p}, \mathbf{q})$. Considering for simplicity the case of a single particle in an external potential, the SC Hamiltonian takes the form

$$H_P^{\text{SC}}(\mathbf{p}, \mathbf{q}) = H_P^0(\mathbf{p}, \mathbf{q}) + V_P^{\text{SC}}(\mathbf{q}) \quad (3)$$

where

$$H_P^0(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^P \frac{[\mathbf{p}^{(j)}]^2}{2m} + \sum_{j=1}^P \frac{1}{2} m \omega_P^2 [\mathbf{q}^{(j)} - \mathbf{q}^{(j+1)}]^2$$

is the ring polymer Hamiltonian of a free particle, subjected to cyclic boundary conditions ($j + P = j$), and

$$V_P^{\text{SC}}(\mathbf{q}) = \sum_{j=1}^{P/2} \left[\frac{2}{3} V(\mathbf{q}^{(2j-1)}) + \frac{4}{3} V(\mathbf{q}^{(2j)}) + \frac{1}{9} \tilde{V}(\mathbf{q}^{(2j)}) \right] \quad (4)$$

Note that the odd and even replicas feel the physical potential $V(\mathbf{q}^{(j)})$ scaled by factors of 2/3 and 4/3 respectively and that the high-order term $\tilde{V}(\mathbf{q}^{(j)}) = \omega_P^{-2} m^{-1} |\mathbf{f}^{(j)}|^2$, that depends on the modulus of the force $\mathbf{f}^{(j)} \equiv -\partial V(\mathbf{q}^{(j)})/\partial \mathbf{q}^{(j)}$, only acts on the even replicas.

The improved efficiency of the high-order scheme is demonstrated by studying the convergence of the total energy and its temperature derivative for a harmonic model of MOF-5—obtained by computing the dynamical matrix associated with the first-principles-derived force field described in Section 2.2—with respect to the number of replicas. The analysis is done analytically at two different temperatures: $T = 100$ and 300 K, as described in ref 45. As shown in Figure 2, the high-

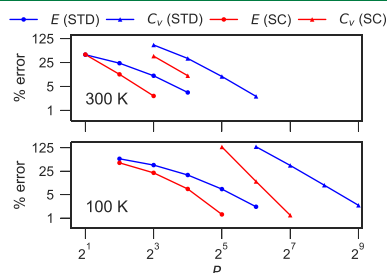


Figure 2. Fractional error in the standard (blue) and Suzuki–Chin (red) path integral estimators of the energy (circles) and the heat capacity (triangles) of the empty MOF-5 modeled by the corresponding Debye crystal potential, as a function of the number of beads P at 100 K (bottom) and 300 K (top). The values of the energy and the heat capacity were obtained analytically.⁴⁵

order scheme improves the convergence of both the energy and the heat capacity by a factor of 2 at room temperature. In the low temperature or high accuracy regime where quantum effects dominate, the efficiency of the high-order scheme is even more significant.

The high accuracy afforded by the SC scheme makes it particularly useful to compute the heat capacity. Thus far, however, it has only been successfully applied to relatively simple systems,⁴⁶ and heat capacities in particular have only been reported for small clusters of molecules and constant-volume conditions.⁴⁷ The difficulty in applying fourth-order schemes to complex materials can be understood by considering the fact that the force and virial contain derivatives of $\tilde{V}$ with respect to the atomic positions and the cell parameters

$$\tilde{\mathbf{f}}^{(j)} \equiv -\frac{\partial \tilde{V}(\mathbf{q}^{(j)})}{\partial \mathbf{q}^{(j)}}, \quad \tilde{\Xi}^{(j)} \equiv \frac{d\tilde{V}(\mathbf{q}^{(j)})}{d\mathbf{h}} \mathbf{h}^T \quad (5)$$

Given that $\tilde{V}(\mathbf{q}^{(0)})$ already contains first-order derivatives of the physical potential, the computation of the forces and the virial, required to sample the isothermal–isobaric ensemble by means of path integral dynamics, also demands the evaluation of higher-order derivatives of the potential, which is often cumbersome and computationally prohibitive. Much of the work on the practical implementation of high-order path integrals has therefore focused on avoiding the calculation of these terms, by sampling the standard path integral Hamiltonian and introducing fourth-order schemes by reweighting.^{24,46} Unfortunately, reweighting schemes have poor statistical performance for large systems,^{24,48} so the application of the SC scheme has until now been limited to small systems and to constant-volume sampling.

To circumvent these limitations, we evaluate the virial using a finite-difference scheme that has recently been introduced by some of the present authors, to sample the SC canonical partition function directly. We discuss the essential ingredients of this scheme in [Appendix A](#) and report a detailed derivation in the [SI](#). Direct access to the instantaneous force and virial allows us to develop an integration scheme that samples the quantum isothermal–isobaric ensemble. This scheme can be regarded as an extension of the second-order scheme introduced in the pioneering work of Martyna and co-workers.³¹ The rather cumbersome derivation and the equations of motion are given in the [SI](#). It should be noted that our implementation in `i-PT`⁴⁹ is also fully compatible with multiple time stepping^{28,50} and stochastic thermostating, extending the integrators introduced in [ref 51](#) to the isothermal–isobaric ensemble.

By using the finite-difference expressions, only $P/2$ additional force evaluations are needed instead of $P/2$ Hessians. It is also useful to note that these components have a P^{-2} prefactor, which means that they become small and slowly varying for typical values of P used in SC simulations.²⁶ This facilitates the use of a long time step for integrating the high-order forces and virials, enabling us to sample the ensemble while evaluating the expensive terms rather infrequently.

To further reduce the computational effort, we combine this scheme with other accelerated PIMD methods that rely on the separation of the total potential into a cheap short-ranged term and an expensive long-ranged term, which is the case in our study, as discussed in [Subsection 2.2](#). We consider in particular ring polymer contraction (RPC)²⁷ and multiple time stepping (MTS).⁵⁰ Within the first method, the long-ranged components can be computed separately on a smaller ring polymer of P' beads, which are subsequently, without loss of accuracy, extrapolated to the case of P beads. The second method reduces the frequency at which the long-ranged interactions are computed by the use of a longer time step for the integration. The two methods can also be used together to achieve substantial computational savings²⁸ and can be seamlessly combined with our high-order constant pressure scheme.

2.5. Calculation of Thermodynamic Observables.

Within the SC scheme, the thermodynamic averages of all structural observables A are estimated by an ensemble average over the odd replicas

$$\mathcal{A}^{\text{OP}} = \frac{2}{P} \left\langle \sum_{j=1}^{P/2} A(\mathbf{q}^{(2j-1)}) \right\rangle \quad (6)$$

as first demonstrated by Jang and Voth.²⁴ These estimators are commonly referred to as “operator” (OP) estimators, as opposed to the “thermodynamic” estimators obtained by derivation of the path integral partition function, that often have pathological statistical behavior. The simplicity of OP estimators makes the SC scheme very appealing in comparison to other high-order schemes, in which *ad hoc* estimators need to be constructed for simple structural observables.^{46,52} The OP estimators for the total energy ($\mathcal{E}$) and enthalpy ($\mathcal{H}$) are listed in [Appendix B](#). Since the standard estimators for the heat capacity in path integral methods tend to be very complex and exhibit a large variance, we derive an OP double-virial estimator for the isobaric (and isochoric) heat capacity $C_p = \frac{\partial \mathcal{H}}{\partial T}$. The derivation is presented in the [SI \(Section S3.2\)](#), and the resulting expression is given in [Appendix B](#), where it is also shown that this estimator has very good statistical properties and outperforms existing heat capacity estimators.⁴⁷ However, in this study we computed thermo-physical properties over a broad range of temperatures and found it more convenient to estimate C_p by means of a finite difference approximation to the temperature derivative of the enthalpy:

$$C_p(T) = \frac{\partial \mathcal{H}}{\partial T} \approx \frac{\mathcal{H}_{T+\Delta T} - \mathcal{H}_{T-\Delta T}}{2\Delta T} \quad (7)$$

A dedicated estimator will prove useful in simulations that are targeted at a single, specific temperature.

3. COMPUTATIONAL DETAILS

The required first-principles cluster data for the determination of the covalent terms in the force field are generated with Gaussian 16⁵³ using the B3LYP⁵⁴ exchange-correlation functional. A 6-311G(*d,p*) basis set⁵⁵ is used for the C, O, and H atoms, together with the LanL2DZ basis set for Zn.⁵⁶ The atomic charges are derived with the Minimal Basis Iterative Stockholder (MBIS) partitioning scheme.⁵⁷ The atomic charges of the MOF-5 clusters are obtained from the PBE⁵⁸ electron density computed with GPAW.⁵⁹ For methane, the atomic charges are derived from the B3LYP all-electron density obtained with Gaussian 16. The parameters of the van der Waals interactions are taken from the MM3 force field.^{60,61} The van der Waals interactions are calculated up to a cutoff of 15 Å, and a tail correction is added to the potential and its derivatives.⁶² The initial configurations of the methane molecules are generated using RASPA⁶³ by inserting methane molecules at random positions, while ensuring that only realistic intermolecular distances are retained. Afterward a canonical Monte Carlo algorithm was used to equilibrate the positions.

For MOF-5 with and without methane, we perform classical and path integral MD simulations at a mechanical pressure of 1 bar and at different temperatures in the range of 100 to 500 K. The classical MD simulations of both loaded and pristine MOF-5 are performed using `Yaff` in the $N\mathcal{P}(\sigma_s = 0)T$ ensemble, i.e. without constraints on the unit cell.¹⁶ While the covalent interactions are calculated by `Yaff`, the expensive long-range interactions are computed by `lammps`⁶⁴ in a computationally efficient manner. The equations of motion are updated via a Verlet scheme, with a time step of 0.5 fs. The temperature is controlled via a single Nosé–Hoover chain consisting of three beads, with a relaxation time of 100 fs.^{65–67} A Martyna–Tobias–Klein barostat with a relaxation time of

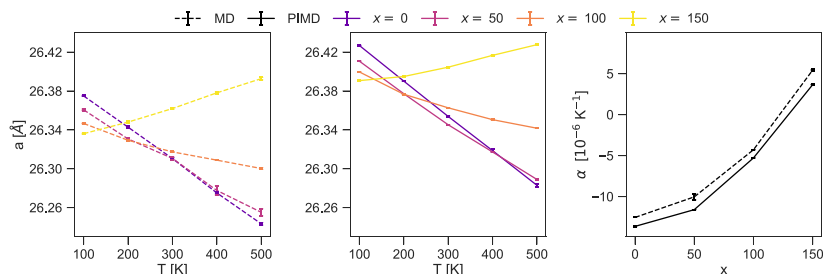


Figure 3. Panels (a) and (b) show the lattice parameter a of MOF-5 with $x = 0, 50, 100$, and 150 molecules of methane as a function of temperature (T), obtained from classical MD and PIMD, respectively. Panel (c) shows the linear thermal expansion coefficient (α) as a function of x . The classical and quantum estimates are respectively shown with dashed and solid lines. Error bars indicate statistical uncertainty.

1000 fs is used to control the pressure.^{16,39,68} We performed five independent runs of 500 ps, starting from a different random seed and from different methane positions. For the empty MOF-5, a single trajectory of 500 ps was used. An equilibration time of 100 ps was considered.

The PIMD simulations are performed with the universal force engine *i-PI*⁴⁹ in the $N\mathcal{P}(\hbar_0)T$ ensemble, in which the cubic symmetry is kept fixed. As shown in the SI (see Section S6.2), the results obtained in the classical limit ($P = 1$) agree perfectly with those obtained in the classical $N\mathcal{P}(\sigma_e = 0)T$ ensemble. This indicates that the effect of cell shape sampling on the heat capacity is negligible for this rigid MOF and thus isotropic barostatting suffices for our PIMD simulations. The evaluation of the forces is carried out by *Yaff* and *lammps*, similar to the classical MD simulations, while the time evolution of the nuclei to sample the appropriate thermodynamic ensemble is done with *i-PI*. To control the temperature, a PILE-L thermostat⁶⁹ is applied to the system, and a white noise Langevin thermostat⁷⁰ is applied to the cell. To control the pressure, a path-integral version of the Bussi-Zykova-Parinello (BZP) barostat,^{32,71} adapted to the SC scheme, is used. The time constants for the thermostats and the barostats are the same as the ones used in the classical simulations. A BAOAB type⁵¹ MTS scheme⁵⁰ (see SI Section S2.3) is used to integrate the equations of motion. The computationally cheap short-range terms of the force field are computed on 64 replicas and integrated with a time step of 0.25 fs. The remainder of the interactions, i.e. the expensive long-range interactions, are computed on 8 replicas using RPC and integrated with a time step of 1 fs. As discussed above, a finite differences strategy is adopted to determine the heat capacity from the enthalpy with a temperature interval of 25 K. We performed 30 independent runs of 50 ps, starting from a different random seed and from different methane positions. For the empty MOF-5, five independent trajectories of 125 ps were used. An equilibration time of 25 ps was considered.

4. RESULTS

Having developed an accelerated integration scheme for the quantum isothermal–isobaric ensemble, we now focus on the structural and thermal properties of methane-loaded MOF-5. Extensions toward other MOFs and adsorbates will be the topic of future studies. The importance of the inclusion of NQEs and anharmonicities in the modeling of the heat capacity is probed by comparing the results with other

methods such as classical MD, which neglects NQEs, and the harmonic approximation, which neglects anharmonicity. We discuss the accuracy of these commonly adopted approximations and provide empirical relations, which might resolve the general lack of knowledge of the heat capacity of this class of materials.

4.1. Structural Properties. To unravel the influence of adsorbates on the framework and finally on the heat capacity, we start by investigating the structural response of MOF-5 for various loadings and temperatures. Here, one could already expect to observe significant NQEs, as zero-point effects were recently found to substantially increase the volume of MOF-5 when comparing classical MD with PIMD.²¹ Additionally, NQEs have previously been observed to change the volume of bulk alkanes by about 10%.^{72–74} A comparison of Figures 3(a) and (b) indeed reveals that the inclusion of NQEs increases the volume by almost 1% for all loadings and temperatures. Horizontally, this shift corresponds to a substantial temperature reduction of about 100 K.

Interestingly, the qualitative changes in the volume as a function of loading at different temperatures do not change appreciably with or without the inclusion of NQEs. At low temperatures, the material slightly shrinks in the presence of methane. The observed adsorption-induced deformation can be understood by attractive van der Waals interactions between the framework and the adsorbed methane.^{75,76} At higher temperatures, by contrast, the empty framework has the lowest volume, as entropic and kinetic effects start dominating and the adsorbed molecules increase the internal pressure, which leads to a volumetric expansion when increasing the loading. The main effect of NQEs on the volume of the guest-loaded system is thus an upward volume shift,²¹ which is to a large extent independent of the number of guest molecules and the temperature.

Varying the concentration and the type of adsorbates in the framework was suggested by Calero and co-workers¹⁵ as a way to control and tune the thermal expansion of a system based on classical MD simulations. We confirm that with methane it is possible to go from the well-known negative thermal expansion behavior of the empty framework^{57–79} toward positive thermal expansion. A proper inclusion of NQEs in our molecular dynamics simulations does not influence the predictions in this temperature window,²¹ and this conclusion still holds with methane in the pores, as shown in Figure 3(c).

A more surprising picture emerges when looking at the distribution of methane inside MOF-5. Recent PIMD

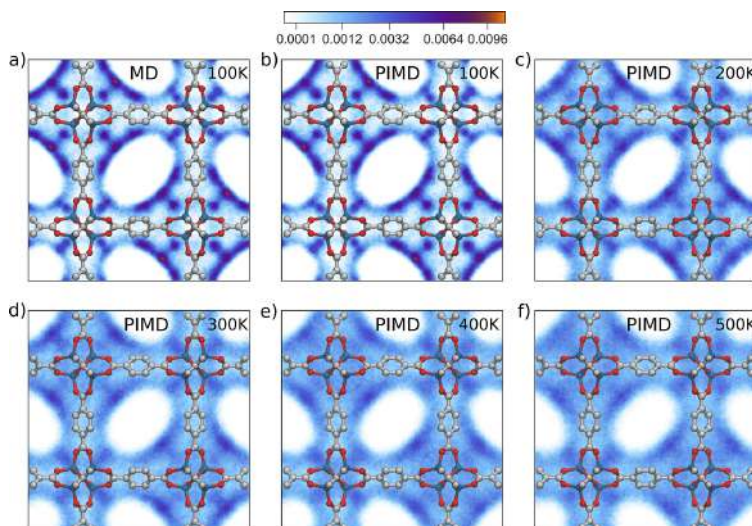


Figure 4. Methane distribution in the pores of MOF-5 at different temperatures as obtained from PIMD simulations. Orange spots indicate high probability adsorption sites. Other colors show the distribution of the low probability methane positions in the conventional unit cell and visualize the probability representation (from very high (orange), to high (dark blue), to low (white) probability). The results are displayed for a loading x of 100 methane molecules per conventional unit cell ($8(\text{Zn}_4\text{O}(\text{CO}_2)_6)$).

simulations⁷³ of bulk methane (at 110 K) have shown that NQEs lead to significant changes in the structure of methane at low temperature, corresponding to an overall softening of the structure and an increase in the intermolecular distance by about 0.1 Å. In contrast, in our study of methane confined in the pores of MOF-5, even at 100 K—where NQEs are expected to be the greatest—there is no appreciable difference between the shape of the classical and quantum distribution functions of methane, as shown in Figure 4. This can be understood by the fact that the change in the structure of bulk methane comes entirely from the isotropic expansion of the gas.⁸⁰ In the case of methane molecules confined in the pores, the low compressibility of the framework makes the expansion as observed in bulk methane when including NQEs impossible.

This discussion shows that the structural response of MOF-5 to a varying number of methane molecules and temperature is largely unaffected by NQEs, except for the zero-point lattice fluctuations. Our observations also corroborate the common practice of ignoring NQEs when studying the loading of porous materials by Grand Canonical Monte Carlo simulations.⁶³ Nevertheless, this conclusion cannot be generalized to other adsorbates, especially those possessing stronger intermolecular interactions such as hydrogen bonding.

4.2. Heat Capacity. MOF-5 has been the subject of a few experimental heat capacity studies^{12,13,81,82} which have shown that the material has a low specific (or molar) heat capacity, about 0.7 J/g·K at room temperature, even when compared to other MOFs. Depending on the type of the application, a large (e.g., for ANG to limit temperature fluctuations) or a small (e.g., for CCS to limit the energy penalty) heat capacity is sought after. It is thus important to understand how this property changes at different levels of loading and temperature

and to determine the factors influencing the heat capacity, which is now possible using our high-order PIMD scheme.

In the previous section, it has been shown that classical MD can—at least qualitatively—be used to model the structural response of MOF-5 in the presence of methane at various temperatures. This approach is however expected to fail for the description of the heat capacity since the heat capacity of most solids is dominated by NQEs at room temperature, as evidenced by experimental deviations from the classical Dulong-Petit law. The most common way of including NQEs for solids is the static harmonic approximation, using Einstein or Debye harmonic model for solids, which is usually able to reproduce the heat capacity semi-quantitatively and will therefore also be used for comparison.

We begin by presenting the estimates of the temperature dependence of the isobaric heat capacity of the empty MOF-5 framework. As shown in Figure 5, the classical MD estimates (dashed line) are in agreement with the Dulong-Petit law. The simulations yield an almost constant value of $3 k_B$ per degree of freedom, which indeed results in large deviations from the experimental values.^{12,13,81,82} Upon inclusion of NQEs with our PIMD scheme (solid line), we find that the results follow the experimental measurements reasonably well up to almost 400 K. This agreement is remarkable, as these measurements are typically carried out on the as-synthesized sample, which possibly includes solvents¹² and differs from the perfect crystal that we have simulated.

Figure 5 also reveals that the results obtained using the simple and computationally inexpensive harmonic approximation (dotted line) are in good agreement with the exact values computed with PIMD. This implies that anharmonic quantum contributions to the heat capacity and the effect of an adequate anharmonic sampling are small for the empty MOF. Moreover,

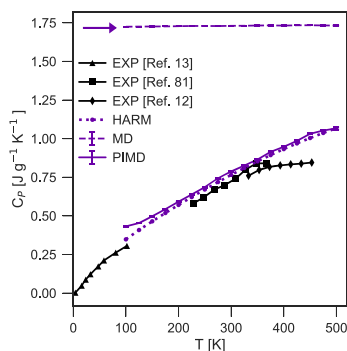


Figure 5. Heat capacity C_p of the empty MOF-5 as a function of temperature (T) computed using classical MD (dashed), PIMD (solid), and the harmonic approximation (dotted). The right pointing arrow shows the Dulong-Petit limit. Different experimental results are shown in black using triangular,¹³ square,⁸¹ and diamond¹² markers. Error bars indicate statistical uncertainty.

the harmonic approximation using the UFF4MOF force field⁸³ yields largely similar results (see SI Section S6.1), so that a less accurate and generic model for the potential energy surface is capable of reproducing the heat capacity of the empty framework.

Another notable detail of our calculations is that the harmonic approximation was used to estimate the isochoric heat capacity instead of the isobaric one. As the isobaric and isochoric heat capacities are almost the same, the MOF behaves like a regular solid, despite its large negative thermal expansion coefficient. The harmonic approximation could therefore serve as an efficient procedure to accurately estimate the heat capacity of the empty framework in the increasing number of high-throughput MOF screenings.^{9,84}

In order to study the effect of adsorbates, we start by considering the case of a loading x of 100 methane molecules per conventional unit cell ($8(\text{Zn}_4\text{O}(\text{CO}_2)_6) \cdot 100\text{CH}_4$). Contrary to the case of the empty framework, we could not find published experimental data for the heat capacity of the guest-loaded framework. Although a high-level PIMD strategy might

not be required to estimate the heat capacity of the empty MOF host, PIMD proves to be crucial to capture the correct temperature dependence of the loaded system, as can be seen in the left panel of Figure 6. Here, anharmonic effects become important as we observe differences between the PIMD results and the harmonic approximation. The discrepancy in the qualitative behavior of the heat capacity between both techniques can be understood through the mobility of the guest molecules in the large pores of the framework, which cannot be adequately captured by a harmonic approximation.⁸⁵ These low-frequency anharmonic motions explain why we find at the classical MD level a similar low-temperature dependence as in PIMD, but only PIMD simulations include both anharmonic and nuclear quantum effects correctly. Interestingly, the combination of both effects yields a heat capacity that does not change monotonically but exhibits a minimum at about 200 K.

Extending toward other loadings of methane in the middle panel of Figure 6, it becomes clear that the heat-capacity minimum as a function of temperature depends strongly on the number of guests and becomes more pronounced at higher loadings. Even when expressing the heat capacity normalized to the total mass of the system, one can see that at a fixed temperature C_p increases almost linearly with the loading (see Figure 6(c) at 300 K). For the volumetric heat capacity, i.e., the heat capacity per unit of volume of the system, similar results are obtained (see SI Section S6.4).

To rationalize the origin of the nonmonotonic temperature dependence of the heat capacity, we determine which interactions give the most substantial contribution to C_p . To this end, the force-field energy contributions are decomposed in terms of the host, host–guest, and guest–guest interactions (see SI Section S6.3). Figure 7 displays the most important results of this analysis. The host and guest–guest contributions to the specific heat capacity are visualized in panels (a) and (c). The shape of the different host curves appears to be independent of the loading. In fact, when rescaled to the mass of the empty MOF, the curves coincide with one another and with the curve obtained within the harmonic approximation. This demonstrates that the degrees of freedom of the MOF-5 framework, which are more strongly quantized, are predominantly harmonic and do not change significantly due to the interaction with methane. Their contribution to the total heat capacity per unit mass, however, decreases with the loading

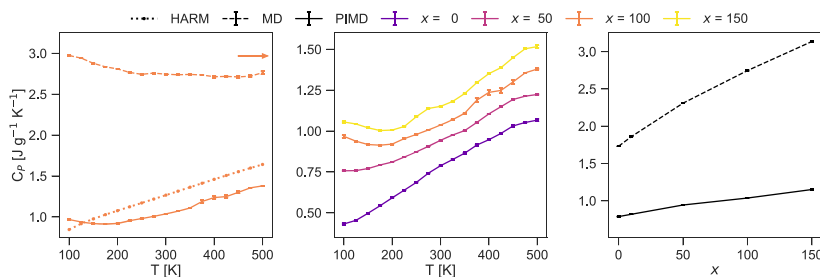


Figure 6. Panel (a) shows the comparison of the classical (dashed), quantum (solid), and harmonic estimates (dotted) of the isobaric heat capacity C_p of MOF-5 with 100 molecules of methane, as a function of the temperature T . Panel (b) shows the temperature dependence of the quantum isobaric heat capacity of MOF-5 with x molecules of methane. Panel (c) shows the quantum isobaric heat capacity of the MOF with x molecules of methane as a function of x at 300 K. Error bars indicate statistical uncertainty.

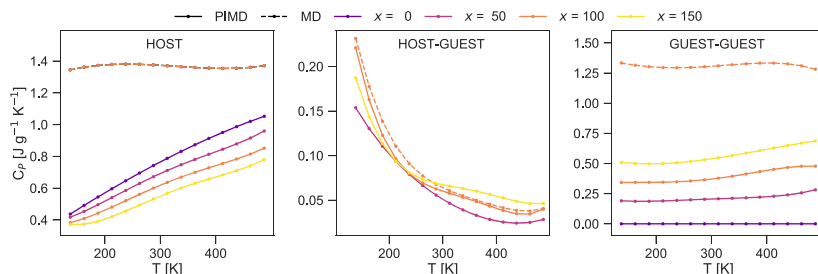


Figure 7. Panels (a), (b), and (c) respectively show the decomposition of the specific heat capacity of the MOF and the adsorbate system into host, host-guest, and guest-guest contributions for different gas loadings (x). The curves were obtained by deriving a polynomial fit to the energy as a function of temperature.

due to a change in the mass balance. The guest-guest interactions, on the other hand, are relatively constant and only show a small increase when going from 100 to 500 K, due to the activation of high-frequency vibrational modes. The most interesting contribution arises from the host-guest interactions, which explains the nonmonotonic behavior of the specific heat capacity of the guest-loaded system. The contribution of these interactions decreases with a sharp temperature dependence when sufficient guest molecules are present inside the pores. The large heat capacity at temperatures lower than 100 K originates from the known first-order structural phase transition of methane in MOF-5 at 60 K,^{86,87} from which we observe the decreasing tail. Since the methane molecules are more localized at low temperatures, the attractive host-guest interactions allow for efficiently storing thermal energy. At higher temperatures, from 250 to 500 K, the host-guest contributions become negligible as the confined guests become more mobile and less bound to the framework, so that the increase in thermal energy can no longer be stored in the physical interactions between the methane guests and the MOF-5 host.

Another decomposition of the force-field energy in terms of the covalent, electrostatic, and van der Waals interactions shows that the short-range covalent interactions and thus the network of chemical bonds (Figure 8) dominates the contributions to the heat capacity. For the empty MOF-5 framework, the noncovalent interactions are negligible (see SI Section S6.3). This confirms that the heat capacity of empty MOF-5 can be approximated by considering only contributions from the separate molecular fragments of the material¹² and suggests why the harmonic approximation works well for this material. For the loaded framework, the noncovalent part starts to play a role, which is especially true for the host-guest interactions. Not surprisingly, in the case of nonpolar methane molecules, these interactions are dominated by the van der Waals terms in the force field (see SI Section S6.3). This suggests that the use of different, more polar, guests in which electrostatic interactions play a more prominent role (e.g., CO₂) could give rise to other interesting phenomena. However, care must be taken in interpreting these different terms, as a separation is not unambiguously defined and might be force-field dependent. Nevertheless, simulations using a different force-field model for the guest-host and guest-guest interactions display the same qualitative behavior (see SI Section S6.5), suggesting that our conclusions are rather robust.

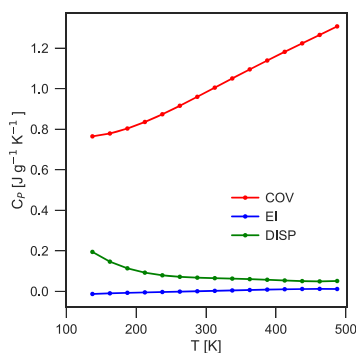


Figure 8. Decomposition of the total heat capacity of MOF-5 with 100 methane molecules per unit cell into covalent (COV), electrostatic (EI), and van der Waals (DISP) contributions. The curves were obtained by deriving a polynomial fit to the energy as a function of temperature.

4.3. The Interplay of Gas Loading, Anharmonicities, and Quantum Effects. Our analysis of the structural and thermal properties of methane-loaded MOF-5 shows that the total system does not always need a full treatment of anharmonicities and NQEs. This suggests that a full path integral sampling of the entire system may not be necessary, especially if qualitative trends are to be studied. Hence, inspired by our results, we propose an empirical formula for the volume and the heat capacity in which the most important effects, i.e., anharmonicities and/or NQEs, are captured and which might prove to be beneficial for future studies of guest-loaded MOFs.

As discussed above, the main difference between the volume with or without NQEs comes from zero-point effects in the lattice.²¹ The correct volume can therefore be estimated as follows

$$\mathcal{V} \approx \mathcal{V}_{\text{qn}}^{\text{anh}}[\text{MOF-5}] - \mathcal{V}_{\text{cl}}^{\text{anh}}[\text{MOF-5}] + \mathcal{V}_{\text{cl}}^{\text{anh}}[\text{MOF-5} + \text{CH}_4]$$

where anh stands for the inclusion of anharmonicities with MD, and cl and qn denote the use of classical or path integral MD, respectively. The left most panel of Figure 9 indicates that this approximate volume agrees very well with the exact results obtained from PIMD simulations. A more stringent test is the

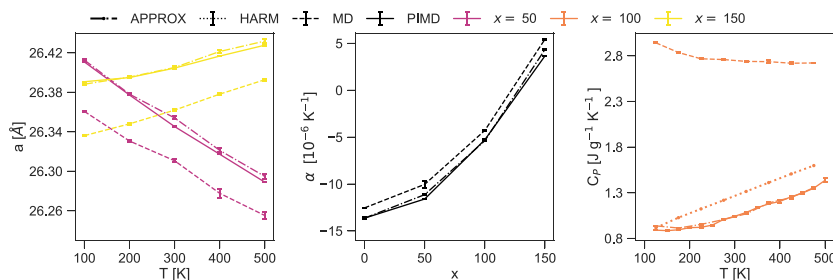


Figure 9. Panels (a), (b), and (c) respectively show the temperature dependence of the cell parameter (a) for MOF-5 with 50 and 150 molecules of methane, the linear thermal expansion coefficient α of MOF-5 as a function of methane loading x , and the isobaric heat capacity C_p of MOF-5 with 100 molecules of methane, obtained with classical MD (dashed), PIMD (solid), and the approximation introduced in the work (dot-dashed). Error bars indicate statistical uncertainty.

thermal expansion coefficient, which is—as shown in Figure 9(b)—also in excellent agreement with the PIMD results. For systems where a first-principles treatment of the potential energy surface is required and PIMD simulations are too expensive, other approximate techniques such as the quasi-harmonic approximation or classical MD with a quantum thermostat could be used to estimate the zero-point effects.²¹

In contrast, we observed in the previous section that the heat capacity of the framework could be estimated with a harmonic approximation, while the guest–host interactions are dominated by anharmonicities. For that reason, we propose

$$C \approx (C_{\text{qn}}^{\text{har}} - C_{\text{cl}}^{\text{har}} + C_{\text{cl}}^{\text{anh}})[\text{MOF-5} + \text{CH}_4]$$

in which the high frequency modes of adsorbate and the MOF are treated in a harmonic fashion and the host–guest interactions are treated classically. For $C_{\text{cl}}^{\text{har}}$, the Dulong-Petit law can be used. The proposed relation is analogous to similar corrections that are routinely used to compare the heat capacity obtained from classical simulations with experimental data.⁸⁸ As shown in the rightmost panel of Figure 9, this approximation works really well for this system and is even able to qualitatively reproduce the heat capacity minimum for a loading of 100 methane molecules. Beyond 200 K, the agreement between the empirical expression and the exact PIMD becomes quantitatively correct. This method could thus be an inexpensive route to estimate the heat capacity of guest-loaded MOFs.

5. CONCLUSIONS

To summarize, we developed an efficient and accurate methodology to calculate the isobaric thermophysical properties of materials, that is generally applicable and therefore ideally suited to the study of guest-loaded MOFs. For this purpose, we derived and implemented the necessary algorithms in i-PI⁴⁹ to perform simulations in the quantum isothermal–isobaric ensemble using the Suzuki-Chin path integral molecular dynamics framework. The method is rigorous and can be seamlessly combined with other cost-reduction techniques, which facilitates a huge reduction of the computational cost compared to standard techniques.

We demonstrated the applicability of our approach by investigating the heat capacity of the prototypical MOF-5 loaded with different numbers of methane molecules. We observed that the level of statistical sampling that is needed to

achieve quantitative accuracy depends on the property of interest. For all the cases we considered, we found the framework to behave in a strongly quantized manner but to be largely amenable to a harmonic treatment. The adsorbates, on the other hand, show only mild quantum effects in their intermolecular interactions but require a full anharmonic description. The heat capacity shows a particularly subtle interplay of quantum and anharmonic fluctuations, that results in a nonmonotonic temperature dependence of the heat capacity, with a minimum around 200 K.

Through a decomposition of the heat capacity into molecular interactions, we find that the host–guest interactions are responsible for this behavior, as their contribution to the total heat capacity decreases with temperature. By comparing the behavior of different classes of framework materials and guest molecules, this may reveal new design rules to optimize the thermal behavior of a storage material over a broad range of temperatures and levels of loading. Our approach provides an affordable route to perform benchmark studies and approximation strategies to carry out the high-throughput studies that are needed to obtain a complete understanding of the interplay between framework, adsorbate, and quantum mechanical and anharmonic fluctuations that determine the thermophysical properties of MOFs.

■ APPENDIX A: SUZUKI-CHIN FORCES AND VIRIALS

Recently, some of the present authors showed that the high-order force can be estimated in a finite difference fashion,²⁶ without computing the full Hessian (see SI Section S1.5)

$$\begin{aligned} \tilde{\mathbf{f}}^{(2j)} &= \omega_p^{-2} m^{-1} \frac{\partial}{\partial \mathbf{q}^{(2j)}} |\mathbf{f}^{(2j)}|^2 \\ &= -2\omega_p^{-2} \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon \delta} \left(\mathbf{f}^{(2j)}|_{\mathbf{q}^{(2j)} + \epsilon \delta \mathbf{u}^{(2j)}} - \mathbf{f}^{(2j)} \right) \end{aligned} \quad (8)$$

where $\mathbf{u}^{(2j)} = \mathbf{f}^{(2j)}/m$ and $\delta = \left[(3NP)^{-1} \sum_{j=1}^P \mathbf{u}^{(j)} \cdot \mathbf{u}^{(j)} \right]^{-1/2}$ is a normalization factor, so that ϵ represents the root-mean-square displacement applied to each atom. This avoids the explicit calculation of the Hessian and allows for the direct sampling of the Suzuki-Chin canonical ensemble. Following a similar strategy (see SI Section S1.6), we show that the high-order component of the virial can be estimated as

$$\begin{aligned} \mathbf{m}^{(2j)} &= \left[-\sum_{j=1}^N \mathbf{q}_i^{(2j)} \otimes \tilde{\mathbf{f}}_i^{(2j)} + \frac{\partial \tilde{V}(\mathbf{q}^{(2j)})}{\partial \mathbf{h}} \mathbf{h}^T \right] \\ &= -2\omega_p^{-2} \left[\sum_{j=1}^N \mathbf{f}_i^{(2j)} \otimes \mathbf{f}_i^{(2j)} / m \right. \\ &\quad \left. + \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon \delta} (\Xi^{(2j)}|_{\mathbf{q}+\epsilon\delta\mathbf{u}^{(2j)}} - \Xi^{(2j)}) \right] \end{aligned} \quad (9)$$

■ APPENDIX B: SUZUKI-CHIN ESTIMATORS

The operator (OP) and thermodynamic (TD) estimators of the energy for Suzuki-Chin isothermal–isobaric PIMD simulations of a single particle system, described in Section 2.4, are given by

$$\mathcal{E}^{\text{OP}} = \frac{3}{2\beta} + \frac{2}{P} \sum_{j=1}^{P/2} \left\langle -\frac{1}{2} (\mathbf{q}^{(2j-1)} - \bar{\mathbf{q}}) \cdot \mathbf{f}^{(2j-1)} \right\rangle + \frac{2}{P} \sum_{j=1}^{P/2} \langle V(\mathbf{q}^{(2j-1)}) \rangle \quad (10)$$

$$\begin{aligned} \mathcal{E}^{\text{TD}} &= \frac{3}{2\beta} + \frac{1}{P} \sum_{j=1}^P \left\langle -\frac{1}{2} (\mathbf{q}^{(j)} - \bar{\mathbf{q}}) \cdot \mathbf{f}^{\text{sc}(j)} \right\rangle \\ &\quad + \frac{1}{P} \sum_{j=1}^{P/2} \left\langle \frac{3}{9} \tilde{V}(\mathbf{q}^{(2j)}) \right\rangle + \frac{1}{P} \sum_{j=1}^P \langle w_j V(\mathbf{q}^{(j)}) \rangle \end{aligned} \quad (11)$$

where $\bar{\mathbf{q}} \equiv \frac{1}{P} \sum_{j=1}^P \mathbf{q}^{(j)}$ is the position of the centroid, $\mathbf{f}^{\text{sc}(j)} \equiv -\partial V^{\text{sc}}(\mathbf{q}^{(j)})/\partial \mathbf{q}^{(j)}$ is the total Suzuki-Chin force, and $\langle \cdot \rangle$ denotes a thermodynamic average over the quantum isothermal–isobaric ensemble. The generalization to a many particle system is straightforward. The $\square = \text{OP}$ or $\square = \text{TD}$ estimators of the enthalpy are obtained through the simple expression:

$$\mathcal{H}^{\square} = \mathcal{E}^{\square} + \mathcal{P} \langle V \rangle \quad (12)$$

The $\square = \text{OP}$ or $\square = \text{TD}$ (that we will refer to as the Yamamoto estimator⁴⁷) double virial estimators of the heat capacity take the following form

$$\frac{C_p^{\square}}{k_B \beta^2} = \text{Cov}[\mathcal{H}^{\square}, \mathcal{H}^{\text{TD}}] + \mathcal{E}^{\square'} \quad (13)$$

where $\mathcal{E}^{\square'}$ for $\square = \text{TD}$ is given in ref 47 and

$$\mathcal{E}^{\text{OP}'} = \frac{3N}{2\beta^2} + \frac{1}{\beta P} \sum_{j=1}^{P/2} \langle ((\mathbf{q}^{(2j-1)} - \bar{\mathbf{q}}) \cdot \mathbf{f}_{\text{dcv}}^{(2j-1)}) \rangle \quad (14)$$

The double virial force $\mathbf{f}_{\text{dcv}}^{(2j-1)}$, which depends on the Hessian of the physical potential, can be estimated in a computationally efficient way by finite differences:

$$\mathbf{f}_{\text{dcv}}^{(j)} = \frac{3}{2} \mathbf{f}^{(j)} + \lim_{\epsilon \rightarrow 0} \frac{1}{2\epsilon} [\mathbf{f}^{(j)}|_{\mathbf{q}^{(j)}+\epsilon(\mathbf{q}^{(j)}-\bar{\mathbf{q}})} - \mathbf{f}^{(j)}] \quad (15)$$

We tested this estimator on the well-known isobaric heat capacity of liquid water which is 1 cal mol⁻¹ K⁻¹ or 9 k_B per molecule at 300 K. The water molecules are modeled with the q-TIP4P/f force field,⁸⁹ and the heat capacity is estimated with SC PIMD using the aforementioned estimators. As shown in Figure 10, both estimators converge to the same value and are in excellent agreement with the experiments. More impor-

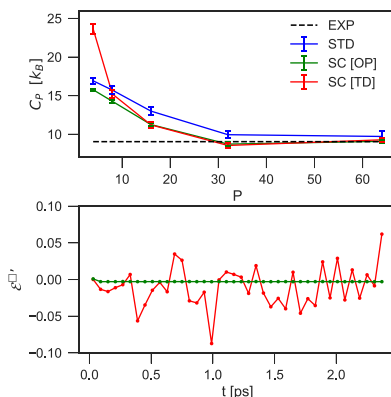


Figure 10. Top panel shows the convergence of the isobaric heat capacity of liquid water at 300 K, modeled by the q-TIP4P/f potential, as a function of the number of replicas. The blue curve was obtained from standard PIMD using the Yamamoto estimator, while the red and green curves were obtained from SC PIMD using the Yamamoto (TD) and OP estimator, respectively. The dashed black line represents the experimental result. Error bars indicate statistical uncertainty. The bottom panel shows instantaneous values of the computationally expensive $\mathcal{E}^{\square'}$ term when computed with the OP and the Yamamoto (TD) estimator.

tantly, however, the variance of the computationally expensive $\mathcal{E}^{\square'}$ term with the OP method is almost two orders of magnitude smaller than with the Yamamoto estimator. The OP estimator also only requires one-fourth of the number of force evaluations than its Yamamoto counterpart and should therefore always be preferred.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.8b01297.

Derivation of Suzuki-Chin partition functions, forces, virials, and total stress; equations of motion and integration schemes for sampling isothermal–isobaric ensemble; derivation of heat capacity estimators; details of generation and validation of first-principles force field; temperature dependence of adsorption isotherms for methane; formula of the harmonic heat capacity; comparison of different barostats; decomposition of total heat capacity into contributions from different physical interactions; temperature dependence of volumetric heat capacity and comparison of host–guest interactions for a different force field (PDF)

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Funding

We acknowledge financial support by the Swiss National Science Foundation (project ID 200021-159896), the Fund for Scientific Research Flanders (FWO), the Research Board of Ghent University, and the European Union's Horizon 2020 research and innovation programme (consolidator ERC grant agreement No. 647755-DYNPOR (2015-2020)). The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by Ghent University, FWO, and the Flemish Government department EWI.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We also want to acknowledge F. Giberti, R. Semino, S. M. J. Rogge, and L. Vanduyfhuys for their valuable input and discussions.

REFERENCES

- (1) Slater, A. G.; Cooper, A. I. Function-led design of new porous materials. *Science* **2015**, *348*, aaa8075.
- (2) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, 1230444.
- (3) Mason, J. A.; Veenstra, M.; Long, J. R. Evaluating metal-organic frameworks for natural gas storage. *Chem. Sci.* **2014**, *5*, 32–51.
- (4) He, Y.; Chen, F.; Li, B.; Qian, G.; Zhou, W.; Chen, B. Porous metal-organic frameworks for fuel storage. *Coord. Chem. Rev.* **2018**, *373*, 167–198.
- (5) de Lange, M. F.; Verouden, K. J. F. M.; Vlucht, T. J. H.; Gascon, J.; Kapteijn, F. Adsorption-Driven Heat Pumps: The Potential of Metal-Organic Frameworks. *Chem. Rev.* **2015**, *115*, 12205–12250.
- (6) Wang, S.; Lee, J. S.; Wahiduzzaman, M.; Park, J.; Muschi, M.; Martineau-Corcios, C.; Tissot, A.; Cho, K. H.; Marrot, J.; Shepard, W.; Maurin, G.; Chang, J.-S.; Serre, C. A robust large-pore zirconium carboxylate metal-organic framework for energy-efficient water-sorption-driven refrigeration. *Nat. Energy* **2018**, *3*, 985–993.
- (7) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781.
- (8) Trickett, C. A.; Helal, A.; Al-Maythaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The chemistry of metal-organic frameworks for CO₂ capture, regeneration and conversion. *Nat. Rev. Mater.* **2017**, *2*, 17045.
- (9) Simon, C. M.; Kim, J.; Gomez-Gualdron, D. A.; Camp, J. S.; Chung, Y. G.; Martin, R. L.; Mercado, R.; Deem, M. W.; Gunter, D.; Haranczyk, M.; Sholl, D. S.; Snurr, R. Q.; Smit, B. The materials genome in action: identifying the performance limits for methane storage. *Energy Environ. Sci.* **2015**, *8*, 1190–1199.
- (10) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. L.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; Llewellyn, P. L.; Masciocchi, N.; Long, J. R. Methane storage in flexible metal-organic frameworks with intrinsic thermal management. *Nature* **2015**, *527*, 357–361.
- (11) Huck, J. M.; Lin, L.-C.; Berger, A. H.; Shahrak, M. N.; Martin, R. L.; Bhowan, A. S.; Haranczyk, M.; Reuter, K.; Smit, B. Evaluating different classes of porous materials for carbon capture. *Energy Environ. Sci.* **2014**, *7*, 4132–4146.
- (12) Mu, B.; Walton, K. S. Thermal Analysis and Heat Capacity Study of Metal-Organic Frameworks. *J. Phys. Chem. C* **2011**, *115*, 22748–22754.
- (13) Kloutse, F. A.; Zacharia, R.; Cossement, D.; Chahine, R. Specific heat capacities of MOF-5, Cu-BTC, Fe-BTC, MOF-177 and MIL-53(Al) over wide temperature ranges: Measurements and application of empirical group contribution method. *Microporous Mesoporous Mater.* **2015**, *217*, 1–5.
- (14) Babaei, H.; Wilmer, C. E. Mechanisms of Heat Transfer in Porous Crystals Containing Adsorbed Gases: Applications to Metal-Organic Frameworks. *Phys. Rev. Lett.* **2016**, *116*, 025902.
- (15) Balestra, S. R. G.; Bueno-Perez, R.; Hamad, S.; Dubbeldam, D.; Ruiz-Salvador, A. R.; Calero, S. Controlling Thermal Expansion: A Metal-Organic Frameworks Route. *Chem. Mater.* **2016**, *28*, 8296–8304.
- (16) Rogge, S. M. J.; Vanduyfhuys, L.; Ghysels, A.; Waroquier, M.; Verstraeten, T.; Maurin, G.; Van Speybroeck, V. A Comparison of Barostats for the Mechanical Characterization of Metal-Organic Frameworks. *J. Chem. Theory Comput.* **2015**, *11*, 5583–5597.
- (17) Vanduyfhuys, L.; Rogge, S. M. J.; Wieme, J.; Vandenbrande, S.; Maurin, G.; Waroquier, M.; Van Speybroeck, V. Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals. *Nat. Commun.* **2018**, *9*, 204.
- (18) Wieme, J.; Lejaeghere, K.; Kresse, G.; Van Speybroeck, V. Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks. *Nat. Commun.* **2018**, *9*, 4899.
- (19) Paesani, F. Water in metal-organic frameworks: structure and diffusion of H₂O in MIL-53(Cr) from quantum simulations. *Mol. Simul.* **2012**, *38*, 631–641.
- (20) Borges, D. D.; Semino, R.; Devautour-Vinot, S.; Jobic, H.; Paesani, F.; Maurin, G. Computational Exploration of the Water Concentration Dependence of the Proton Transport in the Porous UiO-66(Zr)-(CO₂H)₂ Metal-Organic Framework. *Chem. Mater.* **2017**, *29*, 1569–1576.
- (21) Lamaire, A.; Wieme, J.; Rogge, S. M. J.; Waroquier, M.; Van Speybroeck, V. On the importance of anharmonicities and nuclear quantum effects in modelling the structural properties and thermal expansion in MOF-5. *J. Chem. Phys.* **2019**, *150*, 094503.
- (22) Parrinello, M.; Rahman, A. Study of an F center in molten KCl. *J. Chem. Phys.* **1984**, *80*, 860.
- (23) Chandler, D.; Wolynes, P. G. Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids. *J. Chem. Phys.* **1981**, *74*, 4078–4095.
- (24) Jang, S.; Jang, S.; Voth, G. A. Applications of higher order composite factorization schemes in imaginary time path integral simulations. *J. Chem. Phys.* **2001**, *115*, 7832–7842.
- (25) Ceriotti, M.; Manolopoulos, D. E. Efficient First-Principles Calculation of the Quantum Kinetic Energy and Momentum Distribution of Nuclei. *Phys. Rev. Lett.* **2012**, *109*, 100604.
- (26) Kapil, V.; Behler, J.; Ceriotti, M. High order path integrals made easy. *J. Chem. Phys.* **2016**, *145*, 234103.
- (27) Markland, T. E.; Manolopoulos, D. E. An efficient ring polymer contraction scheme for imaginary time path integral simulations. *J. Chem. Phys.* **2008**, *129*, 024105.
- (28) Kapil, V.; VandeVondele, J.; Ceriotti, M. Accurate molecular dynamics and nuclear quantum effects at low cost by multiple steps in real and imaginary time: Using density functional theory to accelerate wavefunction methods. *J. Chem. Phys.* **2016**, *144*, 054111.
- (29) Poltavsky, I.; Tkatchenko, A. Modeling quantum nuclei with perturbed path integral molecular dynamics. *Chem. Sci.* **2016**, *7*, 1368–1372.
- (30) Markland, T. E.; Ceriotti, M. Nuclear quantum effects enter the mainstream. *Nat. Rev. Chem.* **2018**, *2*, 0109.
- (31) Martyna, G. J.; Hughes, A.; Tuckerman, M. E. Molecular dynamics algorithms for path integrals at constant pressure. *J. Chem. Phys.* **1999**, *110*, 3275.
- (32) Ceriotti, M.; More, J.; Manolopoulos, D. E. i-PI: A Python interface for ab initio path integral molecular dynamics simulations. *Comput. Phys. Commun.* **2014**, *185*, 1019–1026.
- (33) Vanduyfhuys, L.; Vandenbrande, S.; Verstraeten, T.; Schmid, R.; Waroquier, M.; Van Speybroeck, V. QuickFF: A program for a

quick and easy derivation of force fields for metal-organic frameworks from ab initio input. *J. Comput. Chem.* **2015**, *36*, 1015–1027.

(34) Vanduyfhuys, L.; Vandenbrande, S.; Wieme, J.; Waroquier, M.; Verstraeten, T.; Van Speybroeck, V. Extension of the QuickFF force field protocol for an improved accuracy of structural, vibrational, mechanical and thermal properties of metal-organic frameworks. *J. Comput. Chem.* **2018**, *39*, 999–1011.

(35) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279.

(36) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* **2002**, *295*, 469–472.

(37) Zhou, W.; Wu, H.; Hartman, M. R.; Yildirim, T. Hydrogen and methane adsorption in metal-organic frameworks: A high-pressure volumetric study. *J. Phys. Chem. C* **2007**, *111*, 16131–16137.

(38) Vandenbrande, S.; Verstraeten, T.; Gutiérrez-Sevillano, J. J.; Waroquier, M.; Van Speybroeck, V. Methane adsorption in Zr-based MOFs: Comparison and critical evaluation of force fields. *J. Phys. Chem. C* **2017**, *121*, 25309–25322.

(39) Martyna, G. J.; Tobias, D. J.; Klein, M. L. Constant pressure molecular dynamics algorithms. *J. Chem. Phys.* **1994**, *101*, 4177.

(40) Shiga, M.; Shinoda, W. Calculation of heat capacities of light and heavy water by path-integral molecular dynamics. *J. Chem. Phys.* **2005**, *123*, 134502.

(41) Takahashi, M.; Imada, M. Monte Carlo calculation of quantum systems. II. Higher order correction. *J. Phys. Soc. Jpn.* **1984**, *53*, 3765–3769.

(42) Chin, S. A. Symplectic integrators from composite operator factorizations. *Phys. Lett. A* **1997**, *226*, 344–348.

(43) The standard fourth-order Suzuki-Chin Splitting contains an α parameter which can be used to share the high order term between odd and even beads. In this case we have set it to zero so that the high order term is evaluated only on the even beads reducing the computational cost by a factor of 2.

(44) Suzuki, M. Hybrid exponential product formulas for unbounded operators with possible applications to Monte Carlo simulations. *Phys. Lett. A* **1995**, *201*, 425–428.

(45) Brain, G. *Higher Order Propagators in Path Integral Molecular Dynamics*. Ph.D. thesis, Part II Chemistry Thesis, Oxford University, 2011.

(46) Pérez, A.; Tuckerman, M. E. Improving the convergence of closed and open path integral molecular dynamics via higher order Trotter factorization schemes. *J. Chem. Phys.* **2011**, *135*, 064104.

(47) Yamamoto, T. M. Path-integral virial estimator based on the scaling of fluctuation coordinates: Application to quantum clusters with fourth-order propagators. *J. Chem. Phys.* **2005**, *123*, 104101.

(48) Ceriotti, M.; Brain, G. A. R.; Riordan, O.; Manolopoulos, D. E. The inefficiency of re-weighted sampling and the curse of system size in high order path integration. *Proc. R. Soc. London, Ser. A* **2012**, *468*, 2–17.

(49) Kapil, P.; Rossi, M.; Marsalek, O.; Petraglia, R.; Litman, Y.; Spura, T.; Cheng, B.; Cuzzocrea, A.; Meißner, R. H.; Wilkins, D. M.; Juda, P.; Bienvenue, S. P.; Fang, W.; Kessler, J.; Poltavsky, I.; Vandenbrande, S.; Wieme, J.; Corminboeuf, C.; Kühne, T. D.; Manolopoulos, D. E.; Markland, T. E.; Richardson, J. O.; Tkatchenko, A.; Tribello, G. A.; Speybroeck, V. V.; Ceriotti, M. i-PI 2.0: A universal force engine for advanced molecular simulations. *Comput. Phys. Commun.* **2019**, *236*, 214–223.

(50) Tuckerman, M.; Berne, B. J.; Martyna, G. J. Reversible multiple time scale molecular dynamics. *J. Chem. Phys.* **1992**, *97*, 1990.

(51) Leimkuhler, B.; Matthews, C. Robust and efficient configurational molecular sampling via Langevin dynamics. *J. Chem. Phys.* **2013**, *138*, 174102.

(52) Poltavsky, I.; DiStasio, R. A., Jr.; Tkatchenko, A. Perturbed path integrals in imaginary time: Efficiently modeling nuclear quantum effects in molecules and materials. *J. Chem. Phys.* **2018**, *148*, 102325.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian16*, Revision B.01; Gaussian Inc.: Wallingford, CT, 2016.

(54) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(55) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 20. Basis Set for Correlated wave-Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.

(56) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270.

(57) Verstraeten, T.; Vandenbrande, S.; Heidari-Zadeh, F.; Vanduyfhuys, L.; Van Speybroeck, V.; Waroquier, M.; Ayers, P. W. Minimal Basis Iterative Stockholder: Atoms in molecules for force-field development. *J. Chem. Theory Comput.* **2016**, *12*, 3894–3912.

(58) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(59) Mortensen, J. J.; Hansen, L. B.; Jacobsen, K. W. Real-space grid implementation of the projector augmented wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 035109.

(60) Lü, J. H.; Allinger, N. L. Molecular mechanics. The MM3 force field for hydrocarbons. 3. The van der Waals Potentials and crystal data for aliphatic and aromatic hydrocarbons. *J. Am. Chem. Soc.* **1989**, *111*, 8576–8582.

(61) Allinger, N. L.; Zhou, X.; Bergsma, J. Molecular mechanics parameters. *J. Mol. Struct.: THEOCHEM* **1994**, *312*, 69–83.

(62) Sun, H. COMPASS: An ab initio force-field optimized for condensed-phase applications - Overview with details on alkane and benzene compounds. *J. Phys. Chem. B* **1998**, *102*, 7338–7364.

(63) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials. *Mol. Simul.* **2016**, *42*, 81–101.

(64) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.

(65) Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.* **1984**, *52*, 255–268.

(66) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A: At, Mol, Opt. Phys.* **1985**, *31*, 1695–1697.

(67) Martyna, G. J.; Klein, M. L.; Tuckerman, M. Nose-Hoover Chains - the Canonical Ensemble Via Continuous Dynamics. *J. Chem. Phys.* **1992**, *97*, 2635–2643.

(68) Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. Explicit reversible integrators for extended systems dynamics. *Mol. Phys.* **1996**, *87*, 1117–1157.

(69) Ceriotti, M.; Parrinello, M.; Markland, T. E.; Manolopoulos, D. E. Efficient stochastic thermostatting of path integral molecular dynamics. *J. Chem. Phys.* **2010**, *133*, 124104.

(70) Bussi, G.; Parrinello, M. Accurate sampling using Langevin dynamics. *Phys. Rev. E* **2007**, *75*, 067007.

(71) Bussi, G.; Zykova-Timan, T.; Parrinello, M. Isothermal-isobaric molecular dynamics using stochastic velocity rescaling. *J. Chem. Phys.* **2009**, *130*, 074101.

(72) Balog, E.; Hughes, A. L.; Martyna, G. J. Constant pressure path integral molecular dynamics studies of quantum effects in the liquid state properties of n-alkanes. *J. Chem. Phys.* **2000**, *112*, 870–880.

- (73) Pereyaslavets, L.; Kurnikov, I.; Kamath, G.; Butin, O.; Illarionov, A.; Leontyev, I.; Olevanov, M.; Levitt, M.; Kornberg, R. D.; Fain, B. On the importance of accounting for nuclear quantum effects in ab initio calibrated force fields in biological simulations. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 8878–8882.
- (74) Veit, M.; Jain, S. K.; Bonakala, S.; Rudra, I.; Hohl, D.; Csányi, G. Equation of state of fluid methane from first principles with machine learning potentials. *J. Chem. Theory Comput.* **2019**, *15*, 2574–2586.
- (75) Ravikovitch, P. I.; Neimark, A. V. Density Functional Theory Model of Adsorption Deformation. *Langmuir* **2006**, *22*, 10864–10868.
- (76) Joo, J.; Kim, H.; Han, S. S. Volume shrinkage of a metal-organic framework host induced by the dispersive attraction of guest gas molecules. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18822–18826.
- (77) Zhou, W.; Wu, H.; Yildirim, T.; Simpson, J. R.; Hight Walker, A. R. Origin of the exceptional negative thermal expansion in metal-organic framework-5 $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78*, 054114.
- (78) Lock, N.; Wu, Y.; Christensen, M.; Cameron, L. J.; Peterson, V. K.; Bridgeman, A. J.; Kepert, C. J.; Iversen, B. B. Elucidating Negative Thermal Expansion in MOF-5. *J. Phys. Chem. C* **2010**, *114*, 16181–16186.
- (79) Lock, N.; Christensen, M.; Wu, Y.; Peterson, V. K.; Thomsen, M. K.; Plitz, R. O.; Ramirez-Cuesta, A. J.; McIntyre, G. J.; Norén, K.; Kutteh, R.; Kepert, C. J.; Kearley, G. J.; Iversen, B. B. Scrutinizing negative thermal expansion in MOF-5 by scattering techniques and ab initio calculations. *Dalton Trans* **2013**, *42*, 1996–2007.
- (80) A 10% increase in volume due to NQEs, assuming the molecules to be spherical, is associated with a $(1.10)^{1/3}$ times increase in the effective radius. The classical “radius” is close to 4 Å, and thus the increase in the intermolecular distance due to NQEs coming from the isotropic expansion of the gas is $(1.10)^{1/3} \times 4 - 4 \approx 0.13$ Å.
- (81) Ming, Y.; Purewal, J.; Liu, D.; Sudik, A.; Xu, C.; Yang, J.; Veenstra, M.; Rhodes, K.; Soltis, R.; Warner, J.; Gaab, M.; Müller, U.; Siegel, D. J. Thermophysical properties of MOF-5 powders. *Microporous Mesoporous Mater.* **2014**, *185*, 235–244.
- (82) Liu, D.; Purewal, J. J.; Yang, J.; Sudik, A.; Maurer, S.; Müller, U.; Ni, J.; Siegel, D. J. MOF-5 composites exhibiting improved thermal conductivity. *Int. J. Hydrogen Energy* **2012**, *37*, 6109–6117.
- (83) Addicoat, M. A.; Vankova, N.; Akter, I. F.; Heine, T. Extension of the Universal Force Field to metal-organic frameworks. *J. Chem. Theory Comput.* **2014**, *10*, 880–891.
- (84) Tabor, D. P.; Roch, L. M.; Saikin, S. K.; Kreisbeck, C.; Sheberla, D.; Montoya, J. H.; Dwaraknath, S.; Aykol, M.; Ortiz, C.; Tribukait, H.; Amador-Bedolla, C.; Brabec, C. J.; Maruyama, B.; Persson, K. A.; Aspuru-Guzik, A. Accelerating the discovery of materials for clean energy in the era of smart automation. *Nat. Rev. Mater.* **2018**, *3*, 5–20.
- (85) Tsivion, E.; Head-Gordon, M. Methane storage: molecular mechanisms underlying room-temperature adsorption in $\text{Zn}_4\text{O}(\text{BDC})_3$ (MOF-5). *J. Phys. Chem. C* **2017**, *121*, 12091–12100.
- (86) Wu, H.; Zhou, W.; Yildirim, T. Methane sorption in nanoporous metal-organic frameworks and first-order phase transition of confined methane. *J. Phys. Chem. C* **2009**, *113*, 3029–3035.
- (87) Kuchta, B.; Dundar, E.; Formalik, F.; Llewellyn, P. L.; Firlej, L. Adsorption-Induced Structural Phase Transformation in Nanopores. *Angew. Chem., Int. Ed.* **2017**, *56*, 16243–16246.
- (88) Levitt, M.; Hirshberg, M.; Sharon, R.; Laidig, K. E.; Daggett, V. Calibration and Testing of a Water Model for Simulation of the Molecular Dynamics of Proteins and Nucleic Acids in Solution. *J. Phys. Chem. B* **1997**, *101*, S051–S061.
- (89) Habershon, S.; Markland, T. E.; Manolopoulos, D. E. Competing quantum effects in the dynamics of a flexible water model. *J. Chem. Phys.* **2009**, *131*, 024501.

Paper IX

**Pillared-layered metal-organic frameworks for
mechanical energy storage applications**

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Journal of Materials Chemistry A, **2019**, 7, 22663-22674

J. Wieme performed DFT and force field simulations, interpreted the results and wrote the manuscript.

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Cite this: *J. Mater. Chem. A*, 2019, **7**, 22663
Accepted 19th August 2019

Received 11th February 2019
Accepted 19th August 2019

DOI: 10.1039/c9ta01586h

rsc.li/materials-a

Pillared-layered metal–organic frameworks for mechanical energy storage applications†

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Herein we explore the unique potential of pillared-layered metal–organic frameworks of the DMOF-1 family for mechanical energy storage applications. In this work, we theoretically predict for the guest-free DMOF-1 a new contracted phase by exerting an external mechanical pressure of more than 200 MPa with respect to the stable phase at atmospheric pressure. The breathing transition is accompanied by a very large volume contraction of about 40%. The high transition pressures and associated volume changes make these materials highly promising with an outstanding mechanical energy work. Furthermore, we show that changing the nature of the metal allows to tune the behavior under mechanical pressure. The various phases were revealed by a combination of periodic density-functional theory calculations, force field molecular dynamics simulations and mercury intrusion experiments for DMOF-1(Zn) and DMOF-1(Cu). The combined experimental and theoretical approach allowed to discover the potential of these materials for new technological developments.

1 Introduction

The exceptional flexibility displayed by breathing metal–organic frameworks (MOFs) has attracted much attention over the past few years.^{1–5} Such materials – belonging to the class of soft porous crystals² – feature an enormous shift in volume upon external stimuli without breaking chemical bonds. Various triggers such as temperature, pressure and guest adsorption have been used to initiate a breathing transition in a limited number of frameworks (e.g. ref. 6–9). The drastic change of the volume accompanying the breathing transition makes these peculiar materials extremely enticing for a large variety of applications such as gas storage, separation and detection,^{10–12} controlled drug release¹³ and mechanical energy storage.^{14,15}

Given these remarkable properties, extensive efforts have also been spent to unravel the origin of flexibility from a theoretical point of view. Some of us recently showed that fundamental insight into the macroscopic conditions at which MOFs display

flexibility can be gained through knowledge of the thermodynamic potential.⁵ However, despite the enormous progress made in recent years, the automated, computer-aided detection of flexible materials is still very challenging.^{16,17} For other properties such as gas storage and separation, high-throughput screening allowed to identify new structures that outperform the current materials (e.g. ref. 18–20), but most computational studies on flexible materials still tend to focus only on understanding the flexibility of specific case studies (e.g. ref. 21–27).

In this study, we investigate the dehydrated DMOF-1 framework^{28,29} with either copper or zinc at the metal nodes belonging to the subclass of pillared-layered MOFs.^{30,31} This class of hybrid porous materials has already demonstrated to be an excellent testing platform for flexible behavior with a high tunability of physical and chemical properties through standard MOF synthesis routes such as functionalization or substitution of the metal and/or organic ligand. In DMOF-1, the two-dimensional layers are formed by paddle wheels composed of divalent metal cations, which are bridged by 1,4-benzenedicarboxylate (BDC) organic linkers (Fig. 1). The layers are connected through 1,4-diazabicyclo[2.2.2]octane (DABCO) pillar ligands via the axial sites of the paddle wheels. This material has been synthesized with various types of metal ions (Fe,³² Co,^{33,34} Ni,^{35,36} Cu,²⁸ Zn²⁹) and mixed-metal variants exist.³⁷ While theoretical investigations of DMOF-1 are relatively limited,^{5,17,21,38,39} the unusual and reversible breathing behavior has been highlighted by several experimental groups.^{29,40–54} On the one hand, with guests present in the pores, DMOF-1(Zn) was found to contract upon adsorption. Specific guest molecules

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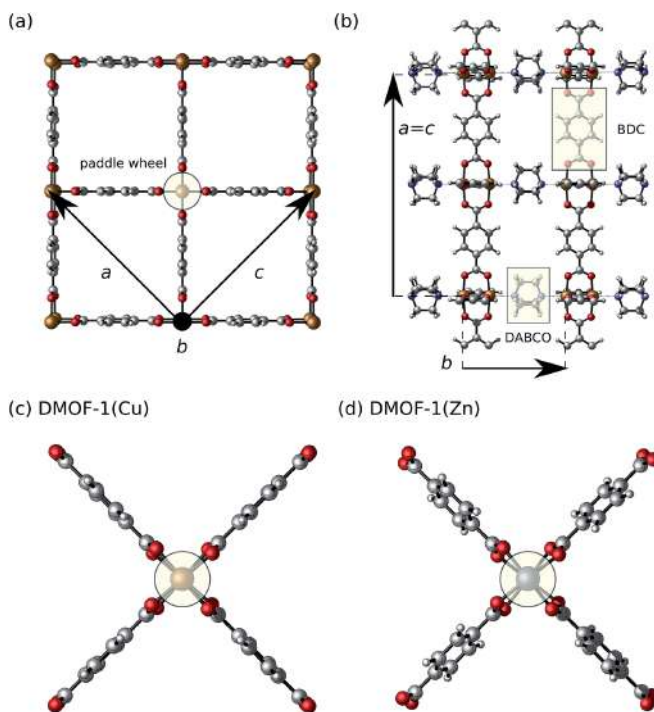


Fig. 1 Molecular representation of the open-pore phase of DMOF-1 and its building blocks (paddle wheel, 1,4-benzenedicarboxylate (BDC) and 1,4-diazabicyclo[2.2.2]octane (DABCO)). The definition of the unit cell parameters is indicated. (a) Two-dimensional layer formed by paddle wheels connected through BDC organic linkers. The a and c lattice vectors are aligned along the diagonals of the pores. (b) The connection of the two-dimensional layers through DABCO pillar ligands along the b -direction. (c and d) Paddle wheel present in the equilibrium unit cell of (c) DMOF-1(Cu) and (d) DMOF-1(Zn), obtained at the PBE + D3(BJ) level of theory at 0 K.

such as benzene, methanol, ethanol and isopropanol (IPA) trigger breathing,^{29,40,42,50} while N,N -dimethylformamide (DMF) distorts the structure in a different way.^{29,50} Nevertheless, this material is rather weakly responsive to most guests. On the other hand, no temperature-induced breathing transitions have been reported for this jungle-gym-type framework. Kim *et al.* did find that the Zn variant displays a slight anisotropic negative thermal expansion between 150 K and 298 K with a symmetry group change at low temperatures.⁵⁰ The thermo-responsive and guest-dependent behavior of DMOF-1 – especially for the Zn variant – can thus be considered well-studied from an experimental point of view. More interestingly, enormous thermal expansion behavior and breathing transitions could be obtained when functionalizing the BDC linker.^{39,48,51,53} Particularly, the attachment of pendant alkoxy chains greatly modified the structural flexibility. Functionalization also allowed to influence the guest-dependent behavior.^{41–44,47,49,51,52} Very recently, Fischer and co-workers discussed into detail the significant impact of the metal ion on the breathing mechanisms in a functionalized DMOF-1.⁵³ Previous studies highlighted how the threshold gas pressure and transition

temperature for the breathing transition can be tuned by the choice of the functional groups and metal ion. So far the response of this MOF upon mechanical pressure has barely been investigated.^{5,55–57}

Therefore, we want to further explore the potential of these highly tailorable frameworks for mechanical energy storage. To this end, we examined the pressure-induced flexibility of empty DMOF-1(Zn) and DMOF-1(Cu) through a combination of theoretical and experimental techniques. Using first-principles and force field simulations, we predict a breathing transition for both prototypical pillared-layered materials with very appealing features such as a high transition pressure and a massive volume contraction. Subsequently, to validate these theoretical findings, mercury intrusion experiments have been accomplished on both variants. This technique was originally used to detect pressure-induced structural transitions in several wine-rack MOFs,^{5,14,15,58–61} and it has been applied to characterize the structural transitions in other flexible frameworks such as ZIF-4 (ref. 62) and DUT-48/49.⁶³ The experiments confirmed some of the interesting features found by theory. This study highlights the complementary power of theory and experiment

to unravel the behavior of flexible MOFs for promising technological applications.

2 Methods

2.1 Theory/computational details

DMOF-1 was investigated using two types of simulation strategies, namely periodic density-functional theory (DFT) calculations and force field simulations which allow to simulate at realistic conditions of pressure and temperature. The periodic plane-waves DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP)⁶⁴ using the projector-augmented wave (PAW) method.⁶⁵ We used the PBE⁶⁶ exchange–correlation functional combined with the DFT-D3 dispersion scheme using Becke–Johnson damping.^{67,68} We recently showed that PBE + D3(BJ)^{ATM} resulted in the best agreement with a high-level many-electron treatment for an energy profile as a function of the volume for a breathing MOF.²⁵ Therefore, we added three-body Axilrod–Teller–Muto (ATM) contributions^{69,70} (D3(BJ)^{ATM}) to the energy with the DFT-D3 program as they have not yet been implemented in VASP. The energy profile as a function of the volume was constructed by fixed-volume relaxations in which the atomic positions and cell shape were optimized.^{15,71} We also calculated the dynamical matrix at the Γ -point for the stable open-pore phase of DMOF-1(Zn). More technical details on the DFT simulations can be found in the ESI.†

For the force field simulations, a new force field was derived from the dynamical matrix with QuickFF^{72,73} for DMOF-1(Zn) including covalent, electrostatic and van der Waals interactions. The covalent interactions were fitted with QuickFF and include anharmonic bond and bend terms, out-of-plane terms, dihedral terms, and cross terms. The electrostatic interactions are modeled with Gaussian smeared MBIS⁷⁴ point charges, which were derived with Horton.⁷⁵ The MM3-Buckingham potential^{76,77} is used to model the van der Waals interactions. The force field parameters and detailed force field energy expression are included in the ESI Section II.† The force field is able to qualitatively describe the flexibility of DMOF-1(Zn) under mechanical pressure. An exact quantitative correspondence between the DFT and the force field energy curves at 0 K is very challenging. First, the force field only includes pairwise dispersion interactions and therefore lacks potentially important many-body dispersion effects at low volumes included in our DFT results.²⁵ Furthermore, the force field was fitted on the open-pore phase of DMOF-1(Zn) and is intrinsically less accurate for anharmonic atomic displacements in the low-volume region. A more detailed comparison and validation is taken up in the ESI (Section II.B†). The DMOF-1(Zn) force field was used to perform molecular dynamics (MD) simulations with Yaff⁷⁸ in both the $(N, V, \sigma_a = 0, T)$ and $(N, P, \sigma_a = 0, T)$ ensembles.^{23,79} Simulations were carried out for different volumes at a temperature of 150 K, 300 K and 450 K allowing the cell shape to fluctuate.^{23,79} We constructed the pressure profile $P(V)$ and Helmholtz free energy profile $F(V)$ as a function of the volume for these temperatures. The procedure to derive these profiles is explained in detail elsewhere.^{5,23} Additional computational details are given in the ESI.†

2.2 Experiments

DMOF-1(Zn) was synthesized from a mixture of terephthalic acid (H_2BDC) (3.37 mol, 560 mg), DABCO (1.67 mmol, 187 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (3.36 mmol, 1000 mg) in 40 mL of DMF in a conical flask and stirred at room temperature for 20 minutes, followed by a sonication of 20 minutes. The mixture was transferred into a Teflon-lined autoclave and heated to 120 °C for 48 hours. Thereafter, the colorless crystalline precipitate was cooled down to room temperature. The as-synthesized DMOF-1(Zn) was further purified by a two-step procedure using DMF and hot ethanol. To remove the residual unreacted substances, the solid was immersed into DMF for 3 hours and subsequently in hot ethanol at 60 °C for 3 hours. The highly purified solid was evacuated in vacuum at room temperature for 12 hours. DMOF-1(Cu) was synthesized following the same protocol starting with a mixture of BDC (3 mmol, 498 mg), DABCO (2.49 mmol, 279 mg) and $Cu(NO_3)_2 \cdot 3H_2O$ (3 mmol, 725 mg) in 60 mL of DMF.

Both DMOF-1(Zn) and DMOF-1(Cu) samples were evacuated under secondary vacuum during 8 hours at 150 °C. The sample preparations were performed using a glove box (Jacomex P-BOX) under argon atmosphere ($H_2O < 1$ ppm). The structural features of both DMOF-1 solids were investigated by laboratory powder X-ray diffraction (PXRD) using a PANalytical X'Pert equipped with an X'Celerator detector and a Si (111) monochromator ($Cu-K_{\alpha 1}$ wavelength, $\lambda = 1.54059 \text{ \AA}$ with an operating voltage of 40 kV and a beam current of 40 mA). The samples were loaded into a 1 mm glass capillary in a glove box and sealed before collecting their PXRD patterns (ESI Fig. 12 and 13†). These diffraction patterns were successfully indexed in the tetragonal system with the space group $P4/nbm$ (no. 125). The resulting unit cell parameters (ESI Table VI†) and associated volume (DMOF-1(Zn): $2301.1(1) \text{ \AA}^3$, DMOF-1(Cu): $2266.2(1) \text{ \AA}^3$) were obtained using a LeBail fit by the Jana2006 software.⁸⁰

Compression of the two solids was carried out using mercury intrusion. To avoid rehydration, the powders were loaded into a penetrometer of 3.1126 mL volume with a stem volume of 0.4120 mL into a glove box (Jacomex P-BOX) under argon atmosphere $H_2O < 5$ ppm. The mercury intrusion experiments were carried out using a Micromeritics AutoPore IV 9500 allowing a range of applied pressure from 0.003 MPa to 420 MPa. Prior to the experiments, the powder was outgassed at 6.5 Pa during 15 minutes. The collected volume of intruded mercury was corrected by a blank recorded under the same temperature and pressure conditions using the same penetrometer to obtain the absolute contracted volume as a function of the applied pressure. Two compression–decompression cycles were collected in this range of pressure for two distinct scenarios: (i) consecutive cycles and (ii) cycles separated by a time interval of 48 hours (ESI Fig. 14 and Table VI†).

After the compression by mercury intrusion the powders of both solids were carefully collected, separated from the mercury and their structural features were analyzed with PXRD following the same protocol described above (ESI Fig. 15 and 16†).

More details on the experiments can be found in the ESI.†

3 Results and discussion

3.1 Equilibrium structures of DMOF-1(Zn) and DMOF-1(Cu)

First, we optimized the crystallographic unit cells of DMOF-1(Zn)²⁹ and DMOF-1(Cu)²⁸ in the open-pore (op) state with cuboidal-shaped pore channels by constructing a local energy profile as a function of the volume using DFT calculations⁷¹ (ESI Fig. 1†). The op state of DMOF-1(Zn) at 0 K contains twisted DABCO pillar ligands, and twisted and slanted BDC linkers in agreement with the crystal structure solved experimentally^{30,81} (Fig. 1(c) and (d)). Our optimized structure of DMOF-1(Cu) does not feature such pronounced local symmetry breakings as the zinc variant. While the equilibrium structures of the two metal variants show some differences, the energy profiles near equilibrium are very similar (ESI Fig. 1†). An equation of state is fitted following the procedure of Vanpoucke *et al.*⁷¹ and the resulting properties are tabulated in Table 1. The Zn variant has a slightly larger unit cell volume and it is less rigid, as reflected in the equilibrium volume V_0 and bulk modulus B_0 , respectively. The simulated values are in good agreement with the experimental data (at room temperature) obtained from PXRD (volume) and mercury porosimetry (bulk modulus) (Table 1). In particular, it is experimentally confirmed that the bulk modulus

for DMOF-1(Cu) is higher than for its Zn-analogue. The higher rigidity of the copper paddle wheel as compared to a zinc paddle wheel was previously ascribed to electronic effects^{38,53} such as orbital directing effects only present in the copper variant. For the latter, we considered various possible magnetic configurations (ESI Section I.C†), as each metal ion has one unpaired d-electron. This did not have much influence on V_0 and B_0 as found for other copper paddle-wheel MOFs (*e.g.* HKUST-1 (ref. 82)), but in contrast to the flexible MIL-47(V) with a magnetic 1D chain.⁸³ Our computational results confirm that an antiferromagnetic Cu–Cu coupling in the paddle wheel is preferred, together with negligible ferromagnetic interactions along the BDC and DABCO linkers (ESI Section I.C†), which was also measured by Kozlova *et al.*⁸⁴ The obtained equilibrium lattice parameters of DMOF-1(Cu/Zn) are reported in Table VII in the ESI.† Our DFT results slightly overestimate the experimental lattice parameters (definition see Fig. 1), but we find overall a good agreement and a reproduction of the qualitative trends ($a_{\text{Cu}} \approx c_{\text{Cu}} < a_{\text{Zn}} \approx c_{\text{Zn}}$, $b_{\text{Cu}} > b_{\text{Zn}}$ and $V_{\text{Cu}} < V_{\text{Zn}}$). This emphasizes that our computational DFT approach succeeds in reproducing the experimentally reported structural features.

3.2 Prediction of pressure-induced breathing

Beyond this stable op phase at 0 K, DMOF-1 and functionalized forms have displayed different metastable states under influence of temperature and guests as mentioned in the introduction. To clearly distinguish between the various states observed in our calculations, we have extended the nomenclature of the possible configurations of the material as shown in Fig. 2. We differentiate between the open pore (op), large pore (lp), narrow pore (np) and closed pore (cp) states for which the pore angle α (definition see Fig. 2) and unit cell volume decrease. In the stable op state, the pore channels have a rectangular cross

Table 1 Equilibrium parameters of DMOF-1 fitted to a Rose–Vinet equation of state. The equilibrium volume V_0 , the bulk modulus B_0 and the first derivative to the volume of the bulk modulus B_1 are given. Our experimental results at room temperature are also given

Material	V_0 (Å ³)		B_0 (GPa)		B_1 (—)
	Theory	Exp.	Theory	Exp.	
DMOF-1(Cu)	2318	2266	16.4	18.8	11.0
DMOF-1(Zn)	2334	2301	13.7	16.9	0.2

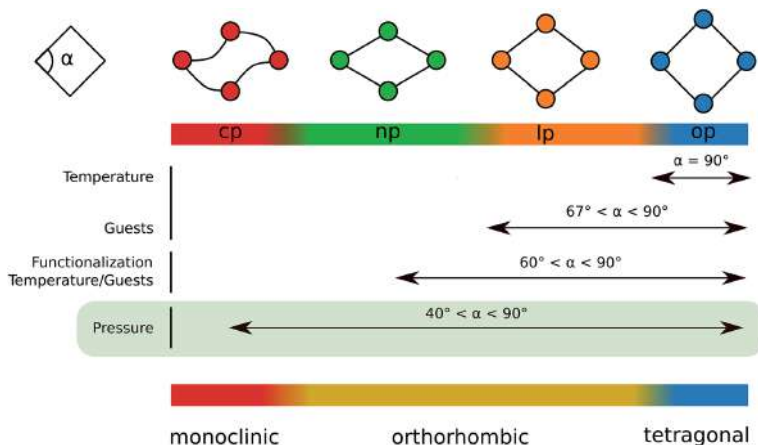


Fig. 2 Schematic overview of the reported flexibility in DMOF-1 illustrated as a function of the pore angle α . Our definition of the different states is indicated. The crystal system of the different states is indicated at the bottom, distinguishing between tetragonal (op), orthorhombic (lp and np) and monoclinic (cp).

section and the lattice parameters a and c are approximately equal (Fig. 1). Previous studies showed that various guest molecules (e.g. benzene²⁹) may cause a contraction of a , with a symmetry lowering from a tetragonal ($a \approx c$) to an orthorhombic ($a > c$) lattice. Following our nomenclature, guest-induced breathing leads to a lp state with lozenge-shaped pore channels. The pore angle remains higher than 67 degrees, which is to the best of our knowledge the lowest value reported for DMOF-1 in the presence of guests.⁴⁵ We denote the state with an even lower α as the np state, which is the continuation of the lp at lower volumes where no guests can enter DMOF-1. Such large contractions have, however, been reported when functionalizing the organic linkers.⁴⁷ Lastly, the cp state represents the configuration in which the channels become distorted and deviate from a lozenge. Such distortions were already found in other MOFs with one-dimensional pore channels such as MIL-53(Sc) and MIL-53(Al)-ADP.^{85,86}

We now focus on the intrinsic flexibility of the empty DMOF-1 framework. This is first achieved by constructing the energy profile as a function of the volume using DFT calculations at 0 K.^{15,25,71} These DFT $E(V)$ profiles are shown in the top left panel of Fig. 3 for DMOF-1(Zn) and DMOF-1(Cu), together with the

indication of various states as introduced earlier. It is immediately clear that the energy curves strongly resemble the breathing curves of other flexible MOFs.⁵ Recently we have shown that the shape of the Helmholtz free energy profile is indicative for the expected flexible behavior under the influence of various triggers.^{5,25,87} The now observed curves do not include temperature corrections, yet they already give an indication of the expected mechanical behavior.

More specifically and according to our earlier classification,⁵ DMOF-1(Cu) has a Type III energy profile and corresponds to a lossy spring with a back and forth transition from one phase to the other when increasing or releasing the mechanical pressure. Fig. 3(b) displays the pressure profile $P(V)$ as a function of the volume, which can be derived by differentiation of the simulated DFT energy profile at 0 K. These calculations predict that at a pressure of about 240 MPa ($P_{\max}$ for DMOF-1(Cu)) the structural transition takes place from the op phase towards a dense state with a unit cell volume of about 1200 Å³, which represents a remarkable volume contraction of 40%. A new dense configuration appears in a cp state, which is only stable at high pressures. The simulations for DMOF-1(Cu) thus predict that this structural transformation is reversible and

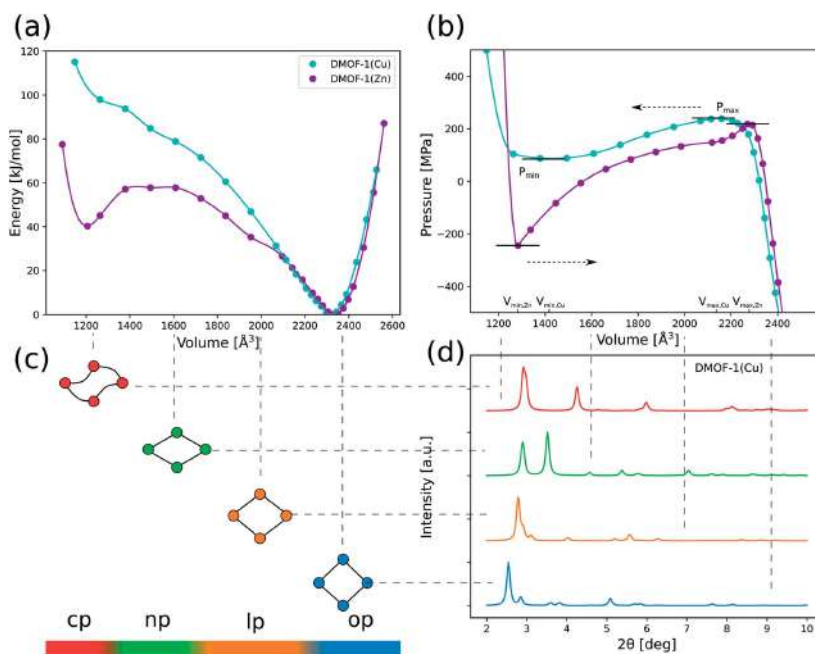


Fig. 3 (a) DFT energy profiles $E(V)$ as a function of the volume for DMOF-1(Cu) and DMOF-1(Zn) at 0 K (PBE + D3(BJ)^{ATM}). The lines only represent a guide to the eye. (b) Pressure profiles $P(V)$ (at 0 K) as a function of the volume obtained by numerically deriving the energy profiles via $P(V) = -\frac{\partial E(V)}{\partial V}$. $P_{\max}$ is 239 MPa for DMOF-1(Cu) and 222 MPa for DMOF-1(Zn). $P_{\min}$ is 86 MPa for DMOF-1(Cu) and -238 MPa for DMOF-1(Zn). (c) The definition of the states (open pore (op), large pore (lp), narrow pore (np) and closed pore (cp)) used in this work is inspired by the pore angle α as defined in Fig. 2. (d) Simulated XRD patterns for different representative phases of DFT-optimized DMOF-1(Cu) ($\lambda = 0.4859$ Å).

displays a hysteresis of about 150 MPa. According to our 0 K DFT calculations we find a cp like state with distorted channels. An example is shown in ESI Fig. 4.† However, it needs to be validated by simulations at higher temperatures to what extent such shapes are still valid (*vide infra*).

Based on its $E(V)$ curve, DMOF-1(Zn) can be classified as a Type IIa material, where the material suddenly switches to a contracted state but never returns. The pressure profile reveals a slightly lower critical pressure $P_{\max}$ (≈ 220 MPa) as compared to DMOF-1(Cu). Moreover, the dense state is even found to be a metastable phase at 0 K in this case. Therefore, this material is predicted to behave as a nanoshock absorber as it displays an irreversible pressure-induced transition (a negative $P_{\min}$ is experimentally not yet accessible).⁵

Significant energetic differences can also be observed in the dense structure of the two DMOF-1 materials (Fig. 3(a)). The dense state of the Cu variant is much less stable than the Zn variant (± 100 kJ mol⁻¹ with respect to the stable open phase *versus* ± 40 kJ mol⁻¹), which was also reflected in the bulk modulus at 0 K (Table 1). This clearly emphasizes that changing the nature of the metal allows to tune the mechanical behavior of DMOF-1 (lossy spring or nanoshock absorber).

Finally, a valuable figure of merit to characterize the potential of a MOF for mechanical energy storage applications is the relation $P_{\max}\Delta V$ for energy work. It presents a theoretical upper bound for the energy stored during the pressure-induced breathing process. As both the predicted transition pressure $P_{\max}$ (more than 200 MPa) and the associated volume change ($\approx 40\%$) of DMOF-1 are among the highest reported so far for flexible frameworks, this material could thus potentially be interesting for mechanical energy storage. We find a predicted energy work of approximately 119 J g⁻¹ and 130 J g⁻¹ for DMOF-1(Cu) and DMOF-1(Zn), respectively.

3.3 Molecular-level characterization of the phase transition at operando conditions

To extend our predictions towards experimental conditions at higher temperature, we performed force field MD simulations as described in the Methods section on DMOF-1(Zn) with a new QuickFF force field^{72,73} The Helmholtz free energy profiles are shown in Fig. 4. Only in cases where DMOF-1 materials were additionally functionalized, for example with pendant alkoxy groups,^{39,48,51,53} the relative stability between the various phases could be drastically changed. In these specific cases, additional interactions between the functional groups allowed to stabilize the contracted phase at low temperatures. The op state could then only be retrieved at high temperatures. A similar balance between dispersion and entropy was recently rationalized by some of us on the MIL-53(Al).²⁵ More important for the current study, however, is that we find that both transition pressures $P_{\max}$ and $P_{\min}$ increase with temperature from 169 MPa at 150 K to 200 MPa and 210 MPa at 300 K and 450 K, respectively (Fig. 4), and that the metastable dense phase of DMOF-1(Zn) is expected to disappear. The $P_{\max}\Delta V$ energy work increases from 91 J g⁻¹ to 108 J g⁻¹ over this temperature range.

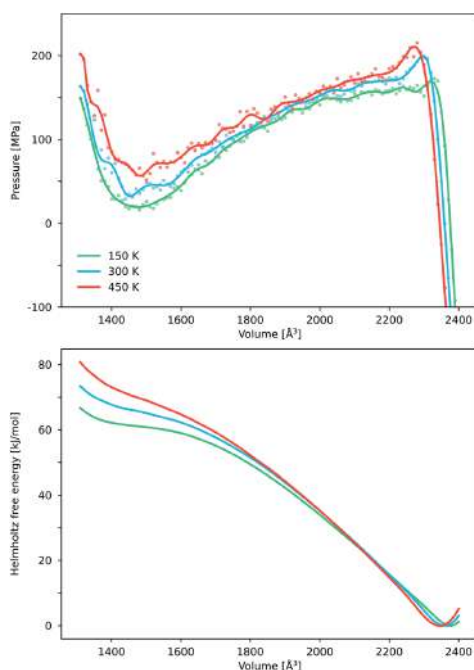


Fig. 4 The pressure $P(V)$ and Helmholtz free energy $F(V)$ profiles as a function of the volume obtained through force field MD simulations for DMOF-1(Zn) at 150 K, 300 K and 450 K.

Until now, we have focused on the macroscopic conditions of breathing in DMOF-1. In order to gain more molecular-level insight in the pressure-induced breathing process, we studied the behavior of some important structural parameters as a function of the volume. A first impression is achieved through monitoring the final structures of the geometry optimizations used to construct the DFT energy profile as a function of volume for both the copper and zinc variants at 0 K. This procedure allows us to easily examine the evolution of the shape of the unit cell and the results are displayed in Fig. 5. In the stable op phase, both materials adopt a tetragonal lattice system. When the volume decreases, the system goes abruptly over to an orthorhombic symmetry ($a \neq c$), as the pores start to anisotropically contract instead of isotropically shrinking in the 2D layer. At very small volumes – when the pores become distorted, *i.e.* the cp phase – the structure deviates from an orthorhombic symmetry. During the entire transition process from the op to the cp structure, the metal-DABCO axis remains nearly constant, indicating that the volume reduction entirely results from breathing in the 2D layers. On the molecular level, the pores mainly shrink due to a knee-cap motion, accompanied by slanting of the BDC linkers, which is shown in the right panel of Fig. 5. This is suggested by the evolution of the dihedral M–O–C–C angle in the DFT optimized structures. This dihedral angle

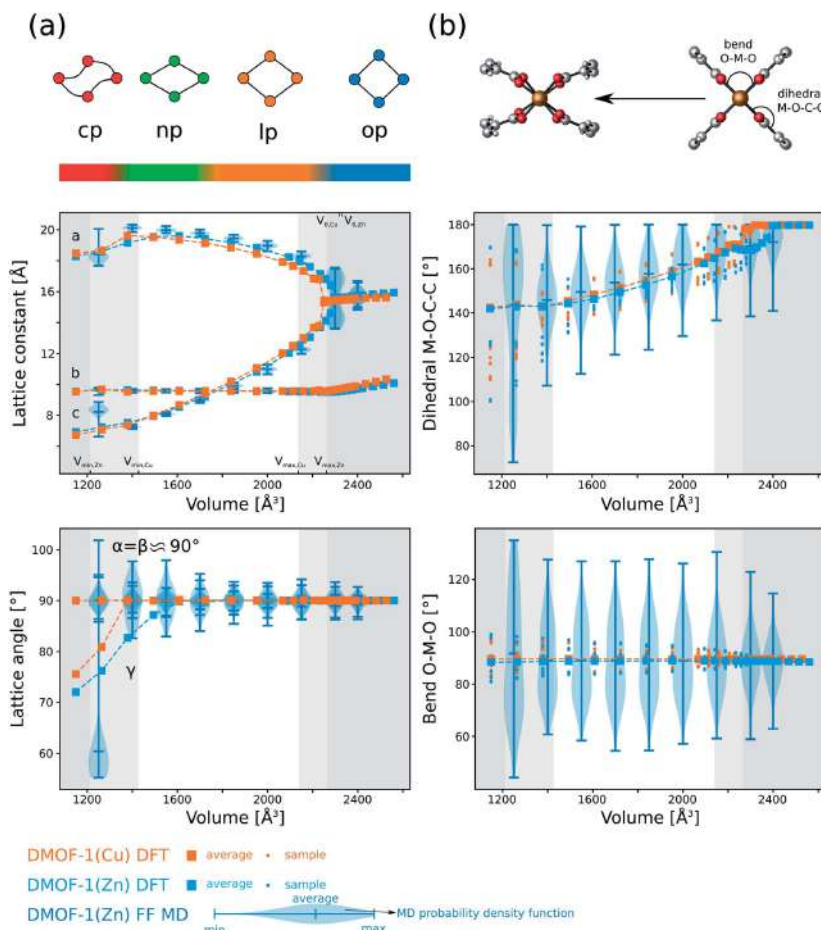


Fig. 5 The lattice parameters and internal coordinates of DMOF-1(Cu) and DMOF-1(Zn), obtained through DFT optimization at 0 K. The DMOF-1(Zn) force field (FF) molecular dynamics (MD) results are indicated *via* violin plots. They show the probability density function of the property obtained through $(N, V, \sigma_a = 0, T)$ simulations at different volumes and at 300 K. (a) Evolution of the lattice parameters (as defined in Fig. 1) as a function of the volume. The different states (cp, np, lp and op) are again schematically indicated. (b) Evolution of important internal coordinates as a function of the volume. The definition of the bend and dihedral are indicated in the top right panel. The transparent grey regions indicate the mechanically (meta)stable volume regions for pressures above $P_{\min}$ and below $P_{\max}$, as obtained in Fig. 3(b). The light grey region only encompasses DMOF-1(Cu), while the darker region includes both DMOF-1(Zn) and DMOF-1(Cu).

was previously identified as an important internal coordinate for the breathing motion in members of the MIL-53 family.^{23,88} Contrarily, the square-planar coordination environment around the copper and zinc ions remains relatively intact on average.

Essential insights in the pressure-induced breathing process at operating conditions can be obtained by looking at the system at room temperature. Then, the system runs through different molecular configurations during the energetically preferred knee-cap motion according to our force field MD simulations on DMOF-1(Zn). Although the lattice constants vary

only mildly at room temperature, the internal coordinates describing the structure of the paddle wheels, *i.e.* O–M–O bends, can fluctuate in a surprisingly wide range from 60 degrees to 125 degrees. For the cp state, the distribution becomes even wider. We display this by violin plots in Fig. 5, which show the probability density function as obtained *via* $(N, V, \sigma_a = 0, T)$ simulations at 300 K. This unveils that a static picture (DFT at 0 K) might be misleading, and that at realistic conditions both knee-cap and paddle wheel deformations are present during the breathing process.

We further analyzed the structural properties based on our force field simulations. Focusing on the evolution of the symmetry of the DMOF-1(Zn) unit cell as a function of the volume at 300 K, as indicated in Fig. 6, a similar picture as the one at 0 K emerges. Starting at high volumes, the material adopts the tetragonal crystal system (op state). When decreasing the volume, the material undergoes a tetragonal-to-orthorhombic symmetry breaking around $2300 \text{ \AA}^3$. As the states with an orthorhombic symmetry are mechanically unstable (positive $\partial P/\partial V$ slope in Fig. 4) this volume region is not directly attainable by applying a pressure to the material, as also schematically depicted in Fig. 2. Finally when decreasing the volume below *ca.* $1300 \text{ \AA}^3$, the material undergoes a further symmetry breaking towards a monoclinic phase, observed in the mechanically stable cp state. Hence, while the inclusion of temperature at operating conditions clearly allows for larger fluctuations in the internal coordinates, the sequence of phases and crystal systems at room temperature is the same as those observed earlier with DFT at 0 K.

3.4 Experimental contraction of DMOF-1(Zn) and DMOF-1(Cu) through mercury intrusion measurements

Motivated by the predictions so far, we investigated the isostructural DMOF-1(Zn) and DMOF-1(Cu) materials using mercury intrusion experiments to verify the possible contraction of the two pristine phases under mechanical pressure and to further confirm their promise for mechanical energy storage. Fig. 7 shows the evolution of the cumulative volume of intruded mercury as a function of the applied pressure for the two materials. Two consecutive intrusion–extrusion, *i.e.*, compression–decompression, cycles, from 10^{-3} MPa to 420 MPa, were applied to the samples. While the first two steps of the curve at 0.01 MPa and ~ 12 MPa correspond to the compaction of the powder and the filling of interparticle grains, the increase in

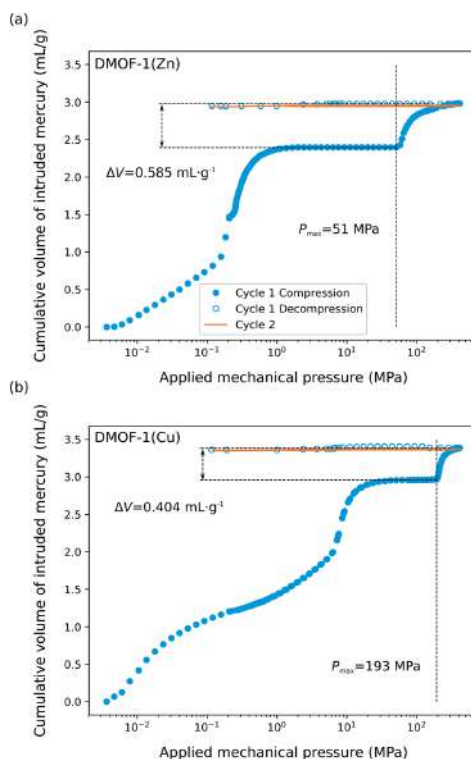


Fig. 7 Cumulative volume of intruded mercury in an intrusion–extrusion experiment with two consecutive cycles as a function of the applied mechanical pressure obtained for the (a) DMOF-1(Zn) and (b) DMOF-1(Cu) sample. The measured transition pressure P_{max} and associated volume change are indicated in the figure. The results of the two cycles separated by a time interval of 48 hours are given in ESI Fig. 14.†

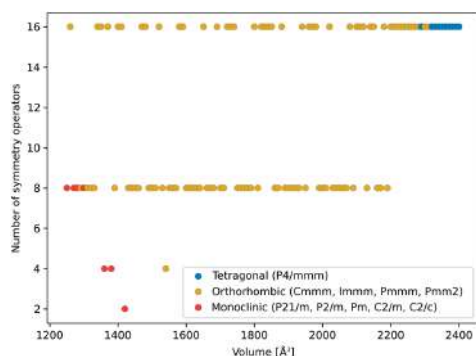


Fig. 6 Evolution of the DMOF-1(Zn) cell symmetry at 300 K, as indicated by the number of symmetry operators as a function of the volume during the breathing process obtained through $(N, V, \sigma_a = 0, T)$ simulations. For each volume, the crystal system of the material is indicated with a color code, distinguishing between the tetragonal (op), orthorhombic (lp and np) and monoclinic (cp) crystal systems.

volume of mercury observed at ~ 51 MPa and ~ 193 MPa for DMOF-1(Zn) and DMOF-1(Cu), respectively, can only be associated with a contraction of these microporous materials since Hg does not enter the pores. The resulting volume variations (ΔV) of 0.59 mL g^{-1} and 0.41 mL g^{-1} correspond to a contraction of $\sim 48\%$ and $\sim 34\%$ of the unit cell volume for DMOF-1(Zn) and DMOF-1(Cu), respectively. It can be noted that the transition pressure (P_{max}) of DMOF-1(Cu) is significantly higher than the one of DMOF-1(Zn). The trend that the copper version is more rigid than the zinc variant is qualitatively consistent with the predictions, and with the simulated and experimental bulk moduli. Furthermore, we observed that this structural change is irreversible for both materials as evidenced by the superposition of the experimental data collected during the first decompression and the second compression/decompression steps. To probe possible kinetic effects on the (ir)reversibility of the structural contraction, two compression–decompression cycles were performed with a time interval of 48 hours between the first

and the second cycle (ESI Fig. 14†). Both experimental conditions lead to very similar Hg-porosimetry curves (transition pressure, volume change) for both solids, indicating that more time does not allow a reopening of the contracted structures.

Considering the initial mass of the samples and the unit cell volumes determined from our laboratory PXRD (Table 1), the volumes of the contracted phases are expected to be about 1200 Å³ (DMOF-1(Zn)) and 1500 Å³ (DMOF-1(Cu)), which seem to be situated around the theoretical volumes at $P_{\min}$. The $\Delta P\Delta V$ energy work associated to this structural contraction can be estimated to be about 30 J g⁻¹ and 80 J g⁻¹. The latter value is among the highest performances reported for a MOF so far, which makes DMOF-1(Cu) highly attractive for mechanical energy storage applications, and more specifically as a nano-shock absorber.⁵

Since the Hg-induced structural transformation of the two materials is irreversible, we collected the PXRD patterns of the corresponding powders obtained after compression. ESI Fig. 15 and 16† show that this irreversible contraction is accompanied by an amorphization of the polycrystalline sample, which makes it impossible to determine the unit cell parameters of the experimentally contracted structure. This behavior is similar to a very recent study some of us performed on the pressure-induced contraction of DUT-48/DUT-49.⁶³ In this specific case, Hg-porosimetry confirmed the characteristics of the theoretically predicted transition (the relative volume contraction and the transition pressure), but the contracted structure previously evidenced by *in situ* gas adsorption⁸⁹ was not observed after mercury intrusion. For DMOF-1, it is known that under the influence of specific guests (e.g. water vapor, air), the 3D structure can break down at the pillar ligands towards 2D layers.^{90–92} Additionally, mechanical nano-indentation experiments have shown that the direction along the DABCO linker is brittle and can start to plastically deform,⁵⁵ which could also explain the structural collapse and irreversibility of DMOF-1. In our case, it remains to be verified if the amorphization takes place during the structural contraction or due to compression beyond the contracted phase as the applied pressure during an intrusion experiment is varied up to 420 MPa.

Given these experimental findings, we can return to our computational predictions and evaluate their validity. As the powders after Hg-intrusion have become amorphous, we cannot conclusively confirm the reversible or irreversible nature of the structural transition. Nevertheless, the experimentally measured volume contractions for both materials are in agreement with the simulations. The computational transition pressure is slightly overestimated (239 MPa *versus* 193 MPa) for DMOF-1(Cu). For DMOF-1(Zn), in contrast, theory did predict an irreversible crystalline transformation, but the experimental transition pressure does not coincide well with the DFT or force field MD simulations. This discrepancy could also be related to the difficulty of getting accurate predictions for the relative stability between different phases without the use of computationally very heavy methodologies,²⁵ or by other effects present in the sample which are not well understood. For instance, the crystal size has shown to modify the hysteresis behavior and

corresponding threshold values in flexible MOFs in different ways.^{93–95}

3.5 Theoretical characterization of the contracted phase

To further characterize the evolution of DMOF-1 under pressure, we calculated the XRD patterns of our DFT-optimized structures (at 0 K) as a function of the volume to predict the evolution of an ideal *in situ* high-pressure powder X-ray diffraction experiment. These theoretical results may serve as a useful tool in future experimental characterization studies targeted to unravel the contracted phase. Based on the estimated volumes from the mercury intrusion experiments, we cannot distinguish between a cp or a np state. Below, we only discuss the results for DMOF-1(Cu), as the predicted behavior of the Zn variant is nearly identical (ESI Fig. 10†). In Fig. 3(d), the simulated XRD pattern is indicated for a representative structure with different characteristic volumes as obtained from 0 K DFT simulations. Our simulated low angle XRD patterns illustrate that especially the first peaks should change in relative intensity when the structure contracts. This trend is also observed in experimental *in situ* studies of guest- or temperature-induced breathing of pillared-layered MOFs.^{44,49,53,96} Going from the op state to the lp state, we predict a general shift of the peaks towards higher angles in agreement with the volume contraction. The first peaks shift further to the right in the np and cp configurations, but a second large peak arises in the latter, which may be used in experiment to identify the state of the sample. The transition from a np to a cp state should be clearly visible according to the simulated XRD patterns. In the ESI, we furthermore show that temperature and the use of force field MD techniques only have a small impact on the XRD patterns and accompanying conclusions (ESI Fig. 10†) in the case of the orthorhombic and tetragonal crystal systems. In the cp state, some extra peaks arise under influence of temperature.

Reliably modeling pressure-induced amorphization is a difficult task.⁸⁷ To shed light on a possible amorphization of DMOF-1, we performed a symmetry analysis similar to the one on UiO-66-type materials in ref. 97. Therefore, we determined the radial distribution functions (RDFs) of the different atoms in DMOF-1(Zn) with respect to the center of the zinc paddle-wheel cluster at 300 K for three volumes: at 2400 Å³ (tetragonal), at 1800 Å³ (orthorhombic), and at 1270 Å³ (monoclinic). As indicated in ESI Section II.C.2,† the RDFs in the tetragonal and orthorhombic phases are defined by well-defined peaks for distances up to about 10 Å. At a volume of 1800 Å³, the new zinc peak at 10 Å is a direct result of the decreased symmetry when going from the tetragonal to the orthorhombic phase. When going to the contracted monoclinic phase at 1270 Å³, the peaks are much more spread out and start to overlap, revealing that the symmetry of this contracted phase is reduced. This could hint toward loss of crystallinity, but does not decisively show that amorphization should occur.

Despite these efforts, however, it remains unclear which phase is experimentally found after the large experimental volume contraction through mercury intrusion experiments,

and it will require experimental validation and future in-depth studies on the rigidity of paddle wheel frameworks.

4 Conclusion

Herein we have shown the unique potential for DMOF-1 belonging to the class of pillared-layered MOFs to be used for mechanical energy storage applications. To date, materials of this class were shown to exhibit breathing behavior under influence of guest molecules such as benzene, IPA and DMF with large volume changes. However, the influence of mechanical pressure upon guest-free DMOF-1 was not known.

In this work, we predicted pressure-induced flexibility in empty DMOF-1 materials with copper or zinc at the metal nodes. Under the application of a mechanical pressure, enormous volume contractions were observed. This behavior was analyzed in detail using a combination of 0 K DFT and force field MD simulations. Our theoretical calculations predict a phase transformation towards a contracted state for both copper and zinc variants. In the case of Cu, the phase transformation is predicted to be reversible, whereas with Zn the material maintains a contracted phase after releasing the mechanical pressure. The predicted pressure-induced flexibility was confirmed experimentally by mercury intrusion experiments, which indeed detected a structural contraction. In both cases, however, the Hg-induced structural transformation was found to be irreversible. As the Hg-intruded structures displayed pressure-induced amorphization, we could not validate the reversible or irreversible nature of the structural transition. Nevertheless, the experiments did confirm the potential of these materials as a nanoshock absorber. They associated a high energy of 80 J g⁻¹ to the pressure-induced transition of DMOF-1(Cu), which outperforms many other flexible MOFs to date.

Conflicts of interest

The authors declare no competing interests.

Acknowledgements

This work is supported by the Fund for Scientific Research Flanders (FWO). V. V. S. acknowledges funding from the European Union's Horizon 2020 research and innovation program (consolidator ERC grant agreement no. 647755-DYNPOR (2015–2020)). The work is furthermore supported by the Research Board of Ghent University (BOF). The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by Ghent University, FWO and the Flemish Government department EWI. S.-K. L. and J.-S.C. authors are grateful to the National Research Council of Science & Technology (NST) of Korea (the R&D Convergence Program, CRC-14-1-KRICT) for financial support. P. G. Y. and G. M. acknowledge the ANR MeaCoPa for funding.

References

- 1 G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 1380–1399.

- 2 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704.
- 3 A. Schneemann, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062–6096.
- 4 F.-X. Coudert, *Chem. Mater.*, 2015, **27**, 1905–1916.
- 5 L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier and V. Van Speybroeck, *Nat. Commun.*, 2018, **9**, 204.
- 6 Y. Liu, J.-H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann and C. M. Brown, *J. Am. Chem. Soc.*, 2008, **130**, 11813–11818.
- 7 F. Salles, A. Ghoufi, G. Maurin, R. G. Bell, C. Mellot-Draznicks and G. Férey, *Angew. Chem., Int. Ed.*, 2008, **47**, 8487–8491.
- 8 I. Beurroies, M. Boulhout, P. L. Llewellyn, B. Kuchta, G. Férey, C. Serre and R. Denoyel, *Angew. Chem., Int. Ed.*, 2010, **49**, 7526–7529.
- 9 C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519–13526.
- 10 J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi and J. R. Long, *Nature*, 2015, **527**, 357–361.
- 11 E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren and L. Brammer, *Nat. Chem.*, 2017, **9**, 882–889.
- 12 P. Freund, L. Mielewczyk, M. Rauche, I. Senkovska, S. Ehrling, E. Brunner and S. Kaskel, *ACS Sustainable Chem. Eng.*, 2019, **7**, 4012–4018.
- 13 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232–1268.
- 14 P. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghoufi, T. Devic, C. Serre, G. Dmitriev, G. Férey, G. L. Zhong and G. Maurin, *Chem. Sci.*, 2012, **3**, 1100–1104.
- 15 P. Ramaswamy, J. Wieme, E. Alvarez, L. Vanduyfhuys, J. P. Itié, P. Fabry, V. Van Speybroeck, C. Serre, P. G. Yot and G. Maurin, *J. Mater. Chem. A*, 2017, **5**, 11047–11054.
- 16 L. Sarkisov, R. L. Martin, M. Haranczyk and B. Smit, *J. Am. Chem. Soc.*, 2014, **136**, 2228–2231.
- 17 A. U. Ortiz, A. Boutin, A. H. Fuchs and F.-X. Coudert, *Phys. Rev. Lett.*, 2012, **109**, 195502.
- 18 C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, *Nat. Chem.*, 2012, **4**, 83–89.
- 19 C. M. Simon, J. Kim, D. A. Gomez-Gualdrón, J. S. Carno, Y. G. Chung, R. L. Martin, R. Mercado, M. W. Deem, D. Gunger, M. Haranczyk, D. S. Sholl, R. Q. Snurr and B. Smit, *Energy Environ. Sci.*, 2015, **8**, 1190–1199.
- 20 P. Z. Moghadam, T. Islamoglu, S. Goswami, J. Exley, M. Fantham, C. F. Kaminski, R. Q. Snurr, O. K. Farha and D. Fairen-Jimenez, *Nat. Commun.*, 2018, **9**, 1378.
- 21 J. S. Grosh and F. Paesani, *J. Am. Chem. Soc.*, 2012, **134**, 4207–4215.
- 22 A. U. Ortiz, A. Boutin and F.-X. Coudert, *Chem. Commun.*, 2014, **50**, 5867–5870.

- 23 S. M. J. Rogge, L. Vanduyfhuys, A. Ghysels, M. Waroquier, T. Verstraelen, G. Maurin and V. Van Speybroeck, *J. Chem. Theory Comput.*, 2015, **11**, 5583–5597.
- 24 J. Wieme, L. Vanduyfhuys, S. M. J. Rogge, M. Waroquier and V. Van Speybroeck, *J. Phys. Chem. C*, 2016, **120**, 14934–14947.
- 25 J. Wieme, K. Lejaeghere, G. Kresse and V. Van Speybroeck, *Nat. Commun.*, 2018, **9**, 4899.
- 26 A. E. J. Hoffman, L. Vanduyfhuys, I. Nevestic, J. Wieme, S. M. J. Rogge, H. Depauw, P. Van Der Voort, H. Vrielinck and V. Van Speybroeck, *J. Phys. Chem. C*, 2018, **122**, 2734–2746.
- 27 J.-J. Zheng, S. Kusaka, R. Matsuda, S. Kitagawa and S. Sakaki, *J. Am. Chem. Soc.*, 2018, **140**, 13958–13969.
- 28 K. Seki, S. Takamizawa and W. Mori, *Chem. Lett.*, 2001, **30**, 332–333.
- 29 D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033–5036.
- 30 X.-L. Luo, Z. Yin and M. Kurmoo, *Inorg. Chem. Front.*, 2016, **3**, 1208–1226.
- 31 N. C. Burtch and K. S. Walton, *Acc. Chem. Res.*, 2015, **48**, 2850–2857.
- 32 K. Kongpatpanich, S. Horike, M. Sugimoto, S. Kitao, M. Seto and S. Kitagawa, *Chem. Commun.*, 2014, **50**, 2292–2294.
- 33 T. Takei, T. Li, J. Kawashima, T. Ohmura, M. Ichikawa, M. Hosoe, Y. Shinya, I. Kanoya and W. Mori, *Chem. Lett.*, 2007, **36**, 1136–1137.
- 34 H. Wang, J. Getzschmann, I. Senkovska and S. Kaskel, *Microporous Mesoporous Mater.*, 2008, **116**, 653–657.
- 35 B. Arstad, H. Fjellvåg, K. O. Kongshaug, O. Swang and R. Blom, *Adsorption*, 2008, **14**, 755–762.
- 36 P. Maniam and N. Stock, *Inorg. Chem.*, 2011, **50**, 5085–5097.
- 37 O. Kozachuk, K. Khaletskaya, M. Halbherr, A. Bétard, M. Meilikhov, R. W. Seidel, B. Jee, A. Pöpl and R. A. Fischer, *Chem.–Eur. J.*, 2012, **18**, 1688–1695.
- 38 S. Bureekaew, S. Amirjalayer and R. Schmid, *J. Mater. Chem.*, 2012, **22**, 10249–10254.
- 39 M. Alaghemandi and R. Schmid, *J. Phys. Chem. C*, 2016, **120**, 6835–6841.
- 40 K. Uemura, Y. Yamasaki, Y. Komagawa, K. Tanaka and H. Kita, *Angew. Chem., Int. Ed.*, 2007, **46**, 6662–6665.
- 41 Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2009, **131**, 16675–16677.
- 42 K. Uemura, Y. Yamasaki, F. Onishi, H. Kita and M. Ebihara, *Inorg. Chem.*, 2010, **49**, 10133–10143.
- 43 S. Henke, R. Schmid, J. D. Grunwaldt and R. A. Fischer, *Chem.–Eur. J.*, 2010, **16**, 14296–14306.
- 44 S. Henke, F. D. C. Wieland, M. Meilikhov, M. Paulus, C. Sternemann, K. Yussenko and R. A. Fischer, *CrystEngComm*, 2011, **13**, 6399–6404.
- 45 N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, *Nat. Mater.*, 2011, **10**, 787–793.
- 46 N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda and S. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 4501–4504.
- 47 S. Henke, A. Schneemann, A. Wütscher and R. A. Fischer, *J. Am. Chem. Soc.*, 2012, **134**, 9464–9474.
- 48 S. Henke, A. Schneemann and R. A. Fischer, *Adv. Funct. Mater.*, 2013, **23**, 5990–5996.
- 49 V. Bon, J. Pallmann, E. Eisbein, H. C. Hoffmann, I. Senkovska, I. Schwedler, A. Schneemann, S. Henke, D. Wallacher, R. A. Fischer, G. Seifert, E. Brunner and S. Kaskel, *Microporous Mesoporous Mater.*, 2015, 64–74.
- 50 Y. Kim, R. Haldar, H. Kim, J. Koo and K. Kim, *Dalton Trans.*, 2016, **45**, 4187–4192.
- 51 I. Schwedler, S. Henke, M. T. Wharmby, S. R. Bajpe, A. K. Cheetham and R. A. Fischer, *Dalton Trans.*, 2016, **45**, 4230–4241.
- 52 A. Schneemann, Y. Takahashi, R. Rudolf, S.-i. Noro and R. A. Fischer, *J. Mater. Chem. A*, 2016, **4**, 12963.
- 53 A. Schneemann, P. Vervoots, I. Hante, M. Tu, S. Wannapaiboon, C. Sternemann, M. Paulus, D. C. F. Wieland, S. Henke and R. A. Fischer, *Chem. Mater.*, 2018, **30**, 1667–1676.
- 54 S. Wannapaiboon, A. Schneemann, I. Hante, M. Tu, K. Epp, A. L. Semrau, C. Sternemann, M. Paulus, S. J. Baxter, G. Kieslich and R. A. Fischer, *Nat. Commun.*, 2019, **10**, 346.
- 55 S. Henke, W. Li and A. K. Cheetham, *Chem. Sci.*, 2014, **5**, 2392–2397.
- 56 M. Andrzejewski, N. Casati and A. Katrusiak, *Dalton Trans.*, 2017, **46**, 14795–14803.
- 57 T. Iizuka, K. Honjo and T. Uemura, *Chem. Commun.*, 2019, **55**, 691–694.
- 58 P. G. Yot, Z. Boudene, J. Macia, D. Granier, L. Vanduyfhuys, T. Verstraelen, V. V. Speybroeck, T. Devic, C. Serre, G. Férey, N. Stock and G. Maurin, *Chem. Commun.*, 2014, **50**, 9462–9464.
- 59 P. G. Yot, L. Vanduyfhuys, E. Alvarez, J. Rodriguez, J.-P. Itié, P. Fabry, N. Guillou, T. Devic, I. Beurroies, P. L. Llewellyn, V. Van Speybroeck, C. Serre and G. Maurin, *Chem. Sci.*, 2016, 446–450.
- 60 M. Wahiduzzaman, N. Reimer, J.-P. Itié, N. Stock, G. Maurin and P. G. Yot, *Polyhedron*, 2018, **155**, 144–148.
- 61 P. G. Yot, M. Wahiduzzaman, E. Elkaim, P. Fertey, P. Fabry, C. Serre and G. Maurin, *Dalton Trans.*, 2019, **48**, 1656–1661.
- 62 S. Henke, M. T. Wharmby, G. Kieslich, I. Hante, A. Schneemann, Y. Wu, D. Daisenberger and A. K. Cheetham, *Chem. Sci.*, 2018, **9**, 1654–1660.
- 63 S. Krause, J. D. Evans, V. Bon, I. Senkovska, S. Ehrling, U. Stoeck, P. G. Yot, P. Iacomi, P. L. Llewellyn, G. Maurin, F.-X. Coudert and S. Kaskel, *J. Phys. Chem. C*, 2018, **122**, 19171–19179.
- 64 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 65 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- 66 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 67 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 15104.
- 68 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **132**, 1456–1465.
- 69 B. M. Axilrod and E. Teller, *J. Chem. Phys.*, 1943, **11**, 1943.
- 70 Y. Muto, *Proc. Phys.-Math. Soc. Jpn*, 1944, **17**, 629.

- 71 D. E. P. Vanpoucke, K. Lejaeghere, V. Van Speybroeck, M. Waroquier and A. Ghysels, *J. Phys. Chem. C*, 2015, **119**, 23752–23766.
- 72 L. Vanduyfhuys, S. Vandenbrande, T. Verstraelen, R. Schmid, M. Waroquier and V. Van Speybroeck, *J. Comput. Chem.*, 2015, **36**, 1015–1027.
- 73 L. Vanduyfhuys, S. Vandenbrande, J. Wieme, M. Waroquier, T. Verstraelen and V. Van Speybroeck, *J. Comput. Chem.*, 2018, **39**, 999–1011.
- 74 T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Speybroeck, M. Waroquier and P. W. Ayers, *J. Chem. Theory Comput.*, 2016, **12**, 3894–3912.
- 75 T. Verstraelen, P. Tecmer, F. Heidar-Zadeh, C. E. González-Espinoza, M. Chan, T. D. Kim, K. Boguslawski, S. Fias, S. Vandenbrande, D. Berrocal and P. W. Ayers, *Horton 2.1.0*, 2017, <http://theochem.github.com/horton/>.
- 76 J. H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, 1989, **111**, 8576–8582.
- 77 N. L. Allinger, X. Zhou and J. Bergsma, *J. Mol. Struct.: THEOCHEM*, 1994, **312**, 69–83.
- 78 T. Verstraelen, L. Vanduyfhuys, S. Vandenbrande and S. M. J. Rogge, *Yaff, yet another force field*, <http://molmod.ugent.be/software/>, accessed 2019-01-25.
- 79 S. M. J. Rogge, S. Caroes, R. Demuyne, M. Waroquier, V. Van Speybroeck and A. Ghysels, *J. Chem. Theory Comput.*, 2018, **14**, 1186–1197.
- 80 V. Petříček, M. Dušek and L. Palatinus, *Z. Kristallogr.–Cryst. Mater.*, 2014, **229**, 345–352.
- 81 S. G. Kozlova and S. P. Gabuda, *Sci. Rep.*, 2017, **7**, 11505.
- 82 M. R. Ryder, B. Civalieri, G. Cinque and J.-C. Tan, *CrystEngComm*, 2016, **18**, 4303–4312.
- 83 D. E. P. Vanpoucke, J. W. Jaeken, S. De Baerdemacker, K. Lejaeghere and V. Van Speybroeck, *Beilstein J. Nanotechnol.*, 2014, **5**, 1738–1748.
- 84 S. G. Kozlova, D. G. Samsonenko, I. A. Tkachenko, A. B. Slobodyuk, D. A. Stepnov and A. S. Yunoshev, *Phys. Status Solidi B*, 2016, **253**, 2252–2256.
- 85 L. Chen, J. P. S. Mowat, D. Fairen-Jimenez, C. A. Morrison, S. P. Thompson, P. A. Wright and T. Dören, *J. Am. Chem. Soc.*, 2013, **135**, 15763–15773.
- 86 H. Reinsch, R. S. Pillai, R. Siegel, J. Senker, A. Lieb, G. Maurin and N. Stock, *Dalton Trans.*, 2016, **45**, 4179–4186.
- 87 S. M. J. Rogge, M. Waroquier and V. Van Speybroeck, *Acc. Chem. Res.*, 2017, **51**, 138–148.
- 88 C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk and G. Férey, *Science*, 2007, **315**, 1828–1931.
- 89 S. Krause, V. Bon, I. Senkovska, U. Stoeck, D. Wallacher, D. M. Többs, S. Zander, R. S. Pillai, G. Maurin, F.-X. Coudert and S. Kaskel, *Nature*, 2016, **532**, 348–352.
- 90 K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2012, **24**, 3153–3167.
- 91 Z. Chen, S. Xiang, D. Zhao and B. Chen, *Cryst. Growth Des.*, 2009, **9**, 5293–5296.
- 92 N. C. Burtch, A. Torres-Knoop, G. S. Foo, J. Leisen, C. Sievers, B. Ensing, D. Dubbeldam and K. S. Walton, *J. Phys. Chem. Lett.*, 2015, **6**, 812–816.
- 93 Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka and O. Sakata, *Science*, 2013, **339**, 193–196.
- 94 N. Kavooosi, V. Bon, I. Senkovska, S. Krause, C. Atzori, F. Bonino, J. Pallmann, S. Paasch, E. Brunner and S. Kaskel, *Dalton Trans.*, 2017, **46**, 4685–4695.
- 95 S. Krause, V. Bon, I. Senkovska, D. M. Többs, D. Wallacher, R. S. Pillai, G. Maurin and S. Kaskel, *Nat. Commun.*, 2018, **9**, 1573.
- 96 V. Bon, N. Klein, I. Senkovska, A. Heerwig, J. Getzschmann, D. Wallacher, I. Zizak, M. Brzhezinskaya, U. Mueller and S. Kaskel, *Phys. Chem. Chem. Phys.*, 2015, **17**, 17471–17479.
- 97 S. M. J. Rogge, J. Wieme, L. Vanduyfhuys, T. Verstraelen, S. Vandenbrande, G. Maurin, M. Waroquier and V. Van Speybroeck, *Chem. Mater.*, 2016, **28**, 5721–5732.

Paper X

**Thermal engineering of metal-organic frameworks
for adsorption applications: a molecular simulations
perspective**

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ACS Applied Materials & Interfaces, **2019**, 11, 38697-38707

J. Wieme performed the research and wrote the manuscript.

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Thermal Engineering of Metal–Organic Frameworks for Adsorption Applications: A Molecular Simulation Perspective

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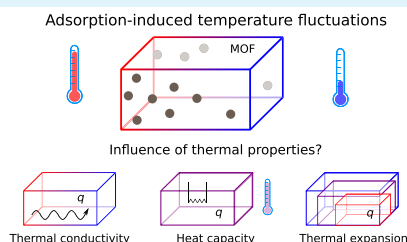
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S Supporting Information

ABSTRACT: Thermal engineering of metal–organic frameworks for adsorption-based applications is very topical in view of their industrial potential, in particular, since heat management and thermal stability have been identified as important obstacles. Hence, a fundamental understanding of the structural and chemical features underpinning their intrinsic thermal properties is highly sought-after. Herein, we investigate the nanoscale behavior of a diverse set of frameworks using molecular simulation techniques and critically compare properties such as thermal conductivity, heat capacity, and thermal expansion with other classes of materials. Furthermore, we propose a hypothetical thermodynamic cycle to estimate the temperature rise associated with adsorption for the most important greenhouse and energy-related gases (CO₂ and CH₄). This macroscopic response on the heat of adsorption connects the intrinsic thermal properties with the adsorption properties and allows us to evaluate their importance.

KEYWORDS: metal–organic frameworks, heat capacity, thermal conductivity, thermal expansion, gas adsorption, molecular simulations, thermal engineering



1. INTRODUCTION

Metal–organic frameworks (MOFs)¹ belong to the class of the most promising porous materials envisioned to play a role in gas storage and separation.^{2,3} These porous, hybrid inorganic–organic crystalline frameworks possess excellent chemical and physical properties and may, therefore, contribute to solutions for present-day world problems, such as the reduction of the greenhouse effect and the use of sustainable energy.^{4,5} Hence, much fundamental research effort has been devoted to the development of MOFs with a particular emphasis on the improvement of their adsorption properties for carbon capture and methane storage. As MOFs are slowly progressing toward industrial applications,^{6–9} attention increasingly turns toward important thermal engineering issues, such as thermal stability¹⁰ and heat management.^{11–13} This is particularly relevant as these adsorbents are exposed to large thermal fluctuations, since the adsorption and desorption of guests implies the release or consumption of energy. While efficient heat transport in MOFs will ultimately be limited by their inherent porosity, it is, nevertheless, essential to understand and improve the intrinsic thermal characteristics to reduce the costs of, for instance, compensating heat exchangers.¹⁴

The released heat of adsorption during charging needs to be dissipated quickly, as an increase in temperature severely diminishes the maximum uptake. In other words, to avoid the system from heating up, the charging rate needs to be constrained. During discharging, a decrease in temperature due to the heat of desorption will increase the number of unusable adsorbates remaining in the pores at the depletion pressure. The amount of gas stored or delivered under realistic dynamical conditions is always lower than that under perfect isothermal conditions. Therefore, for applications based on pressure swing adsorption (PSA), small temperature changes have a detrimental influence on their performance. This bottleneck is often mentioned when considering adsorbed natural gas as an alternative to conventional petroleum-based fuels for transportation vehicles.^{15–17} This problem is not limited to MOFs but extends to other candidate materials, such as activated carbon or zeolites, as well.^{18,19} Nevertheless, for some technologies, it is possible to take advantage of the thermal properties of MOFs. An example is the removal of

Received: July 17, 2019

Accepted: September 26, 2019

Published: September 26, 2019

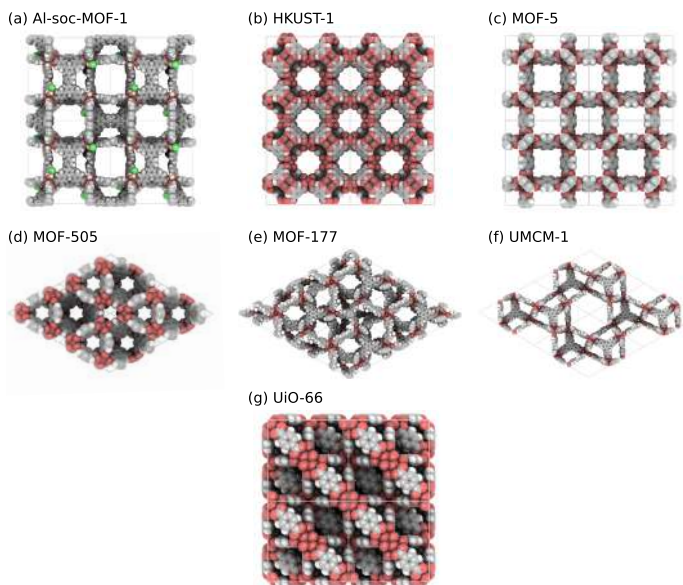


Figure 1. Overview of the MOFs investigated in this study. Al-soc-MOF-1²⁹ is an aluminum-based MOF. HKUST-1³⁰ and MOF-505³¹ (or NOTT-100³²) are copper-paddle wheel MOFs. UiO-66³³ is a zirconium MOF ($Zr_6O_4(OH)_4$). MOF-5,³⁴ MOF-177,³⁵ and UMCM-1³⁶ are Zn-based MOFs (ZnO_4). The simulated and experimental unit cell parameters of these MOFs are given in the [Supporting Information](#) (SI). The figures are generated with iRASP.³⁷

carbon dioxide from flue gas streams using temperature swing adsorption (TSA),^{20,21} where MOFs would have a lower energy penalty to heat to the regeneration temperature than the currently used monoethanolamine technology, as MOFs have a much lower heat capacity.²² To compensate for the limited availability of pilot-scale measurements of MOF applications,^{14,19} system performance studies to monitor the thermal effects have started to appear.^{23,24} These studies are mostly based on computational fluid dynamics and require the design of the system (e.g., geometry of the storage tank) together with the adsorbent material's properties. However, there are no systematic studies available mapping simultaneously the various thermal properties, i.e., the thermal conductivity, the heat capacity, and the thermal expansion coefficient, of MOFs. Except for the thermal stability, which is typically measured for every new material,¹⁰ experimental and even computational data about these properties are mainly limited to the well-known MOFs. This is in sharp contrast to gas adsorption, catalytic, and even mechanical properties. For these properties, large-scale computational screenings of structures have pinpointed important structure–property relations,^{25,26} whereas studies of thermal properties remain limited to toy models^{13,27} or very specific classes of MOFs.²⁸

Motivated by this, we evaluated the thermal conductivity, the isobaric specific heat capacity, and the volumetric thermal expansion coefficient from a molecular perspective, by applying molecular simulation techniques to a diverse set of materials representing widely studied classes of rigid MOFs for storage applications ([Figure 1](#)).² We included examples with the most important inorganic building blocks, such as the copper-paddle

wheel (HKUST-1³⁰ and MOF-505³¹) and ZnO_4 (MOF-5,³⁴ MOF-177,³⁵ and UMCM-1³⁶). Furthermore, we selected UiO-66³³ and Al-soc-MOF-1²⁹ to represent the Zr-based and Al-based MOFs, respectively. The set under study includes a number of MOFs for which experimental data on thermal properties have been reported ([Table S2](#)).^{14,38–44} To investigate the effect of elongating the organic linkers, we also tested IRMOF-10 and IRMOF-16 as longer linker equivalents of MOF-5 (i.e., IRMOF-1).⁴⁵ The key goal is to obtain insight into how the overall thermal properties are affected by the nanoscale design. In this way, we present the first systematic study of these important properties, giving a broader view on the thermal performance of MOFs and their associated limitations. Additionally, we present a materials property chart, where the thermal properties of MOFs are visualized alongside other classes of materials, such as metals, polymers, and ceramics.

Based on the thermal properties obtained at the molecular level, we, furthermore, propose a thermodynamic cycle to estimate how adsorption impacts the temperature of the adsorbent. This thermodynamic cycle mimics the initial charging process and allows quantifying an upper bound for the intrinsic temperature rise of the system resulting from the release of the heat of adsorption. We investigate the influence of adsorbing the most important greenhouse and energy-related gases (CO_2 and CH_4) on the material's temperature by applying our protocol on the same set of MOFs, while probing the impact of the intrinsic thermal properties of the MOF on the observed behavior.

2. COMPUTATIONAL METHODS

2.1. Force-Field Derivation. As the computational cost of extracting the thermal properties of MOFs with first-principles molecular dynamics techniques is too high, we instead rely on force-field simulations. Therefore, new system-specific force fields were derived from first-principles cluster data for all MOFs under study. To that end, the quantum mechanical potential energy surface is approximated by a sum of analytic functions of the nuclear coordinates that describe the covalent, electrostatic, and van der Waals interactions. The covalent interactions were fitted using QuickFF,^{46,47} an in-house developed protocol for deriving force fields from first-principles input that has been tested for its adequacy in describing structural, vibrational, mechanical, and thermal properties of MOFs. The underlying idea of QuickFF is to mimic the quantum mechanical potential energy surface in the neighborhood of the equilibrium structure, which is defined by the provided optimized geometry and Hessian, by fitting the unknown parameters featuring in the covalent interactions. The electrostatic interactions were modeled by a Coulomb interaction between Gaussian charge distributions. The van der Waals interactions were described by the MM3-Buckingham model⁴⁸ up to a finite cutoff of 12 Å and were supplemented with tail corrections.

The required first-principles data for the determination of the covalent terms were generated with Gaussian 16⁴⁹ using the B3LYP⁵⁰ exchange-correlation functional. The 6-311G(d,p) basis set⁵¹ was used for the H, C, O, Al, and Cu atoms, together with the LanL2DZ basis set for Zn and Al.⁵² The atomic charges were derived with the Minimal Basis Iterative Stockholder (MBIS) partitioning scheme⁵³ from the all-electron density obtained with Gaussian 16. The MBIS atomic charges of the Zn- and Zr-clusters were obtained from the PBE⁵⁴ all-electron density computed with GPAW.⁵⁵ The cluster models for the different MOFs under study are shown in Figures S1–S4. A similar approach was followed for CH₄ and CO₂.

More details on the force-field energy expression, derivation, and validation can be found in SI Section S1. The force fields and input structures are also added to the Supporting Information.

2.2. Molecular Dynamics Simulations. To compute the heat capacity and thermal expansion coefficient, Suzuki–Chin (SC) path integral molecular dynamics (PIMD) simulations^{56,57} were performed at a controlled mechanical pressure of 1 bar and at different temperatures in the range of 100–600 K. PIMD is the method of choice to calculate the equilibrium properties of distinguishable particles with inclusion of nuclear quantum effects at a finite temperature by mapping the quantum partition function onto the classical partition function of an extended system of interacting replicas.⁵⁸ Nevertheless, the inclusion of nuclear quantum effects in molecular dynamics typically comes at a large computational cost. Hence, cost-reduction techniques are required to enable simulations on large systems, such as guest-loaded MOFs.⁵⁷ In this study, we used a combination of multiple-time stepping and ring-polymer contraction to reduce the number of force evaluations⁵⁹ together with the Suzuki–Chin high-order factorization of the quantum partition function to reduce the number of necessary replicas.⁵⁶ The simulations were performed with the universal force engine, i-PI,^{60,61} a code that efficiently implements PIMD in the appropriate thermodynamic ensemble. The evaluation of the forces is carried out by other external codes: the covalent interactions are computed with our in-house Yaff code⁶² and the long-range interactions are evaluated with LAMMPS.⁶³

These SC PIMD simulations were used to determine the thermal properties, following the procedure of ref 57. In this advanced PIMD scheme,⁵⁸ all important effects related to the anharmonic and quantum nature of the atomic movements are accounted for, which is necessary to obtain a reliable heat capacity estimate in the presence of guests.^{57,64}

Furthermore, the Green–Kubo approach^{65,66} was used to compute the classical thermal conductivity of the empty frameworks. This method provides a relation between a transport coefficient (thermal conductivity) and an integral over a time-correlation function (heat

flux) and is based on the fluctuation–dissipation theorem in nonequilibrium statistical mechanics. This formalism yields a method capable of obtaining a transport property from a simulation of a system in thermodynamic equilibrium. In our case, the thermal conductivity is extracted from the heat current autocorrelation function (HCACF). Data used to approximate this property are collected from hundred independent simulations in the classical microcanonical ensemble (NVE) performed with LAMMPS. To obtain the thermal conductivity at room temperature, the system has to be equilibrated first at the desired temperature in the $NV(\bar{h}_0)/T$ ensemble⁶⁷ before going over to the NVE ensemble. The equilibrium crystallographic unit cell at 300 K was taken from the SC PIMD simulations. The simulations were performed on super cells to limit finite size effects.⁶⁸ The same approach as that applied on MOF-5 by McGaughey et al. was followed to estimate the thermal conductivity from the HCACF.^{69,70}

More details on the molecular dynamics simulations are provided in SI Section S2. A comparison of the simulated thermal properties with experiment is tabulated in Table S2.

2.3. Thermodynamic Cycle. A detailed thermodynamic analysis of our hypothetical cycle is presented in SI Section S3. The main ingredients that need to be computed using molecular simulations are the heat capacity of the guest-loaded structure (see the previous section) and the total heat of adsorption when the empty MOF adsorbs n guest molecules at a temperature T . To compute the latter, we note that this can be written as (SI Section S3)

$$\Delta H_{\text{ib}} = \Delta U^S(0 \rightarrow n) + P\Delta V^S(0 \rightarrow n) - n(U_T^R(1) + k_B T) \quad (1)$$

The first term in this expression, i.e., $\Delta U^S(0 \rightarrow n)$, is the change in internal energy of the thermodynamic system S , which corresponds to the difference in energy between the guest-loaded MOF and the empty MOF under isothermal–isobaric conditions. The second term is typically rather small and is associated with the mechanical work determined by the product of the controlled mechanical pressure P and the change in volume ΔV of the system when adsorbing n guest molecules. Both terms can straightforwardly be extracted from the SC PIMD simulations required for the heat capacity of the empty and guest-loaded MOF. The last term coincides with the enthalpy change of an ideal gas reservoir R , from which n gas molecules are removed. The internal energy $U_T^R(1)$ can be found by performing a SC PIMD simulation on a single gas molecule at a temperature T .

Four different loadings of CH₄ and CO₂ are considered to enable a consistent comparison between the different MOFs, namely, 20, 50, 75, and 100% of the equilibrium loading at 300 K and 100 bar. This high-pressure loading was computed using Grand Canonical Monte Carlo (GCMC) simulations with RASPA.⁷¹ Snapshots from these GCMC simulations were subsequently used in the SC PIMD simulations of the guest-loaded MOFs. More details on the GCMC simulations and a comparison with experimental isotherms can be found in SI Section S3.2.

3. RESULTS AND DISCUSSION

3.1. Thermal Properties of MOF Adsorbents. Before comparing the properties of MOFs with other classes of materials, such as metals, polymers, and ceramics, the three investigated thermal properties are discussed separately for our diverse set of MOFs.

3.1.1. Thermal Conductivity. Heat dissipation and efficient thermal transport are big issues in the context of storage applications with charge and discharge cycles.^{2,73} Hence, the low thermal conductivity of MOFs is perceived as a fundamental problem of the materials. The main origins of the bad thermal conductance in MOFs are known and result from the intrinsic chemical diversity and porosity.^{13,74,75} Chemical diversity or heterogeneity introduces a mismatch between atomic masses and bond strengths, which results in phonon scattering. Moreover, the large empty voids hinder the

Table 1. Structural and Thermal Properties of a Number of MOFs^a

material	Al-soc-MOF-1	HKUST-1	MOF-505	UiO-66	MOF-5	IRMOF-10	IRMOF-16	UMCM-1	MOF-177
ρ (kg m ⁻³)	343	851	888	1162	555	304	193	366	406
ASA (m ² g ⁻¹)	5016	2229	2423	1246	3894	5230	6123	4584	4899
void fraction (%)	80	66	64	47	77	86	90	83	80
κ (W m ⁻¹ K ⁻¹)	0.22	0.45	1.16–1.26	0.87	0.29	0.09	0.07	0.07–0.13	0.08–0.09
C_p (J kg ⁻¹ K ⁻¹)	1051	774	800	758	786	860	913	865	894
β_V (10 ⁻⁶ K ⁻¹)	-19	-15	-17	-9	-41	-48	-52	-47	-39

^aThe structural properties (density ρ , accessible surface area (ASA), and probe-occupiable void fraction) were derived from the optimal structure at 0 K using Zeo++⁷² (N₂ probe molecule with kinetic diameter 3.64 Å). The thermal properties are simulated at room temperature (300 K): thermal conductivity κ , isobaric heat capacity C_p , and volumetric thermal expansion coefficient β_V . A comparison of the simulated thermal properties with experiments is tabulated in Table S2.

efficient propagation of phonons through the porous crystal structures. While a high thermal conductivity for these materials might, therefore, not be realistic, it should be possible to identify structural and chemical descriptors that describe the best-performing frameworks.

The thermal conductivity is often defined through the empirical Fourier's law for heat conduction

$$\vec{q} = -\bar{\kappa} \cdot \nabla T \quad (2)$$

where $\vec{q}$ is the local heat flux density, ∇T is the local temperature gradient, and $\bar{\kappa}$ is the second-order thermal conductivity tensor. The thermal conductivity coefficient can depend on the crystal direction in MOFs,¹³ but most structures in our set are isotropic and can be described by one thermal conductivity coefficient (Table 1). For MOF-505, UMCM-1, and MOF-177, we have indicated the limited spread on the coefficients due to the anisotropic cell directions in Table 1.

Within the class of MOFs, there are some important trends to be noted in Figure 2 regarding κ . First, to systematically investigate the effect of elongating the linkers or increasing the size of the pores, IRMOF-10 and IRMOF-16 were compared with MOF-5 (blue dotted line). As the low thermal conductivity of MOFs mainly stems from the large empty voids, it is not a surprise that the coefficient of heat conduction decreases with increasing linker length. Indeed, it goes down

from MOF-5 toward IRMOF-16, in line with the toy model predictions of Babaei et al.¹³

The suggested correlation between the size of the pores and the thermal conductivity appears to be relatively independent of the underlying chemical structure. MOFs with a density below 500 kg m⁻³ have ultralow thermal conductivities. Unfortunately, these are the most porous frameworks, which can store the largest amount of gas at high pressure (see textural properties in Table 1). Moreover, MOF-5, HKUST-1, and UiO-66 have a similar linker length in between the inorganic nodes, but their performance seems to be solely dominated by the density. MOF-505 with copper-paddle wheels in the popular NbO-topology has a significantly higher value than the other frameworks and could be an interesting topology with improved thermal characteristics to start from.

3.1.2. Specific Heat Capacity. Another thermal property that has been recognized to influence the actual performance of adsorption-based technologies is the heat capacity. As mentioned in the Introduction, for applications based on TSA, a low value is desired as the adsorbent heat capacity largely affects the energy penalty to heat the system to the regeneration temperature. In contrast, for PSA processes, a high adsorbent heat capacity is beneficial, as it limits the temperature peaks during charging and discharging.^{15,76}

The specific heat capacity (J kg⁻¹ K⁻¹) describes the amount of energy required to increase the material's temperature and is defined as

$$C_p = \frac{1}{M} \left(\frac{\partial H}{\partial T} \right)_p \quad (3)$$

where H is the molar enthalpy of the system and M is the molar mass. It has previously been measured for a selected number of MOFs,^{14,39,40} and these reported values suggested a specific heat capacity in between 700 and 1000 J kg⁻¹ K⁻¹ at room temperature.⁷⁷ It is sensitive to the temperature and can change by more than 65% in the interval between 200 and 400 K.⁵⁷

The results in Table 1 are evidently in line with the proposed experimental range (and with the available experimental results (Figure S5)). Figure 2 shows that MOFs possessing the lowest density, i.e., Al-soc-MOF-1, MOF-177, and UMCM-1, have a larger specific heat capacity. This is also reflected in the IRMOF-series. The inverse correlation between specific heat capacity on a mass basis and the density is also found in regular solids (Figure S13). A different picture emerges when considering the volumetric heat capacity ($=\rho C_p$, Figure S7), where the most porous frameworks possess the lowest value and vice versa.

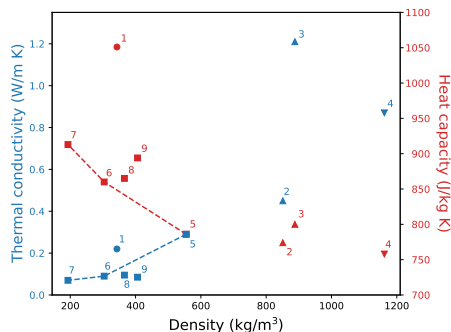


Figure 2. Thermal conductivity (blue) and heat capacity (red) as a function of the density at room temperature. The markers indicate the inorganic node: Zr₆O₈H₄ (down-triangle), ZnO₄ (square), Cu₆O₈ (up-triangle), and Al (circle). The IRMOF-series (MOF-5, IRMOF-10, and IRMOF-16) are connected by a line. 1 = Al-soc-MOF-1, 2 = HKUST-1, 3 = MOF-505, 4 = UiO-66, 5 = MOF-5, 6 = IRMOF-10, 7 = IRMOF-16, 8 = UMCM-1, and 9 = MOF-177.

The aluminum-based Al-soc-MOF-1 has the highest value per gram MOF, which is due to the lighter inorganic node, as compared to zinc, copper, and zirconium, and the presence of a tetratopic linker containing many light atoms. This can be understood by realizing that the specific heat capacity is a measure for the available degrees of freedom on a mass basis.

3.1.3. Thermal Expansion. A third thermal property that needs to be dealt with in applications is the thermal expansion behavior. This is characterized by a volumetric thermal expansion coefficient β_V

$$\beta_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (4)$$

The difference between the thermal expansion coefficients of the materials in contact with the adsorbent bed may give rise to mechanical failure. This thermal expansion mismatch is an important issue that has been mentioned before, mainly in the context of thin-film-based applications of MOFs.⁷⁸ MOFs such as MOF-5 and HKUST-1 even shrink with increasing temperature as opposed to most other materials possessing a positive thermal expansion.^{41,42} However, the studied MOFs (see Table 1) and an increasing number of reports⁷⁹ suggest that negative thermal expansion is not the exception but might be quite common for MOFs. MOFs containing the ZnO_4 inorganic node have notably larger negative thermal expansion coefficients, whereas UiO-66 exhibits a smaller coefficient that might be explained by the higher connectivity of the inorganic nodes. The origin of negative thermal expansion has been investigated for several of these structures (MOF-5, IRMOF-10, IRMOF-16, HKUST-1, and UiO-66).^{28,41,42,80,81} These studies have suggested that low-energy transverse vibrational modes play an important role, and that it strongly depends on the topology of the structure.⁷⁹

3.1.4. Comparison with Other Materials. To put the obtained values for the different properties into perspective, a comparison is made with more common classes of materials, such as metals, ceramics, and polymers.⁸² This is done in the materials property chart in Figure 3, where a two-dimensional representation based on the simulated specific heat capacity and thermal conductivity is shown for the MOFs under study alongside experimental data for other materials (see SI Section

S4). It should be noted that our simulated results contain intrinsic model uncertainties and that they might quantitatively differ from experimental measurements, which have not been available for most MOFs to date. However, in this work, we will mainly focus on qualitative trends. As such, the data undeniably show that MOFs have thermal properties at the crossing of the ceramics, polymers, and hybrid materials (natural materials and composites). More specifically, the MOFs with the lowest thermal conductivity are relatively unique in this set of materials. The ones with the highest value lie in the neighborhood of typical ceramics, such as borosilicate glass ($\kappa \approx 1\text{--}1.3 \text{ W m}^{-1} \text{ K}^{-1}$, $C_p \approx 800 \text{ J kg}^{-1} \text{ K}^{-1}$) and brick ($\kappa \approx 0.45\text{--}0.75 \text{ W m}^{-1} \text{ K}^{-1}$, $C_p \approx 800 \text{ J kg}^{-1} \text{ K}^{-1}$). Finally, Al-soc-MOF-1 compares relatively well with Teflon.

In the Supporting Information, the separate thermal properties are displayed as a function of the density in a comparison with the same materials (Figures S12–S14). This reveals, for instance, that MOFs provide a heat conduction similar to that of natural materials (e.g., softwood) and specific heat capacities on the order of those of foams (e.g., ceramic foam) for the same density. The thermal expansion behavior is rather exceptional. All other material representatives have positive thermal expansion coefficients, whereas the opposite is true for the investigated MOFs. However, the magnitude of the thermal expansion coefficient is quite similar to that of foams. One might envisage the production of composite materials, which behave as zero thermal expansion materials.

Also note that we evaluated all properties on infinite perfect single crystals, whereas in reality, MOFs are loose powders that will have to be shaped using compaction methods.^{83,84} In principle, the single-crystal thermal conductivity should represent an upper limit for the material and should, therefore, be higher than that of the MOF in powder form. Densification of these MOF powders will, in some cases, improve the heat transfer characteristics of the sample (for example, due to plastic deformation), even though the intrinsic properties of the single-crystal material are not changed.¹⁴ In addition, making MOF composites with expanded natural graphite together with compaction was already shown to enhance the thermal properties of the system.^{85–87} To succeed in system integration of MOF powders together with an acceptable thermal performance, engineering approaches beyond improving the intrinsic MOF thermal properties, such as heat exchangers or MOF composites, will have to be developed.^{88–90}

Furthermore, up to now we have focused on the intrinsic thermal properties of the adsorbent in the absence of guests. Of course, in practical applications the pores will often be filled with adsorbates. How this influences all three thermal properties will be the topic of a future study. On the one hand, for the thermal conductivity and the heat capacity, a limited number of isolated case studies are already available.^{57,73,75,91} They show that the influence can be quite drastic, and more studies are required to explain the observed phenomena. On the other hand, guests have been used to tune the thermal expansion behavior of MOFs,^{92,93} which is not limited to the flexible MOFs that display phase transitions and massive volume changes under guest adsorption.^{94,95}

3.2. Thermodynamic Cycle for Adsorption. So far, a clear overview has been obtained for the thermal properties of several MOFs. However, to use the materials in practical applications, this knowledge should be coupled with the adsorption properties of guests. Herein, we focus on the heat

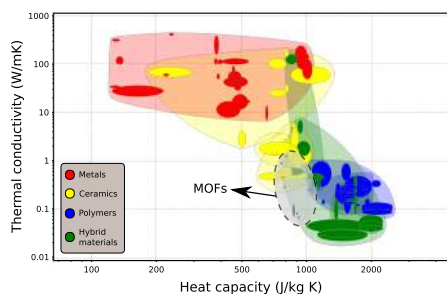


Figure 3. Materials property chart displaying the thermal conductivity and the specific heat capacity of MOFs alongside other classes of materials, namely, metals (and alloys), ceramics (glasses and (non-) technical ceramics), polymers, and hybrid materials (composites, foams, and natural materials). An overview of the used materials is given in the SI.

generated when gas molecules adsorb into the pores of the material. To this end, a hypothetical thermodynamic cycle is presented, which allows predicting the temperature rise within a MOF due to guest adsorption. This quantity depends not only on the intrinsic thermal properties of the adsorbent but also on the guest–host and guest–guest interactions of the adsorbates. This hybrid, computational descriptor could be used in future screenings to probe the thermal performance of a framework.

This thermodynamic cycle starts from an empty MOF at temperature T and ends at a guest-loaded final state at a higher temperature $T + \Delta T$. We consider an idealized scenario in which the framework instantaneously adsorbs the guest molecule as well as instantaneously absorbs the resulting heat of adsorption. During the actual filling process, a complex dynamical combination of mass and thermal transport takes place at the molecular level, which was nicely divided into different phenomena by Babaei et al.⁹⁶ We do not include interface effects but investigate how the bulk material will thermally respond to the adsorption of guest molecules. At the system's level (i.e., including equipment different than the adsorbent), other effects such as compression work and thermal mass from the inlet can play a role.⁹⁰ Below, we describe our idealized process and discuss its assumptions. In the Supporting Information (SI Section S3), we present a detailed thermodynamic analysis of our hypothetical cycle.

Figure 4 displays the different steps and thermodynamic states of the thermodynamic cycle. The initial state (the empty MOF adsorbent) adsorbs n guest molecules (1), a step which

evolves under isothermal and isobaric conditions and is subdivided into

- **1a**: the introduction of n noninteracting molecules in the MOF, i.e., neither guest–guest nor guest–host interactions are already present.
- **1b**: the physisorption of n particles (including all physical interactions).

After step **1a**, the thermodynamic system S is thermally isolated and does not allow for mass and heat transfer with the gas reservoir. The internal energy, U , can still change due to the exchange of $P\Delta V$ work. The heat, Q , required during step **2** to increase the temperature with ΔT can be found by integrating the isobaric heat capacity of the guest-loaded MOF from T to $T + \Delta T$.

We consider an adiabatic process **3** (**1b** + **2**), which enables us to calculate ΔT . Based on the first law of thermodynamics, we can write the following integral equation for the unknown ΔT

$$-\Delta H_{1b} = \Delta H_2 = Q = \int_T^{T+\Delta T} C_p(\mathcal{T}; n) d\mathcal{T} \quad (5)$$

This equation emphasizes the importance of the heat capacity of the adsorbent including adsorbates $C_p(\mathcal{T}; n)$.⁵⁷ As discussed in the Computational Methods Section, all relevant quantities can be extracted from SC PIMD simulations.

In other words, the heat of adsorption released due to the stabilizing guest–host and guest–guest interactions is subsequently used to heat up the thermodynamic system and to increase the temperature during step **2**. We assume adiabatic walls, as this process happens very rapidly, with fast temperature rises.¹⁹ This assumption is supported by a molecular simulation study by Babaei et al.⁹⁶ They showed that the conduction of the heat generated due to adsorption is faster than the diffusion of the guest molecules, making the temperature spatially uniform at any time. The heat can, however, not easily be transferred to the pure gas region in contact with the MOF interface due to the high thermal resistance at this interface. They concluded that the interface presents a bottleneck, making the heat transfer to the surroundings a slow process. Similarly, Beckner and Dailly experimentally observed, in a pilot-scale study for vehicular storage, temperature peaks of 30 K when adsorbing methane at 40 bar and a temperature which only equilibrated after 2 h.¹⁹

The assumption of an adiabatic process presents an ideal limiting case, which will result in an upper bound for a temperature rise at the material's level. The other extreme case is the isothermal process, where the heat is immediately dissipated through its surroundings. In practice, heat exchangers in contact with the adsorbent bed are used to steer the process toward the latter, as this results in a more efficient (dis)charging process.

We display the most important results for our thermodynamic cycle in Figure 5. This graph indicates the increasing temperature ($T + \Delta T$) as a function of loading for our set of materials based on guest-loaded MOF simulations. We find a temperature rise ΔT ranging from 100 to 250 K depending on the framework and the adsorbate at a high-pressure loading of 100 bar. Figure 5 shows that CH_4 has less influence on the material's temperature than CO_2 . It should be noted that more CO_2 molecules are adsorbed than CH_4 at the same gas pressure (Table S5). The copper-paddle wheel MOFs, HKUST-1 and MOF-505, have the highest increase for

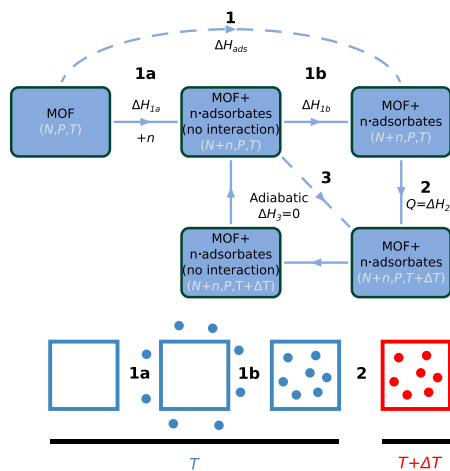


Figure 4. Definition of our hypothetical thermodynamic cycle. After step **1**, n guest molecules are adsorbed in the MOF (N atoms) under isothermal (T) and isobaric (P) conditions. This step is subdivided into two parts. First (**1a**), n noninteracting particles are introduced in the MOF. Subsequently, these guests are physisorbed in **1b**. During step **2**, the released heat of adsorption is used to heat up the thermodynamic system to a temperature $T + \Delta T$. We assume that **1b** + **2** = **3** proceeds adiabatically. Molecular simulations are performed to obtain the relevant quantities.

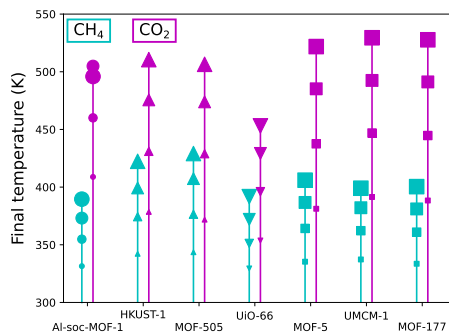


Figure 5. Temperature rise of MOFs when adsorbing CH₄ (cyan) and CO₂ (magenta) at 300 K. The size of the symbols increases with the loading and represents 25, 50, 75, and 100% of the loading at 300 K and 100 bar. The markers indicate the inorganic node: Zr₆O₈H₄ (down-triangle), ZnO₄ (square), CuC₄O₈ (up-triangle), and Al (circle). The numerical results of these data are presented in Table S5.

methane, whereas the Zn-MOFs (MOF-5, UMCM-1, and MOF-177) respond the most to CO₂. UiO-66 has the lowest increase in temperature for both adsorbates. These trends are already visible at lower loadings (25% of the high-pressure loading), and ΔT in general keeps increasing with loading. Although this temperature increase is an idealized upper bound, its magnitude is indicative of the huge temperature fluctuations that are associated with gas adsorption. For some MOFs, it is even on the same order as their decomposition temperature (e.g., 550 K for HKUST-1³⁹) in the case of 100 bar CO₂ adsorption.

Now it becomes possible to assess whether improving the heat capacity is a viable and realistic strategy to reduce the temperature peaks during (dis)charging. Figure 6 displays the correlation between the heat of adsorption ($-\Delta H_{\text{ad}}$) (on a mass basis) and the temperature increase ΔT of the

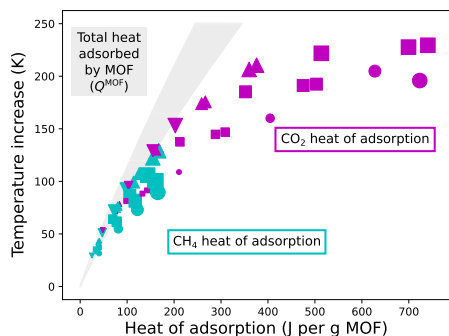


Figure 6. Temperature increase (starting from 300 K) after adsorbing CH₄ and CO₂ as a function of the heat of adsorption. The size of the symbols increases with the loading and represents 25, 50, 75, and 100% of the loading at 300 K and 100 bar. The markers indicate the inorganic node: Zr₆O₈H₄ (down-triangle), ZnO₄ (square), CuC₄O₈ (up-triangle), and Al (circle). The gray shaded area indicates the total heat that can be adsorbed by the MOF.

thermodynamic system containing adsorbent and adsorbates. The symbol size and shape refer to the number of adsorbates and the type of framework, respectively. It comes as no surprise that the temperature rise increases with increasing heat of adsorption. Furthermore, as methane has weaker guest–guest and guest–host interactions than CO₂, the released heat is lower and so is ΔT , as observed above.

To understand how much heat the framework atoms can absorb, we focus here on the heat capacity of the empty framework. The gray shaded area covers the specific heat Q^{MOF} that the MOFs under study can intrinsically absorb (based on the empty framework simulations) according to the following relation:

$$Q^{\text{MOF}}(\Delta T) = \int_{300}^{300+\Delta T} C_p^{\text{MOF}}(T) dT \quad (6)$$

with Q^{MOF} on the horizontal axis and ΔT on the vertical axis of Figure 6. This is a good approximation, as the presence of guests does not significantly modify the contribution of the MOF to the heat capacity.⁵⁷ Hence, the horizontal distance between the gray area and the simulated results illustrates how much heat of adsorption is captured by the adsorbates in the pores. For most loadings of CO₂, this is significantly more than the heat absorbed by the framework itself. The mixture of guests inside the pores, thus, dominates the total heat capacity and, thus, controls the temperature rise. The narrow range of observed heat capacities for MOFs does not offer much potential in limiting temperature spikes by optimizing within the space of known MOFs. Interesting is also the apparent plateau in ΔT for the heat of adsorption in a wide range between 500 and almost 800 J per gram MOF. This suggests that the additional heat of adsorption beyond 500 J g^{−1} MOF can be stored rather efficiently by the inter- and intramolecular interactions of the adsorbates.

Nevertheless, it is clear that for weaker interacting molecules, such as methane, most heat can be adsorbed by the framework. This can be understood by the fact that the gray shaded area is close to the simulated methane-loaded data. However, in this region, the narrow spread on the performance of the diverse set of MOFs again suggests that selecting a MOF with a higher heat capacity within the currently known range will only have a minor impact on the temperature peaks. This will probably also be the case when the adsorbent is coupled with a heat exchanger.

Overall, the analysis thus indicates that replacing a MOF by another MOF with similar adsorption properties but with a higher heat capacity in the studied range will not significantly modify the performance. Rather, new frameworks should be constructed to extend the width of the gray area toward the right, such that the materials are capable of absorbing more heat. As we showed that MOFs are relatively clustered in the materials property chart for thermal properties, conceptually new structures should be devised.

4. CONCLUSIONS

MOFs have been recognized as promising adsorbents. It has been envisioned that these materials will play a key role in adsorption-based technologies such as natural gas storage. However, an actual system is also subjected to thermal effects, as adsorption and desorption processes involve the release or consumption of energy. This will result in large temperature changes that have a detrimental effect on the desired

performance. Engineering strategies exist that can reduce these effects; however, so far it has been unclear as to what extent the intrinsic thermal properties play a role in the thermal effects of the overall process.

In this work, we assessed the thermal conductivity, heat capacity, and thermal expansion of a diverse set of MOFs using molecular simulation methods and indicated how important characteristics such as the density and the chemical nature of their inorganic building blocks influence them. We showed that the thermal conductivity and heat capacity of MOFs are generally low in comparison to other standard materials and that it will be difficult to fundamentally improve the material's properties. The negative thermal expansion behavior of MOFs has already been reported for various structures and was found here as well for a diverse set.

We used the knowledge of these intrinsic thermal properties to estimate as to what extent the temperature of the material would rise when adsorbing CH₄ and CO₂. To this end, a hypothetical thermodynamic cycle was proposed that relies on macroscopic quantities found through simulations at the molecular level. Our thermodynamic considerations reveal significant temperature increases at the material's level. This quantity itself is a relevant materials parameter balancing both thermal and adsorption properties in MOFs. In this way, it was clear that the adsorption of CO₂ has much more impact on the temperature than that of the weaker interacting CH₄. Furthermore, by visualizing the correlation between the increase in temperature and the heat of adsorption, we were able to assess the relevance of the heat capacity of the framework and note its limited impact. Our simulations suggest that selecting a MOF with a higher heat capacity would only be a viable strategy if new and improved MOFs are synthesized.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12533.

Force-field parameters and input structures are added separately (ZIP)

More details on the force-field energy expression, derivation, and validation (Section S1); methods used to calculate the thermal properties (Section S2); thermodynamic cycle (Section S3) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Fund for Scientific Research Flanders (FWO). V.V.S. acknowledges funding from the European Union's Horizon 2020 research and innovation program (consolidator ERC grant agreement No. 647755—

DYNPOR (2015-2020)). This work is furthermore supported by the Research Board of Ghent University (BOF). The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by Ghent University, FWO, and the Flemish Government department EWI. V.K. acknowledges financial support by the Swiss National Science Foundation (project ID 200021–159896).

■ REFERENCES

- (1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, No. 1230444.
- (2) He, Y.; Chen, F.; Li, B.; Qian, G.; Zhou, W.; Chen, B. Porous Metal-Organic Frameworks for Fuel Storage. *Coord. Chem. Rev.* **2017**, *373*, 167–198.
- (3) Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H.-C. Recent Advances in Gas Storage and Separation Using Metal-Organic Frameworks. *Mater. Today* **2018**, *21*, 108–121.
- (4) Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Mac Dowell, N.; Fernández, J. R.; Ferrari, M.-C.; Gross, R.; Hallett, J. P.; Haszeldine, R. S.; Heptonstall, P.; Lyngfelt, A.; Makuch, Z.; Mangano, E.; Porter, R. T. J.; Pourkashanian, M.; Rochelle, G. T.; Shah, N.; Yao, J. G.; Fennell, P. S. Carbon Capture and Storage Update. *Energy Environ. Sci.* **2014**, *7*, 130–189.
- (5) Chu, S.; Cui, Y.; Liu, N. The Path Towards Sustainable Energy. *Nat. Mater.* **2017**, *16*, 16–22.
- (6) Silva, P.; Vilela, S. M. F.; Tomé, J. P. C.; Almeida Paz, F. A. Multifunctional Metal-Organic Frameworks: From Academia to Industrial Applications. *Chem. Soc. Rev.* **2015**, *44*, 6774–6803.
- (7) Beckner, M.; Dailly, A. Adsorbed Methane Storage for Vehicular Applications. *Appl. Energy* **2015**, *149*, 69–74.
- (8) Rubio-Martínez, M.; Avci-Camur, C.; Thornton, A. W.; Imaz, I.; Maspocho, D.; Hill, M. R. New Synthetic Routes Towards MOF Production at Scale. *Chem. Soc. Rev.* **2017**, *46*, 3453–3480.
- (9) DeSantis, D.; Mason, J. A.; James, B. D.; Houchins, C.; Long, J. R.; Veenstra, M. Techno-economic Analysis of Metal-Organic Frameworks for Hydrogen and Natural Gas Storage. *Energy Fuels* **2017**, *31*, 2024–2032.
- (10) Howarth, A. J.; Liu, Y.; Li, P.; Li, Z.; Wang, T. C.; Hupp, J. T.; Farha, O. K. Chemical, Thermal and Mechanical Stabilities of Metal-Organic Frameworks. *Nat. Rev. Mater.* **2016**, *1*, No. 15018.
- (11) de Lange, M. F.; Ottevanger, C. P.; Wiegman, M.; Vlucht, T. J. H.; Kapteijn, F. Crystals for Sustainability - Structuring Al-based MOFs for the Allocation of Heat and Cold. *CrystEngComm* **2015**, *17*, 281–285.
- (12) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; Llewellyn, P. L.; Masciocchi, N.; Long, J. R. Methane Storage in Flexible Metal-Organic Frameworks with Intrinsic Thermal Management. *Nature* **2015**, *527*, 357–361.
- (13) Babaei, H.; McGaughey, A. J. H.; Wilmer, C. E. Effect of Pore Size and Shape on the Thermal Conductivity of Metal-Organic Frameworks. *Chem. Sci.* **2017**, *8*, 583–589.
- (14) Ming, Y.; Purewal, J.; Liu, D.; Sudik, A.; Xu, C.; Yang, J.; Veenstra, M.; Rhodes, K.; Soltis, R.; Warner, J.; Gaab, M.; Müller, U.; Siegel, D. J. Thermophysical Properties of MOF-5 Powders. *Microporous Mesoporous Mater.* **2014**, *185*, 235–244.
- (15) Makal, T. A.; Li, J.-R.; Lu, W.; Zhou, H.-C. Methane Storage in Advanced Porous Materials. *Chem. Soc. Rev.* **2012**, *41*, 7761–7779.
- (16) Mason, J. A.; Veenstra, M.; Long, J. R. Evaluating Metal-Organic Frameworks for Natural Gas Storage. *Chem. Sci.* **2014**, *5*, 32–51.
- (17) Li, B.; Wen, H.-M.; Zhou, W.; Xu, J. Q.; Chen, B. Porous Metal-Organic Frameworks: Promising Materials for Methane Storage. *Chem* **2016**, *1*, 557–580.

- (18) Chang, K. J.; Talu, O. Behavior and Performance of Adsorptive Natural Gas Storage Cylinders During Discharge. *Appl. Therm. Eng.* **1996**, *16*, 359–374.
- (19) Beckner, M.; Dailly, A. A Pilot Study of Activated Carbon and Metal-Organic Frameworks for Methane Storage. *Appl. Energy* **2016**, *162*, 506–514.
- (20) Mason, J. A.; Sumida, K.; Herm, Z. R.; Krishna, R.; Long, J. R. Evaluating Metal-Organic Frameworks for Post-Combustion Carbon Dioxide Capture via Temperature Swing Adsorption. *Energy Environ. Sci.* **2011**, *4*, 3030–3040.
- (21) Trickett, C. A.; Helal, A.; Al-Maythaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The Chemistry of Metal-Organic Frameworks for CO₂ Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017**, *2*, No. 17045.
- (22) Schoedel, A.; Ji, Z.; Yaghi, O. M. The Role of Metal-Organic Frameworks in a Carbon-Neutral Energy Cycle. *Nat. Energy* **2016**, *1*, No. 16034.
- (23) Chakraborty, A.; Kumar, S. Thermal Management and Desorption Modeling of a Cryo-Adsorbent Hydrogen Storage System. *Int. J. Hydrogen Energy* **2013**, *38*, 3973–3986.
- (24) Xiao, J.; Hu, M.; Bénard, P.; Chahine, R. Simulation of Hydrogen Storage Tank Packed with Metal-Organic Framework. *Int. J. Hydrogen Energy* **2013**, *38*, 13000–13010.
- (25) Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q. Large-Scale Screening of Hypothetical Metal-Organic Frameworks. *Nat. Chem.* **2012**, *4*, 83–89.
- (26) Moghadam, P. Z.; Rogge, S. M. J.; Li, A.; Chow, C.-M.; Wieme, J.; Moharrami, N.; Aragones-Anglada, M.; Conduit, G.; Gomez-Gualdron, D. A.; Van Speybroeck, V.; Fairen-Jimenez, D. Structure-Mechanical Stability Relations of Metal-Organic Frameworks via Machine Learning. *Matter* **2019**, *1*, 219–234.
- (27) Sezginel, K. B.; Asinger, P. A.; Babaei, H.; Wilmer, C. E. Thermal Transport in Interpenetrated Metal-Organic Frameworks. *Chem. Mater.* **2018**, *30*, 2281–2286.
- (28) Dubbeldam, D.; Walton, K. S.; Ellis, D. E.; Snurr, R. Q. Exceptional Negative Thermal Expansion in Isoreticular Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2007**, *46*, 4496–4499.
- (29) Alezi, D.; Belmabkhout, Y.; Suyetin, M.; Bhatt, P. M.; Weslinski, L. J.; Solovyeva, V.; Adil, K.; Spanopoulos, I.; Trikalitis, P. N.; Emwas, A.-H.; Eddaoudi, M. MOF Crystal Chemistry Paving the Way to Gas Storage Needs: Aluminum-Based soc-MOF for CH₄, O₂, and CO₂ Storage. *J. Am. Chem. Soc.* **2015**, *137*, 13308–13318.
- (30) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, G. A.; Williams, I. D. A Chemically Functionalizable Nanoporous Material [Cu₃(TMA)₂(H₂O)₃]_n. *Science* **1999**, *283*, 1148–1150.
- (31) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. High H₂ Adsorption in a Microporous Metal-Organic Framework with Open Metal Sites. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745–4749.
- (32) Lin, X.; Jia, J.; Zhao, X.; Thomas, M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. High H₂ Adsorption by Coordination-Framework Materials. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358–7364.
- (33) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.
- (34) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. *Nature* **1999**, *402*, 276–279.
- (35) Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O’Keeffe, M.; Yaghi, O. M. A Route to High Surface Area, Porosity and Inclusion of Large Molecules in Crystals. *Nature* **2004**, *427*, 523–527.
- (36) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. A Crystalline Mesoporous Coordination Copolymer with High Microporosity. *Angew. Chem., Int. Ed.* **2008**, *47*, 677–680.
- (37) Dubbeldam, D.; Calero, S.; Vlugt, T. J. H. iRASP: GPU-Accelerated Visualization Software for Materials Scientists. *Mol. Simul.* **2018**, *44*, 653–676.
- (38) Huang, B. L.; Ni, Z.; Millward, A.; McGaughey, A. J. H.; Uher, C.; Kaviani, M.; Yaghi, O. M. Thermal Conductivity of a Metal-Organic Framework (MOF-5): Part II. Measurement. *Int. J. Heat Mass Transfer* **2007**, *50*, 405–411.
- (39) Mu, B.; Walton, K. S. Thermal Analysis and Heat Capacity Study of Metal-Organic Frameworks. *J. Phys. Chem. C* **2011**, *115*, 22748–22754.
- (40) Kloutse, F. A.; Zacharia, R.; Cossement, D.; Chahine, R. Specific Heat Capacities of MOF-5, Cu-BTC, Fe-BTC, MOF-177 and MIL-53(Al) over Wide Temperature Ranges: Measurements and Application of Empirical Group Contribution Method. *Microporous Mesoporous Mater.* **2015**, *217*, 1–5.
- (41) Lock, N.; Wu, Y.; Christensen, M.; Cameron, L. J.; Peterson, V. K.; Bridgeman, A. J.; Kepert, C. J.; Iversen, B. B. Elucidating Negative Thermal Expansion in MOF-5. *J. Phys. Chem. C* **2010**, *114*, 16181–16186.
- (42) Wu, Y.; Kobayashi, A.; Halder, G. J.; Peterson, V. K.; Chapman, K. W.; Lock, N.; Southon, P. D.; Kepert, C. J. Negative Thermal Expansion in the Metal-Organic Framework Material Cu₃(1,3,5-benzenetricarboxylate)_n. *Angew. Chem., Int. Ed.* **2008**, *47*, 8929–8932.
- (43) Erickson, K. J.; Léonard, F.; Stavila, V.; Foster, M. E.; Spataru, C. D.; Jones, R. E.; Foley, B. M.; Hopkins, P. E.; Allendorf, M. D.; Talin, A. A. Thin Film Thermoelectric Metal-Organic Framework with High Seebeck Coefficient and Low Thermal Conductivity. *Adv. Mater.* **2015**, *27*, 3453–3459.
- (44) Huang, J.; Xia, X.; Hu, X.; Li, S.; Liu, K. A General Method for Measuring the Thermal Conductivity of MOF Crystals. *Int. J. Heat Mass Transfer* **2019**, *138*, 11–16.
- (45) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, *295*, 469–472.
- (46) Vanduyfhuys, L.; Vandenbrande, S.; Verstraeten, T.; Schmid, R.; Waroquier, M.; Van Speybroeck, V. QuickFF: A Program for a Quick and Easy Derivation of Force Fields for Metal-Organic Frameworks from Ab Initio Input. *J. Comput. Chem.* **2015**, *36*, 1015–1027.
- (47) Vanduyfhuys, L.; Vandenbrande, S.; Wieme, J.; Waroquier, M.; Verstraeten, T.; Van Speybroeck, V. Extension of the QuickFF Force Field Protocol for an Improved Accuracy of Structural, Vibrational, Mechanical and Thermal Properties of Metal-Organic Frameworks. *J. Comput. Chem.* **2018**, *39*, 999–1011.
- (48) Lii, J. H.; Allinger, N. L. Molecular Mechanics. The MM3 Force Field for Hydrocarbons. 3. The van der Waals Potentials and Crystal Data for Aliphatic and Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1989**, *111*, 8576–8582.
- (49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, revision E.01; Gaussian Inc.: Wallingford, CT, 2016.
- (50) Becke, A. D. Density-Functional Theorychemochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

- (51) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. 20. Basis Set for Correlated Wave-Functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (52) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, No. 270.
- (53) Verstraelen, T.; Vandenbrande, S.; Heidari-Zadeh, F.; Vanduythuys, L.; Van Speybroeck, V.; Waroquier, M.; Ayers, P. W. Minimal Basis Iterative Stockholder: Atoms in Molecules for Force-Field Development. *J. Chem. Theory Comput.* **2016**, *12*, 3894–3912.
- (54) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (55) Mortensen, J. J.; Hansen, L. B.; Jacobsen, K. W. Real-Space Grid Implementation of the Projector Augmented Wave Method. *Phys. Rev. B* **2005**, *71*, No. 035109.
- (56) Kapil, V.; Behler, J.; Ceriotti, M. High Order Path Integrals Made Easy. *J. Chem. Phys.* **2016**, *145*, No. 234103.
- (57) Kapil, V.; Wieme, J.; Vandenbrande, S.; Lammaire, A.; Van Speybroeck, V.; Ceriotti, M. Modeling the Structural and Thermal Properties of Loaded Metal-Organic Frameworks. An Interplay of Quantum and Anharmonic Fluctuations. *J. Chem. Theory Comput.* **2019**, *15*, 3237–3249.
- (58) Markland, T. M.; Ceriotti, M. Nuclear Quantum Effects Enter the Mainstream. *Nat. Rev. Chem.* **2018**, *2*, No. 0109.
- (59) Kapil, V.; VandeVondele, J.; Ceriotti, M. Accurate Molecular Dynamics and Nuclear Quantum Effects at Low Cost by Multiple Steps in Real and Imaginary Time: Using Density Functional Theory to Accelerate Wavefunction Methods. *J. Chem. Phys.* **2016**, *144*, No. 054111.
- (60) Ceriotti, M.; More, J.; Manolopoulos, D. E. i-PI: A Python Interface for Ab Initio Path Integral Molecular Dynamics Simulations. *Comput. Phys. Commun.* **2014**, *185*, 1019–1026.
- (61) Kapil, V.; Rossi, M.; Marsalek, O.; Petraglia, R.; Litman, Y.; Spura, T.; Cheng, B.; Cuzzocrea, A.; Meißner, R. H.; Wilkins, D. M.; Juda, P.; Bienvue, S. P.; Fang, W.; Kessler, J.; Poltavsky, I.; Vandenbrande, S.; Wieme, J.; Corninboeuf, C.; Kühne, T. D.; Manolopoulos, D. E.; Markland, T. E.; Richardson, J. O.; Tkatchenko, A.; Tribello, G. A.; Speybroeck, V. V.; Ceriotti, M.; et al. i-PI 2.0: A Universal Force Engine for Advanced Molecular Simulations. *Comput. Phys. Commun.* **2019**, *236*, 214–223.
- (62) Verstraelen, T.; Vanduythuys, L.; Vandenbrande, S.; Rogge, S. M. J. *Yaff 1.4.2*, 2017. <http://molmod.github.io/yaff/index.html>.
- (63) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (64) Lammaire, A.; Wieme, J.; Rogge, S. M. J.; Waroquier, M.; Van Speybroeck, V. On the Importance of Anharmonicities and Nuclear Quantum Effects in Modelling the Structural Properties and Thermal Expansion in MOF-5. *J. Chem. Phys.* **2019**, *150*, No. 094503.
- (65) Green, M. S. Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids. *J. Chem. Phys.* **1954**, *22*, 398–413.
- (66) Kubo, R. Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems. *J. Phys. Soc. Jpn.* **1957**, *12*, 570–586.
- (67) Rogge, S. M. J.; Vanduythuys, L.; Ghysels, A.; Waroquier, M.; Verstraelen, T.; Maurin, G.; Van Speybroeck, V. A Comparison of Barostats for the Mechanical Characterization of Metal-Organic Frameworks. *J. Chem. Theory Comput.* **2015**, *11*, 5583–5597.
- (68) Schelling, P. K.; Phillpot, S. R.; Keblinski, P. Comparison of Atomic-Level Simulation Methods for Computing Thermal Conductivity. *Phys. Rev. B* **2002**, *65*, No. 144306.
- (69) McGaughey, A. J. H.; Kaviany, M. Thermal Conductivity Decomposition and Analysis Using Molecular Dynamics Simulations. Part II. Complex Silica Structures. *Int. J. Heat Mass Transfer* **2004**, *47*, 1799–1816.
- (70) Huang, B. L.; McGaughey, A. J. H.; Kaviany, M. Thermal Conductivity of Metal-Organic Framework 5 (MOF-5): Part I. Molecular Dynamics Simulations. *Int. J. Heat Mass Transfer* **2007**, *50*, 393–404.
- (71) Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. RASPA: Molecular Simulation Software for Adsorption and Diffusion in Flexible Nanoporous Materials. *Mol. Simul.* **2016**, *42*, 81–101.
- (72) Willems, T. F.; Rycroft, C. H.; Kazi, M.; Meza, J. C.; Haraczky, M. Algorithms and Tools for High-Throughput Geometry-Based Analysis of Crystalline Porous Materials. *Micro-porous Mesoporous Mater.* **2012**, *149*, 134–141.
- (73) Cui, B.; Audu, C. O.; Liao, Y.; Nguyen, S. T.; Farha, O. K.; Hupp, J. T.; Grayson, M. Thermal Conductivity of ZIF-8 Thin-Film Under Ambient Gas Pressure. *ACS Appl. Mater. Interfaces* **2017**, *9*, 28139–28143.
- (74) Zhang, X.; Jiang, J. Thermal Conductivity of Zeolitic Imidazolate Framework-8: A Molecular Simulation Study. *J. Phys. Chem. C* **2013**, *36*, 18441–18447.
- (75) Han, L.; Budge, M.; Greaney, A. P. Relationship between Thermal Conductivity and Framework Architecture. *Comput. Mater. Sci.* **2014**, *94*, 292–297.
- (76) Kumar, K. V.; Preuss, K.; Titirici, M.-M.; Rodriguez-Reinoso, F. Nanoporous Materials for the Onboard Storage of Natural Gas. *Chem. Rev.* **2017**, *117*, 1796–1825.
- (77) de Lange, M. F.; Verouden, K. J. F. M.; Vlucht, T. J. H.; Gascon, J.; Kapteijn, F. Adsorption-Driven Heat Pumps: The Potential of Metal-Organic Frameworks. *Chem. Rev.* **2015**, *115*, 12205–12250.
- (78) Stassen, I.; Burch, N. C.; Talin, A.; Falcaro, P.; Allendorf, M.; Ameloot, R. An Updated Roadmap for the Integration of Metal-Organic Frameworks with Electronic Devices and Chemical Sensors. *Chem. Soc. Rev.* **2017**, *46*, 3185–3241.
- (79) Coates, C. S.; Goodwin, A. How to Quantify Isotropic Negative Thermal Expansion: Magnitude, Range, or Both? *Mater. Horiz.* **2019**, *6*, 211–218.
- (80) Lock, N.; Christensen, M.; Wu, Y.; Peterson, V. K.; Thomsen, M. K.; Plitz, R. O.; Ramirez-Cuesta, A. J.; McIntyre, G. J.; Norén, K.; Kutteh, R.; Kepert, C. J.; Kearley, G. J.; Iversen, B. B. Scrutinizing Negative Thermal Expansion in MOF-5 by Scattering Techniques and Ab Initio Calculations. *Dalton Trans.* **2013**, *42*, 1996–2007.
- (81) Cliffe, M. J.; Hill, J. A.; Murray, C. A.; Couderc, F.-X.; Goodwin, A. L. Defect-Dependent Colossal Negative Thermal Expansion in UiO-66(Hf) Metal-Organic Frameworks. *Phys. Chem. Chem. Phys.* **2015**, *17*, 11586–11592.
- (82) Tan, J.-C.; Cheetham, A. K. Mechanical Properties of Hybrid Inorganic-Organic Framework Materials: Establishing Fundamental Structure-Property Relationships. *Chem. Soc. Rev.* **2011**, *40*, 1059–1080.
- (83) Nandasiri, M. I.; Jambovane, S. R.; McGrail, P. B.; Schaeff, H. T.; Nune, S. K. Adsorption, Separation, and Catalytic Properties of Densified Metal-Organic Frameworks. *Coord. Chem. Rev.* **2016**, *311*, 38–52.
- (84) Tian, T.; Zeng, Z.; Vulpe, D.; Casco, M. E.; Divitini, G.; Midgley, P. A.; Silvestre-Albero, J.; Tan, J.-C.; Moghadam, P. Z.; Fairen-Jimenez, D. A Sol-Gel Monolithic Metal-Organic Framework with Enhanced Methane Uptake. *Nat. Mater.* **2018**, *17*, 174–179.
- (85) Purewal, J. J.; Liu, D.; Yang, J.; Sudik, A.; Siegel, D. J.; Maurer, S.; Müller, U. Increased Volumetric Hydrogen Uptake of MOF-5 by Powder Densification. *Int. J. Hydrogen Energy* **2012**, *37*, 2723–2727.
- (86) Purewal, J.; Liu, D.; Sudik, A.; Veenstra, M.; Yang, J.; Maurer, S.; Müller, U.; Siegel, D. J. Improved Hydrogen Storage and Thermal Conductivity in High-Density MOF-5 Composites. *J. Phys. Chem. C* **2012**, *116*, 20199–20212.
- (87) Liu, D.; Purewal, J. J.; Yang, J.; Sudik, A.; Maurer, S.; Müller, U.; Ni, J.; Siegel, D. J. MOF-5 Composites Exhibiting Improved Thermal Conductivity. *Int. J. Hydrogen Energy* **2012**, *37*, 6109–6117.
- (88) Jeremias, F.; Henninger, S. K.; Janiak, C. High Performance Metal-Organic Framework Coatings Obtained via Thermal Gradient Synthesis. *Chem. Commun.* **2012**, *48*, 9708–9710.
- (89) He, Y.; Zhou, W.; Qian, G.; Chen, B. Methane Storage in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, 5657–5678.
- (90) Ren, J.; Langmi, H. W.; North, B. C.; Mathe, M. Review on Processing of Metal-Organic Framework (MOF) Materials towards

System Integration for Hydrogen Storage. *Int. J. Energy Res.* **2015**, *39*, 607–620.

(91) Babaei, H.; Wilmer, C. E. Mechanisms of Heat Transfer in Porous Crystals Containing Adsorbed Gases: Applications to Metal-Organic Frameworks. *Phys. Rev. Lett.* **2016**, *116*, No. 025902.

(92) Balestra, S. R. G.; Bueno-Perez, R.; Hamad, S.; Dubbeldam, D.; Ruiz-Salvador, A. R.; Calero, S. Controlling Thermal Expansion: A Metal-Organic Frameworks Route. *Chem. Mater.* **2016**, *28*, 8296–8304.

(93) Auckett, J. E.; Barkhordarian, A. A.; Ogilvie, S. H.; Duyker, S. G.; Chevreau, H.; Peterson, V. K.; Kepert, C. J. Continuous Negative-to-Positive Tuning of Thermal Expansion Achieved by Controlled Gas Sorption in Porous Coordination Frameworks. *Nat. Commun.* **2018**, *9*, No. 4873.

(94) Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nat. Chem.* **2009**, *1*, 695–704.

(95) Vanduyfhuys, L.; Rogge, S. M. J.; Wieme, J.; Vandenbrande, S.; Maurin, G.; Waroquier, M.; Van Speybroeck, V. Thermodynamic Insight into Stimuli-Responsive Behaviour of Soft Porous Crystals. *Nat. Commun.* **2018**, *9*, No. 204.

(96) Babaei, H.; McGaughey, A. J. H. Transient Mass and Thermal Transport during Methane Adsorption into the Metal-Organic Framework HKUST-1. *ACS Appl. Mater. Interfaces* **2018**, *10*, 2400–2406.



List of Publications

Updated December 2019

Publications in international peer-reviewed journals

1. **Thermal engineering of metal-organic frameworks for adsorption applications: a molecular simulations perspective**

Jelle Wieme, Steven Vandenbrande, Aran Lammaire, Venkat Kapil, Louis Vanduyfhuys, and Veronique Van Speybroeck

ACS Appl. Mater. Inter., **2019**, 11, 38697-38707

IF: 8.456. Number of citations: 0

2. **Pillared-layered metal-organic frameworks for mechanical energy storage applications**

Jelle Wieme, Sven M.J. Rogge, Pascal G. Yot, Louis Vanduyfhuys, Su Kyoung Lee, Jong-San Chang, Michel Waroquier, Guillaume Maurin, and Veronique Van Speybroeck

J. Mater. Chem. A, **2019**, 7, 22663-22674

IF: 10.733. Number of citations: 0

3. **Structure-mechanical stability relations of metal-organic frameworks via machine learning**

Peyman Z. Moghadam[†], Sven M.J. Rogge[†], Aurelia Li, Chun-Man Chow, Jelle Wieme, Noushin Moharrami, Marta Aragonés-Anglada,

Diego A. Gomez-Gualdron, Veronique Van Speybroeck, and David Fairen-Jimenez

Matter, **2019**, 1, 219-234

IF: N/A. Number of citations: 0

4. **Modeling the structural and thermal properties of loaded metal-organic frameworks. An interplay of quantum and anharmonic fluctuations**

Venkat Kapil[†], Jelle Wieme[†], Steven Vandenbrande, Aran Lamaire, Veronique Van Speybroeck, and Michele Ceriotti

J. Chem. Theory Comput., **2019**, 15, 3237-3249

IF: 5.313. Number of citations: 2

5. **The impact of lattice vibrations on the macroscopic breathing behavior of MIL-53(Al)**

Alexander E.J. Hoffman, Jelle Wieme, Sven M.J. Rogge, Louis Vanduyfhuys, and Veronique Van Speybroeck

Z. Kristallogr. Cryst., **2019**, 234, 529-545

IF: 1.090. Number of citations: 2

6. **On the importance of anharmonicities and nuclear quantum effects in modelling the structural properties and thermal expansion of MOF-5**

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, Michel Waroquier, and Veronique Van Speybroeck

J. Chem. Phys., **2019**, 150, 094503

IF: 2.997. Number of citations: 3

7. **i-PI 2.0: A universal force engine for advanced molecular simulations**

Venkat Kapil, Mariana Rossi, Ondrej Marsalek, Riccardo Petraglia, Yair Litman, Thomas Spura, Bingqing Cheng, Alice Cuzzocrea, Robert H. Meißner, David M. Wilkins, Benjamin A. Helfrecht, Przemysław Juda, Sébastien P. Bienvenue, Wei Fang, Jan Kessler, Igor Poltavsky, Steven Vandenbrande, Jelle Wieme, Clemence Corminboeuf, Thomas D. Kühne, David E. Manolopoulos, Thomas E. Markland, Jeremy O. Richardson, Alexandre Tkatchenko, Gareth A. Tribello, Veronique Van Speybroeck, and Michele Ceriotti

Comput. Phys. Commun., **2019**, 236, 214-223

IF: 3.309. Number of citations: 15. Highly cited paper

8. **Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks**
Jelle Wieme[†], Kurt Lejaeghere[†], Georg Kresse, and Veronique Van Speybroeck
Nat. Commun., **2018**, 9, 4899
IF: 11.878. Number of citations: 13
9. **Protocol for identifying accurate collective variables in enhanced molecular dynamics simulations for the description of structural transformations in flexible metal-organic frameworks**
Ruben Demuynck, Jelle Wieme, Sven M.J. Rogge, Karen D. Dedecker, Louis Vanduyfhuys, Michel Waroquier, and Veronique Van Speybroeck
J. Chem. Theory Comput., **2018**, 14, 5511-5526
IF: 5.313. Number of citations: 0
10. **Extension of the QuickFF force field protocol for an improved accuracy of structural, vibrational, mechanical and thermal properties of metal-organic frameworks**
Louis Vanduyfhuys, Steven Vandenbrande, Jelle Wieme, Michel Waroquier, Toon Verstraelen, and Veronique Van Speybroeck
J. Comput. Chem., **2018**, 39, 999-1011
IF: 3.224. Number of citations: 15
11. **Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/-computational approach**
Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestic, Jelle Wieme, Sven M.J. Rogge, Hannes Depauw, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck
J. Phys. Chem. C, **2018**, 122, 2734-2746
IF: 4.309. Number of citations: 15
12. **Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals**
Louis Vanduyfhuys, Sven M.J. Rogge, Jelle Wieme, Steven Vandenbrande, Guillaume Maurin, Michel Waroquier, and Veronique Van Speybroeck
Nat. Commun., **2018**, 9, 204
IF: 11.878. Number of citations: 27

13. **Efficient construction of free energy profiles of breathing metal-organic frameworks using advanced molecular dynamics simulations**
Ruben Demuyndck, Sven M.J. Rogge, Louis Vanduyfhuys, Jelle Wieme, Michel Waroquier, and Veronique Van Speybroeck
J. Chem. Theory Comput., **2017**, 13, 5861-5873
IF: 5.313. Number of citations: 14
14. **A series of sulfonic acid functionalized mixed-linker DUT-4 analogues: synthesis, gas sorption properties and catalytic performance**
Guang-Bo Wang, Karen Leus, Kevin Hendrickx, Jelle Wieme, Hannes Depauw, Ying-Ya Liu, Veronique Van Speybroeck, and Pascal Van Der Voort
Dalton Trans., **2017**, 46, 14356-14364
IF: 4.052. Number of citations: 2
15. **Mechanical properties of a gallium fumarate metal-organic framework: a joint experimental-modelling exploration**
Padmini Ramaswamy, Jelle Wieme, Elsa Alvarez, Louis Vanduyfhuys, Jean-Paul Itié, Paul Fabry, Veronique Van Speybroeck, Christian Serre, Pascal G. Yot, and Guillaume Maurin
J. Mater. Chem. A, **2017**, 5, 11047-11054
IF: 10.733. Number of citations: 13
16. **Thermodynamic insight in the high-pressure behavior of UiO-66: effect of linker defects and linker expansion**
Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, Steven Vandenberghe, Guillaume Maurin, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck
Chem. Mater., **2016**, 28, 5721-5732
IF: 10.159. Number of citations: 37
17. **Exploring the flexibility of MIL-47(V)-type materials using force field molecular dynamics simulations**
Jelle Wieme, Louis Vanduyfhuys, Sven M.J. Rogge, Michel Waroquier, and Veronique Van Speybroeck
J. Phys. Chem. C, **2016**, 120, 14934-14947
IF: 4.309. Number of citations: 25
18. **A breathing zirconium metal-organic framework with reversible loss of crystallinity by correlated nanodomain forma-**

tions

Bart Bueken, Frederik Vermoortele, Matthew J. Cliffe, Michael T. Wharmby, Damien Foucher, Jelle Wieme, Louis Vanduyfhuys, Charlotte Martineau, Norbert Stock, Francis Taulelle, Veronique Van Speybroeck, Andrew L. Goodwin, and Dirk De Vos

Chem. Eur. J., **2016**, 22, 3264-3267

IF: 5.160. Number of citations: 20

19. **Fine-tuning the theoretically predicted structure of MIL-47(V) with the aid of powder X-ray diffraction**

Thomas Bogaerts, Louis Vanduyfhuys, Danny E.P. Vanpoucke, Jelle Wieme, Michel Waroquier, Pascal Van Der Voort, and Veronique Van Speybroeck

CrystEngComm, **2015**, 17, 8612-8622

IF: 3.382. Number of citations: 4

Conference contributions

Oral presentations

1. **Towards modeling long-range disorder in MOFs: development of a computational toolbox to extend the length scale in molecular simulations**

Sven M.J. Rogge, Ruben Demuynck, Guillaume Maurin, Steven Vandenbrande, Louis Vanduyfhuys, Toon Verstraelen, Michel Waroquier, Jelle Wieme, and Veronique Van Speybroeck

The Goodwin Group, Research stay @ MMC, Oxford, United Kingdom, June 18, 2019

2. **ZIF-8 as a high-impact shock absorber? Unraveling the anomalous high-rate water intrusion in ZIF-8 by simulation and experiment**

Sven M.J. Rogge, Yueting Sun, Aran Lamaire, Steven Vandenbrande, Jelle Wieme, Jin-Chong Tan, and Veronique Van Speybroeck

Research stay @ MMC, Oxford, United Kingdom, June 18, 2019

3. **Reliably modeling the mechanical stability of MOFs at increasing length scales to unleash their full industrial potential**

Sven M.J. Rogge, Jelle Wieme, Ruben Demuynck, Sander Vandenhaute, Louis Vanduyfhuys, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck

Research stay @ MMC, Oxford, United Kingdom, June 4, 2019

4. **Reliably modeling the mechanical stability of MOFs at increasing length scales to unleash their full industrial potential**

Sven M.J. Rogge, Jelle Wieme, Ruben Demuynck, Sander Vandenhaute, Louis Vanduyfhuys, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck

MOF 2018, Auckland, New Zealand, December 9–13, 2018

5. **Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks**

Jelle Wieme, Kurt Lejaeghere, Louis Vanduyfhuys, Ruben Demuynck, Sven M.J. Rogge, Steven Vandenbrande, Michel Waroquier, and Veronique Van Speybroeck

MOF 2018, Auckland, New Zealand, December 9–13, 2018

6. **Designing temperature-responsive flexible metal-organic frameworks by tuning the balance between dispersion and**

entropy

Kurt Lejaeghere, Jelle Wieme, Georg Kresse, and Veronique Van Speybroeck

International Workshop on Computational Design and Discovery of Novel Materials (COMDI), Lausanne, Switzerland, September 10–12, 2018

7. Towards modeling long-range disorder in MOFs: development of a computational toolbox to extend the length scale in molecular simulations

Sven M.J. Rogge, Ruben Demuynck, Arthur De Vos, Kevin Hendrickx, Kurt Lejaeghere, Guillaume Maurin, Steven Vandenbrande, Sander Vandenhaute, Pascal Van Der Voort, Louis Vanduyfhuys, Toon Verstraelen, Michel Waroquier, Jelle Wieme, and Veronique Van Speybroeck

CECAM workshop: Multi-Scale Modelling of Flexible and Disordered Porous Materials, Paris, France, June 11–13, 2018

8. Towards a molecular level understanding of chemical and physical phenomena in metal-organic frameworks

Jelle Wieme, Chiara Caratelli, Ruben Demuynck, Arthur De Vos, Julianna Hajek, Alexander E.J. Hoffman, Aran Lamaire, Kurt Lejaeghere, Sven M.J. Rogge, Steven Vandenbrande, Louis Vanduyfhuys, and Veronique Van Speybroeck

Premier Congrès Français des MOFs, COFS et Polymères Poreux, Paris, France, May 16–17, 2018

9. A full computational characterization of the impact of defects on the mechanical stability and gas separation ability of MOFs

Sven M.J. Rogge, Jelle Wieme, Ruben Demuynck, Louis Vanduyfhuys, Steven Vandenbrande, Toon Verstraelen, Michel Waroquier, Guillaume Maurin, and Veronique Van Speybroeck

docMOF Symposium on Porous Coordination Polymers and Metal-Organic Frameworks, Munich, Germany, April 29 – May 2, 2018

10. Modelling phase transitions in temperature-responsive flexible metal-organic frameworks: the delicate balance between dispersion and entropy

Kurt Lejaeghere, Jelle Wieme, Ruben Demuynck, Sven M.J. Rogge, Louis Vanduyfhuys, Michel Waroquier, Georg Kresse, and Veronique Van Speybroeck

From Electrons to Phase Transitions 2018, Vienna, Austria, April 4–6, 2018

11. Thermodynamic insight into stimuli-responsive behavior of soft porous crystals

Louis Vanduyfhuys, Sven M.J. Rogge, Jelle Wieme, Steven Vandenberghe, Guillaume Maurin, Michel Waroquier, and Veronique Van Speybroeck

EuroMOF 2017, Delft, The Netherlands, October 29 – November 1, 2017

12. A thermodynamic approach to accurately determine the flexibility and loss of crystallinity in metal-organic frameworks

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, Steven Vandenberghe, Guillaume Maurin, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck

EUROMAT 2017, Thessaloníki, Greece, September 17–22, 2017

13. Impact of the mechanical pressure under various conditions on the flexibility of various metal-organic frameworks

Pascal G. Yot, Padmini Ramaswamy, Jelle Wieme, Louis Vanduyfhuys, Christian Serre, Veronique Van Speybroeck, and Guillaume Maurin

EUROMAT 2017, Thessaloníki, Greece, September 17–22, 2017

14. Exploring the flexibility of MIL-47(V)-type materials using force field molecular dynamics simulations

Jelle Wieme, Louis Vanduyfhuys, Sven M.J. Rogge, Michel Waroquier, and Veronique Van Speybroeck

EUROMAT 2017, Thessaloníki, Greece, September 17–22, 2017

15. A thermodynamic characterization of mechanical, thermal and adsorption properties of flexible metal-organic frameworks

Louis Vanduyfhuys, Sven M.J. Rogge, Jelle Wieme, Steven Vandenberghe, Michel Waroquier, and Veronique Van Speybroeck

EUROMAT 2017, Thessaloníki, Greece, September 17–22, 2017

16. Thermodynamic approach to accurately determine pressure profiles for metal-organic frameworks to assess their flexibility and loss of crystallinity

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, Steven Vandenberghe, Guillaume Maurin, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck

Thermodynamics 2017, Edinburgh, United Kingdom, September 5–8, 2017

17. Exploring the mechanical and thermal properties of MOFs via force field molecular dynamics

Jelle Wieme, Sven M.J. Rogge, Louis Vanduyfhuys, Michel Waroquier, and Veronique Van Speybroeck

Research stay @ COSMO-EPFL, Lausanne, Switzerland, February 7, 2017

18. Insights in the behaviour of MOFs through molecular modeling: from force field derivation to thermodynamic analysis

Louis Vanduyfhuys, Steven Vandenbrande, Ruben Demuynck, Sven M.J. Rogge, Jelle Wieme, An Ghysels, Toon Verstraelen, Guillaume Maurin, Rochus Schmid, Michel Waroquier, and Veronique Van Speybroeck

Research stay @ DAMP, Montpellier, France, November 17, 2016

19. Advanced molecular dynamics simulations to construct free energy profiles of complex transformations in nanoporous materials

Ruben Demuynck, Louis Vanduyfhuys, Sven M.J. Rogge, Jelle Wieme, and Veronique Van Speybroeck

From Molecular Trajectories to Reaction Coordinates, Leiden, The Netherlands, August 29 – September 2, 2016

20. Unraveling the mechanical behaviour of MOFs: a thermodynamic exploration

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, An Ghysels, Michel Waroquier, Toon Verstraelen, Guillaume Maurin, and Veronique Van Speybroeck

Research stay @ DAMP, Montpellier, France, July 18, 2016

21. Metal-organic frameworks under pressure: a thermodynamic exploration

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, An Ghysels, Michel Waroquier, Toon Verstraelen, Guillaume Maurin, and Veronique Van Speybroeck

MolSim 2016: Understanding Molecular Simulation, Amsterdam, The Netherlands, January 4–15, 2016

Poster presentations

1. Structural organisation of water in zirconium-based metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, and Veronique Van Speybroeck

EuroMOF 2019, Paris, France, October 27–30, 2019

2. Structural organisation of water in zirconium-based metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, and Veronique Van Speybroeck

MOFSIM2019, Ghent, Belgium, April 10–12, 2019

3. Nuclear quantum effects in metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, Liesbeth De Bruecker, and Veronique Van Speybroeck

MOFSIM2019, Ghent, Belgium, April 10–12, 2019

4. Understanding the breathing behavior of the flexible metal-organic framework MIL-53(Al) using computational vibrational spectroscopy

Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestic, Jelle Wieme, Sven M.J. Rogge, Hannes Depauw, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck

MOFSIM2019, Ghent, Belgium, April 10–12, 2019

5. Elucidating the dynamics of the intricate stacking behaviour in 2D covalent organic frameworks at finite temperatures using MD simulations

Sander Borgmans, Sven M.J. Rogge, Louis Vanduyfhuys, Jelle Wieme, Ruben Demuynck, Chris V. Stevens, Pascal Van Der Voort, and Veronique Van Speybroeck

MOFSIM2019, Ghent, Belgium, April 10–12, 2019

6. Elucidating the dynamics of the intricate stacking behaviour in 2D covalent organic frameworks at finite temperatures using MD simulations

Sander Borgmans, Sven M.J. Rogge, Louis Vanduyfhuys, Jelle Wieme, Ruben Demuynck, Chris V. Stevens, Pascal Van Der Voort, and Veronique Van Speybroeck

MolSim 2019: Understanding Molecular Simulation, Amsterdam, The Netherlands, January 7–18, 2019

7. Understanding the breathing behavior of the flexible metal-organic framework MIL-53(Al) using computational vibrational spectroscopy

Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestic, Jelle Wieme, Sven M.J. Rogge, Hannes Depauw, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck

Computational spectroscopy: bridging theory and experiment, Como, Italy, September 9–14, 2018

8. Nuclear quantum effects in metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, Liesbeth De Bruecker, and Veronique Van Speybroeck

Ab initio Modeling in Solid State Chemistry, Torino, Italy, September 2–7, 2018

9. Understanding the breathing behavior of the flexible metal-organic framework MIL-53(Al) using computational vibrational spectroscopy

Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestic, Jelle Wieme, Sven M.J. Rogge, Hannes Depauw, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck

Ab initio Modeling in Solid State Chemistry, Torino, Italy, September 2–7, 2018

10. Nuclear quantum effects in metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, Liesbeth De Bruecker, and Veronique Van Speybroeck

Path Integral Quantum Mechanics: From the Basics to the Latest Developments, Lausanne, Switzerland, June 25–29, 2018

11. Nuclear quantum effects in metal-organic frameworks

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, Liesbeth De Bruecker, and Veronique Van Speybroeck

Solvay New Horizons Lectures in Chemistry, Zwijnaarde, Belgium, June 1, 2018

12. On the importance of nuclear quantum effects in modelling the structural properties and thermal expansion of MOF-5

Aran Lamaire, Jelle Wieme, Sven M.J. Rogge, and Veronique Van Speybroeck

MolSim 2018: Understanding Molecular Simulation, Amsterdam, The Netherlands, January 8–19, 2018

13. Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/computational approach

Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestić, Sven M.J. Rogge, Jelle Wieme, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck

MolSim 2018: Understanding Molecular Simulation, Amsterdam, The Netherlands, January 8–19, 2018

14. **On the importance of nuclear quantum effects in modelling the structural properties and thermal expansion of MOF-5**

Aran Lemaire, Jelle Wieme, Sven M.J. Rogge, and Veronique Van Speybroeck

EuroMOF 2017, Delft, The Netherlands, October 29 – November 1, 2017

15. **Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/-computational approach**

Alexander E.J. Hoffman, Louis Vanduyfhuys, Irena Nevjestić, Sven M.J. Rogge, Jelle Wieme, Pascal Van Der Voort, Henk Vrielinck, and Veronique Van Speybroeck

EuroMOF 2017, Delft, The Netherlands, October 29 – November 1, 2017

16. **Assessing the flexibility and loss of crystallinity in metal-organic frameworks from a thermodynamic point of view**

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, Steven Vandenbrande, Guillaume Maurin, Toon Verstraelen, Michel Waroquier, and Veronique Van Speybroeck

EuroMOF 2017, Delft, The Netherlands, October 29 – November 1, 2017

17. **Modeling dispersion interactions in flexible metal-organic frameworks: critical influence on phase stability**

Jelle Wieme, Kurt Lejaeghere, and Veronique Van Speybroeck

EuroMOF 2017, Delft, The Netherlands, October 29 – November 1, 2017

18. **Modeling dispersion interactions in flexible metal-organic frameworks: critical influence on phase stability**

Jelle Wieme, Kurt Lejaeghere, and Veronique Van Speybroeck

EUROMAT 2017, Thessaloníki, Greece, September 17–22, 2017

19. **A thermodynamic approach to accurately determine pressure profiles for MOFs to assess their flexibility and loss of crystallinity**

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, An Ghysels, Michel Waroquier, Toon Verstraelen, Guillaume Maurin, and Veronique Van Speybroeck

MOF-2016: 5th International Conference on Metal-Organic Frameworks & Open Framework Compounds, Long Beach, California, United States of America, September 11–15, 2016

20. Exploring the flexibility of MIL-47(V)-type materials using force field molecular dynamics simulations

Jelle Wieme, Louis Vanduyfhuys, Sven M.J. Rogge, Michel Waroquier, and Veronique Van Speybroeck

MOF-2016: 5th International Conference on Metal-Organic Frameworks & Open Framework Compounds, Long Beach, California, United States of America, September 11–15, 2016

21. A thermodynamic approach to accurately determine pressure profiles for MOFs to assess their flexibility and loss of crystallinity

Sven M.J. Rogge, Jelle Wieme, Louis Vanduyfhuys, An Ghysels, Michel Waroquier, Toon Verstraelen, Guillaume Maurin, and Veronique Van Speybroeck

TACC 2016, Seattle, Washington, United States of America, August 28 – September 2, 2016

22. Investigating the heat capacity of metal-organic frameworks via path integral molecular dynamics simulations

Jelle Wieme, Louis Vanduyfhuys, Sven M.J. Rogge, Steven Vandenberghe, and Veronique Van Speybroeck

CECAM/Psi-k School on Path Integral Quantum Mechanics: Theory, Simulation and Application, Lausanne, Switzerland, June 13–17, 2016

23. Advanced molecular dynamics simulations to accurately characterize metal-organic frameworks

Jelle Wieme, Louis Vanduyfhuys, Kurt Lejaeghere, Sven M.J. Rogge, and Veronique Van Speybroeck

MolSim 2016: Understanding Molecular Simulation, Amsterdam, The Netherlands, January 4–15, 2016

24. Advanced molecular dynamics simulations to accurately characterize metal-organic frameworks

Jelle Wieme, Louis Vanduyfhuys, Kurt Lejaeghere, Sven M.J. Rogge, and Veronique Van Speybroeck

IAP Annual Meeting, Hasselt, Belgium, September 11, 2015

25. Advanced molecular dynamics simulations to accurately characterize metal-organic frameworks

Jelle Wieme, Louis Vanduyfhuys, Kurt Lejaeghere, Sven M.J. Rogge, and Veronique Van Speybroeck

Hands-On Workshop Density-Functional Theory and Beyond: First Principles Simulations of Molecules and Materials, Berlin, Germany, July 13–23, 2015

Master's thesis

Development of accurate force fields for a Pareto screening of high-performance metal-organic frameworks

Jelle Wieme

Master's thesis performed at the Center for Molecular Modeling (CMM), Ghent University, 2014–2015

Supervisors: prof. dr. ir. Veronique Van Speybroeck and prof. dr. Stefaan Cottenier



List of Molecular Modeling Software Packages

In the context of this PhD thesis, various molecular modeling software packages have been used. Below, an overview of these packages is provided.

Gaussian 09 and Gaussian 16

Gaussian 09 and Gaussian 16 are the latest in the Gaussian series of programs used by chemists, chemical engineers, biochemists, physicists and other scientists worldwide. They provide state-of-the-art capabilities for electronic structure modeling and can be used to investigate real-world chemical problems in all of their complexity. Gaussian 09 and Gaussian 16 were adopted in this PhD dissertation to perform electronic structure calculations on MOF cluster models. More information about this software is available in references 295 and 296.

GPAW

GPAW is an open-source density-functional theory Python code based on the projector-augmented wave (PAW) method and the atomic simulation environment, which uses a uniform real-space grid representation of the electronic wave functions. GPAW was adopted in this PhD dissertation to compute all-electron densities of MOF cluster models. More information about this software is available in references 297 and 298.

HORTON

HORTON is a Helpful Open-source Research TOol for N-fermion systems. HORTON is not intended to be a replacement for existing quantum chemistry software, but a helpful supplement to it. The ambition is to provide a research tool that is computationally-efficient enough to be helpful, without compromising code-readability and user-friendliness. HORTON was adopted in this PhD dissertation to derive the atomic charges of MOF unit cells or cluster models from all-electron density calculations. More information about this software is available at <http://theochem.github.io/horton/>.

i-PI

i-PI is a universal force engine interface written in Python, designed to be used together with an ab initio (or force-field based) evaluation of the interactions between the atoms. The main goal is to decouple the problem of evolving the ionic positions to sample the appropriate thermodynamic ensemble and the problem of computing the inter-atomic forces. i-PI was adopted in this PhD dissertation to perform path integral molecular dynamics simulations. More information about this software is available in references 228 and 229.

LAMMPS

LAMMPS is an open-source classical molecular dynamics code, and an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator. LAMMPS has potentials for solid-state materials (metals, semiconductors) and soft matter (biomolecules, polymers) and coarse-grained or mesoscopic systems. It can be used to model atoms or, more generically, as a parallel particle simulator at the atomic, meso, or continuum scale. LAMMPS was adopted in this PhD dissertation to perform classical molecular dynamics simulations. More information about this software is available in reference 206.

MolMod

MolMod is an open-source Python library with many auxiliary modules that are useful for the development of molecular modeling programs. It is the underlying library for many software packages developed at the Center for Molecular Modeling. MolMod was adopted in this PhD dissertation as the underlying software package for QuickFF, TAMkin, Yaff and Zeobuilder. More information about this software is available at <http://molmod.github.io/molmod/>.

phonopy

Phonopy is an open-source software package for phonon calculations at harmonic and quasi-harmonic levels. Phonopy was adopted in this PhD dissertation to compute finite temperature corrections with the harmonic approximation. More information about this software is available at reference 299.

QuickFF

QuickFF is an open-source Python software package developed at the Center for Molecular Modeling, designed to derive accurate force fields for isolated and periodic molecular systems in a quick and easy manner. The force field parameters for the covalent interactions are derived from ab initio data, which need to be provided by the user. QuickFF was adopted in this PhD dissertation to derive force fields for MOFs. More information about this software is available in references 178 and 135.

TAMkin

TAMkin is an open-source post-processing toolkit for normal mode analysis, thermochemistry and reaction kinetics developed at the Center for Molecular Modeling. It uses a Hessian computation from a standard computational chemistry program as its input. TAMkin was adopted in this PhD dissertation for normal mode analysis of force-field simulations of MOFs. More information about this software is available in reference 203.

VASP

The Vienna Ab Initio Simulation Package (VASP) is a computer program for atomic scale materials modeling, e.g. electronic structure calculations and quantum-mechanical molecular dynamics, from first principles. VASP computes an approximate solution to the many-body Schrödinger equation, either within density-functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock approximation, solving the Rothaan equations. Hybrid functionals that mix the Hartree-Fock approach with DFT are implemented as well. Furthermore, Green's functions methods (GW quasiparticles and ACFDT-RPA) and many-body perturbation theory (2nd-order Møller-Plesset) are available in VASP. In VASP, central quantities, like the one-electron orbitals, the electronic charge density, and the local potential are expressed in plane wave basis sets. The interactions between the electrons and ions are described using norm-conserving or ultrasoft pseudopotentials, or the projector-augmented wave method. VASP was adopted in this PhD

dissertation to perform electronic structure calculations on MOFs. More information about this software is available in references 139 and 140.

Yaff

Yaff is a pythonic force-field code developed at the Center for Molecular Modeling to test-drive new force-field models. Its primary intention was to facilitate the implementation of newly developed methods, and therefore it is very flexible and thoroughly tested. Yaff was adopted in this PhD dissertation to perform different types of force field simulations. More information about this software is available at <http://www.github.com/molmod/yaff/>.

Zeo++

Zeo++ is an open-source software package for the analysis of crystalline porous materials. It can be used to perform geometry-based analysis of the structure and the topology of the void space inside a material. Zeo++ can be used to either analyze a single structure or to perform high-throughput analysis of a large database. Zeo++ was adopted in this PhD dissertation to perform a textural analysis of different MOF structures. More information about this software is available in reference 287.

Zeobuilder

Zeobuilder is an open-source user-friendly GUI toolkit for the construction of advanced molecular models (biological, inorganic, reactants in a catalyst, ...) developed at the Center for Molecular Modeling. The program contains several advanced tools to build, align, manipulate and analyze molecular structures. Most of its novel functionality is based on a hierarchical data-structure of reference frames to represent a molecular structure. Zeobuilder was adopted in this PhD dissertation to build and adapt MOF structures. More information about this software is available in reference 300.



High-Performance Computing Infrastructure

The computational resources and services used in this PhD dissertation were provided by Flemish Supercomputer Center (VSC), funded by Ghent University, the Fund for Scientific Research Flanders (FWO) and the Flemish Government Department of Economy, Science and Innovation (EWI). A list of granted computational projects on Tier-1 and a table with infrastructure details (Tier-1/2) are provided below. Figure D.1 displays the computational time that was used on Tier-2, which amounts to more than 2000 core years.

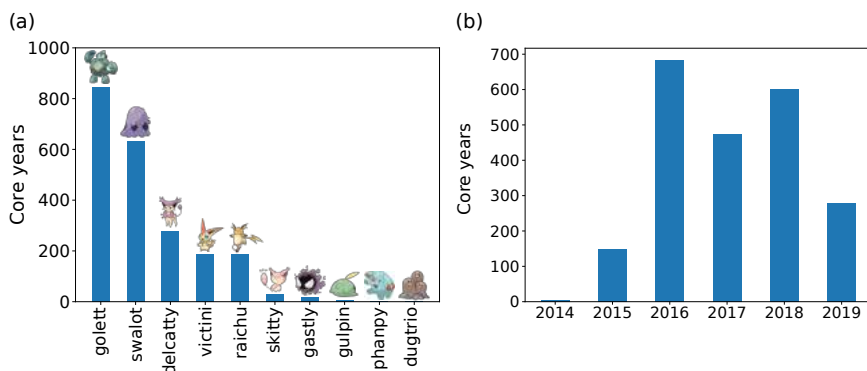


Figure D.1: (a) Computational time used on the Tier-2 clusters. (b) Computational time used per year.

1. *Influence of water on the phase stability of flexible nanoporous materials*
Mar 2019 - Nov 2019, 4897 node days (BrENIAC)
2. *Mechanical deformation of a metal-organic framework using advanced electronic structure calculations*
Mar 2019 - Nov 2019, 4830 node days (BrENIAC)
3. *Investigating the breathing behavior in flexible metal-organic frameworks using computational vibrational spectroscopy*, Jul 2018 - Mar 2019
1800 node days (BrENIAC)
4. *Elucidating the thermal properties of zeolitic imidazolate frameworks*
Jul 2018 - Mar 2019, 2880 node days (BrENIAC)
5. *Structural characterisation of water confined in nanoporous materials*
Jul 2018 - Mar 2019, 4512 node days (BrENIAC)
6. *Investigating the low-frequency vibrational fingerprint of flexible metal-organic frameworks*
Mar 2018 - Nov 2018, 1062 node days (BrENIAC)
7. *Advanced electronic structure calculations of a metal-organic framework*
Mar 2018 - Nov 2018, 1022 node days (BrENIAC)
8. *Benchmarking elastic properties of metal-organic frameworks*
Nov 2017 - Apr 2018, 1296 node days (BrENIAC)
9. *Understanding the high-pressure behavior of a flexible nanoporous material*
Sep 2017 - Dec 2017, 2430 node days (BrENIAC)
10. *Assessing the accuracy of hybrid functionals for the relative stability of a flexible MOF*
Mar 2017 - Aug 2017, 3420 node days (BrENIAC)
11. *Computational exploration of the free energy profile of guest-free $M(\text{bdp})$ ($M=\text{Co, Fe}$)(bdp^{2-} = 1,4-benzenedipyrazolate)*
Nov 2016 - Apr 2017, 2940 node days (BrENIAC)
12. *Construction of ab initio free energy profile for MIL-53-type materials*
Nov 2016 - Apr 2017, 4200 node days (BrENIAC)
13. *Investigating the phases of MIL-53-type materials*
Dec 2015 - Jun 2016, 4644 node days (Muk)

Cluster name	Processor architecture	Memory/node	Interconnect	Tier level
skitty	2×18-core Intel Xeon Gold 6140 (Skylake @ 2.3GHz)	192 GB	EDR Infiniband	Tier-2
victini	2×18-core Intel Xeon Gold 6140 (Skylake @ 2.3GHz)	96 GB	10 GbE	Tier-2
BrENIAC	2×14-core Intel Xeon E5-2680v4 (Broadwell-EP @ 2.4GHz)	128/256 GB	EDR Infiniband	Tier-1
swalot	2×10-core Intel Xeon E5-2660v3 (Haswell-EP @ 2.6 GHz)	128 GB	FDR Infiniband	Tier-2
golett	2×12-core Intel Xeon E5-2660v3 (Haswell-EP @ 2.5 GHz)	64 GB	FDR-10 Infiniband	Tier-2
phanpy	2×12-core Intel Xeon E5-2660v3 (Haswell-EP @ 2.5 GHz)	512 GB	FDR Infiniband	Tier-2
delcatty	2×8-core Intel Xeon E5-2670 (Sandy Bridge @ 2.6 GHz)	64 GB	FDR Infiniband	Tier-2
muk	2×8-core Intel Xeon E5-2670 (Sandy Bridge @ 2.6 GHz)	64 GB	FDR Infiniband	Tier-1
raichu	2×8-core Intel Xeon E5-2670 (Sandy Bridge @ 2.6 GHz)	32 GB	1 GbE	Tier-2
gulin	2×16-core AMD Opteron 6136 (Magny-Cours @ 2.4 GHz)	64 GB	2×QDR Infiniband	Tier-2
gastly	2×4-core Intel Xeon L5520 (Nehalem @ 2.26 GHz)	12 GB	1 GbE	Tier-2
dugtrio	2×6-core Intel Xeon X5675 (Westmere-EP @ 3.06 GHz)	96 GB	2×QDR Infiniband	Tier-2

Bibliography

- [1] “Graphene Flagship,” <https://graphene-flagship.eu>.
- [2] M. Park, J. Ryu, W. Wang, and J. Cho, “Material design and engineering of next-generation flow-battery technologies,” *Nat. Rev. Mater.*, **2**, 16080 (2016).
- [3] A. Schoedel, Z. Ji, and O. M. Yaghi, “The role of metal-organic frameworks in a carbon-neutral energy cycle,” *Nat. Energy*, **1**, 16034 (2016).
- [4] J. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, “Towards the computational design of solid catalysts,” *Nat. Chem.*, **1**, 37 (2009).
- [5] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, “The high-throughput highway to computational materials design,” *Nat. Mater.*, **12**, 191 (2013).
- [6] A. Jain, Y. Shin, and K. A. Persson, “Computational predictions of energy materials using density functional theory,” *Nat. Rev. Mater.*, **1**, 15004 (2016).
- [7] R. Gómez-Bombarelli, J. Aguilera-Iparraguirre, T. D. Hirzel, D. Duvenaud, D. Maclaurin, M. A. Blood-Forsythe, H. S. Chae, M. Einzinger, D.-G. Ha, T. Wu, G. Markopoulos, S. Jeon, H. Kang, H. Miyazaki, M. Numata, S. Kim, W. Huang, S. I. Hong, M. Baldo, R. P. Adams, and A. Aspuru-Guzik, “Design of efficient molecular organic light-emitting diodes by a high-throughput virtual screening and experimental approach,” *Nat. Mater.*, **15**, 1120 (2016).
- [8] H. Furukawa, K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, “The chemistry and applications of metal-organic frameworks,” *Science*, **341**, 1230444 (2013).
- [9] A. G. Slater and A. I. Cooper, “Function-led design of new porous materials,” *Science*, **348**, aaa8075 (2015).

- [10] S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, and J. Gascon, "Metal-organic and covalent organic frameworks as single site catalysts," *Chem. Soc. Rev.*, **46**, 3134 (2017).
- [11] P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, and C. Serre, "Metal-organic frameworks in biomedicine," *Chem. Rev.*, **112**, 1232 (2012).
- [12] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, and K. S. W. Sing, "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," *Pure Appl. Chem.*, **87**, 1051 (2015).
- [13] S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh, and J. Reedijk, "Terminology of metal-organic frameworks and coordination polymers (IUPAC Recommendations 2013)," *Pure Appl. Chem.*, **85**, 1715 (2013).
- [14] B. F. Hoskins and R. Robson, "Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks $[\text{N}(\text{CH}_3)_4] [\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}(\text{CN})_4]$ and $\text{Cu}^{\text{I}}[4,4',4'',4''']\text{-tetracyanotetraphenylmethane}[\text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2]$," *J. Am. Chem. Soc.*, **112**, 1546 (1990).
- [15] S. Subramanian and M. J. Zaworotko, "Porous solids by design: $[\text{Zn}(4,4'\text{-bpy})_2(\text{SiF}_6)]_n \cdot x\text{DMF}$, a single framework octahedral coordination polymer with large square channels," *Angew. Chem. Int. Ed.*, **34**, 2127 (1995).
- [16] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, and S. Kitagawa, "Three-dimensional framework with channeling cavities for small molecules: $[\text{M}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4] \cdot \text{H}_2\text{O}_n$ ($\text{M}=\text{Co}, \text{Ni}, \text{Zn}$)," *Angew. Chem. Int. Ed.*, **36**, 1725 (1997).
- [17] S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, G. A. Orpen, and I. D. Williams, "A chemically functionalizable nanoporous material $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$," *Science*, **283**, 1148 (1999).

- [18] H. Li, M. Eddaoudi, M. O’Keeffe, and O. M. Yaghi, “Design and synthesis of an exceptionally stable and highly porous metal-organic framework,” *Nature*, **402**, 276 (1999).
- [19] M. Li, D. Li, M. O’Keeffe, and O. M. Yaghi, “Topological analysis of metal-organic frameworks with polytopic linkers and/or multiple building units and the minimal transitivity principle,” *Chem. Rev.*, **114**, 1343 (2014).
- [20] P. Z. Moghadam, A. Li, S. G. Wiggins, A. Tao, A. G. P. Maloney, P. A. Wood, S. C. Ward, and D. Fairen-Jimenez, “Development of a Cambridge Structural Database subset: a collection of metal-organic frameworks for past, present, and future,” *Chem. Mater.*, **29**, 2618 (2017).
- [21] C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, and R. Q. Snurr, “Large-scale screening of hypothetical metal-organic frameworks,” *Nat. Chem.*, **4**, 83 (2012).
- [22] K. Barthelet, J. Marrot, D. Riou, and G. Férey, “Organic-inorganic solid with very large pores and high magnetic characteristics,” *Angew. Chem. Int. Ed.*, **41**, 281 (2002).
- [23] Y.-Y. Liu, S. Couck, M. Vandichel, M. Grzywa, K. Leus, S. Biswas, D. Volkmer, J. Gascon, F. Kapteijn, J. F. M. Denayer, M. Waroquier, V. Van Speybroeck, and P. Van Der Voort, “New V^{IV}-based metal-organic framework having framework flexibility and high CO₂ adsorption capacity,” *Inorg. Chem.*, **52**, 113 (2013).
- [24] Y.-Y. Liu, K. Leus, M. Grzywa, D. Weinberger, K. Strubbe, H. Vrielinck, R. Van Deun, V. Van Speybroeck, and P. Van Der Voort, “Synthesis, structural characterization, and catalytic performance of a vanadium-based metal-organic framework (COMOC-3),” *Eur. J. Inorg. Chem.*, **2012**, 2819 (2012).
- [25] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, “A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration,” *Chem.: Eur. J.*, **10**, 1373 (2004).
- [26] C. Volkringer, T. Loiseau, N. Guillou, G. Férey, E. Elkaïm, and A. Vimont, “XRD and IR structural investigations of a particular breathing effect in the MOF-type gallium terephthalate MIL-53(Ga),” *Dalton Trans.*, **0**, 2241 (2009).

- [27] E. Alvarez, N. Guillou, C. Martineau, B. Bueken, B. Van de Voorde, C. Le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. H. Cho, N. Ramsahye, T. Devic, M. Daturi, G. Maurin, and G. Serre, "The structure of the aluminum fumarate metal-organic framework A520," *Angew. Chem. Int. Ed.*, **54**, 3664 (2015).
- [28] P. Ramaswamy, J. Wieme, E. Alvarez, L. Vanduyfhuys, J. P. Itié, P. Fabry, V. Van Speybroeck, C. Serre, P. G. Yot, and G. Maurin, "Mechanical properties of a gallium fumarate metal-organic framework: a joint experimental-modelling exploration," *J. Mater. Chem. A*, **5**, 11047 (2017).
- [29] I. Senkovska, F. Hoffmann, M. Fröba, J. Getzschmann, W. Böhlmann, and S. Kaskel, "New highly porous aluminium based metal-organic frameworks: Al(OH)(ndc) (ndc=2,6-naphthalene dicarboxylate) and Al(OH)(bpdc) (bpdc=4,4'-biphenyl dicarboxylate)," *Micropor. Mesopor. Mater.*, **122**, 93 (2009).
- [30] D. Alezi, Y. Belmabkhout, M. Suyetin, P. M. Bhatt, L. J. Weselinski, V. Solovyeva, K. Adil, I. Spanopoulos, P. N. Trikalitis, A.-H. Emwas, and M. Eddaoudi, "MOF crystal chemistry paving the way to gas storage needs: aluminum-based soc-MOF for CH₄, O₂, and CO₂ storage," *J. Am. Chem. Soc.*, **137**, 13308 (2015).
- [31] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, "Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage," *Science*, **295**, 469 (2002).
- [32] B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, and O. M. Yaghi, "High H₂ adsorption in a microporous metal-organic framework with open metal sites," *Angew. Chem. Int. Ed.*, **44**, 4745 (2005).
- [33] H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, and O. M. Yaghi, "A route to high surface area, porosity and inclusion of large molecules in crystals," *Nature*, **427**, 523 (2004).
- [34] K. Koh, A. G. Wong-Foy, and A. J. Matzger, "A crystalline mesoporous coordination copolymer with high microporosity," *Angew. Chem., Int. Ed.*, **47**, 677 (2008).
- [35] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, and K. P. Lillerud, "A new zirconium inorganic building brick forming

- metal organic frameworks with exceptional stability,” *J. Am. Chem. Soc.*, **130**, 13850 (2008).
- [36] N. Stock and S. Biswas, “Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites,” *Chem. Rev.*, **112**, 933 (2012).
- [37] M. Rubio-Martinez, C. Avci-Camur, A. W. Thornton, I. Imaz, D. Maspoch, and M. R. Hill, “New synthetic routes towards MOF production at scale,” *Chem. Soc. Rev.*, **46**, 3453 (2017).
- [38] S. Yuan, L. Feng, K. Wang, J. Pang, M. Bosch, C. Lollar, Y. Sun, J. Qin, X. Yang, P. Zhang, Q. Wang, L. Zou, Y. Zhang, Y. Fang, J. Li, and H.-C. Zhou, “Stable metal-organic frameworks: design, synthesis, and applications,” *Adv. Mater.*, **30**, 1704303 (2018).
- [39] S. M. Cohen, “Postsynthetic methods for the functionalization of metal-organic frameworks,” *Chem. Rev.*, **112**, 970 (2012).
- [40] S. Han, Y. Wei, C. Valente, I. Lagzi, J. Gassensmith, A. Coskun, F. J. Stoddart, and B. A. Grzybowski, “Chromatography in a single metal-organic framework (MOF) crystal,” *J. Am. Chem. Soc.*, **132**, 16358 (2010).
- [41] A. Bénard and R. A. Fischer, “Metal-organic framework thin films: from fundamentals to applications,” *Chem. Rev.*, **112**, 1055 (2012).
- [42] Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, and O. Sakata, “Shape-memory nanopores induced in coordination frameworks by crystal downsizing,” *Science*, **339**, 193 (2013).
- [43] A. J. Howarth, Y. Liu, P. Li, Z. Li, T. C. Wang, J. T. Hupp, and O. K. Farha, “Chemical, thermal and mechanical stabilities of metal-organic frameworks,” *Nat. Rev. Mater.*, **1**, 15018 (2016).
- [44] P. Z. Moghadam, S. M. J. Rogge, A. Li, C.-M. Chow, J. Wieme, N. Moharrami, M. Aragonés-Anglada, G. Conduit, D. A. Gomez-Gualdrón, V. Van Speybroeck, and D. Fairen-Jimenez, “Structure-mechanical stability relations of metal-organic frameworks via machine learning,” *Matter*, **1**, 219 (2019).
- [45] N. C. Burtch, H. Jasuja, and K. S. Walton, “Water stability and adsorption in metal-organic frameworks,” *Chem. Rev.*, **114**, 10575 (2014).
- [46] K. Leus, T. Bogaerts, J. De Decker, H. Depauw, K. Hendrickx, H. Vrielinck, V. Van Speybroeck, and P. Van Der Voort, “Systematic

- study of the chemical and hydrothermal stability of selected "stable" metal organic frameworks," *Micropor. Mesopor. Mater.*, **226**, 110 (2016).
- [47] L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, and V. Van Speybroeck, "Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals," *Nat. Commun.*, **9**, 204 (2018).
- [48] I. M. Hönicke, I. Senkovska, V. Bon, I. A. Baburin, N. Bönisch, S. Raschke, J. D. Evans, and S. Kaskel, "Balancing mechanical stability and ultrahigh porosity in crystalline framework materials," *Angew. Chem. Int. Ed.*, **57**, 13780 (2018).
- [49] L. J. Murray, M. Dinča, and J. R. Long, "Hydrogen storage in metal-organic frameworks," *Chem. Soc. Rev.*, **38**, 1294 (2009).
- [50] J.-R. Li, J. Sculley, and H.-C. Zhou, "Metal-organic frameworks for separations," *Chem. Rev.*, **112**, 869 (2011).
- [51] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, and J. R. Long, "Carbon dioxide capture in metal-organic frameworks," *Chem. Rev.*, **112**, 724 (2012).
- [52] Y. He, W. Zhou, G. Qian, and B. Chen, "Methane storage in metal-organic frameworks," *Chem. Soc. Rev.*, **43**, 5657 (2014).
- [53] P. Silva, S. M. F. Vilela, J. P. C. Tomé, and F. A. Almeida Paz, "Multifunctional metal-organic frameworks: from academia to industrial applications," *Chem. Soc. Rev.*, **44**, 6774 (2015).
- [54] R. Ricco, C. Pfeiffer, K. Sumida, C. J. Sumby, P. Falcaro, S. Furukawa, N. R. Champness, and C. J. Doonan, "Emerging applications of metal-organic frameworks," *CrystEngComm*, **18**, 6532 (2016).
- [55] I. Stassen, N. C. Burtch, A. Talin, P. Falcaro, M. D. Allendorf, and R. Ameloot, "An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors," *Chem. Soc. Rev.*, **46**, 3185 (2017).
- [56] N. C. Burtch, J. Heinen, T. D. Bennett, D. Dubbeldam, and M. D. Allendorf, "Mechanical properties in metal-organic frameworks: emerging opportunities and challenges for device functionality and technological applications," *Adv. Mater.*, **30**, 1704124 (2018).
- [57] A. Schneemann, I. Schwedler, I. Senkovska, S. Kaskel, and R. A. Fischer, "Flexible metal-organic frameworks," *Chem. Soc. Rev.*, **43**, 6062 (2014).

- [58] F.-X. Coudert, "Responsive metal-organic frameworks and framework materials: under pressure, taking the heat, in the spotlight, with friends," *Chem. Mater.*, **27**, 1905 (2015).
- [59] J. H. Lee, S. Jeoung, Y. G. Chung, and H. R. Moon, "Elucidation of flexible metal-organic frameworks: Research progresses and recent developments," *Coord. Chem. Rev.*, **389**, 161 (2019).
- [60] Y. Liu, J.-H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann, and C. M. Brown, "Reversible structural transition in MIL-53 with large temperature hysteresis," *J. Am. Chem. Soc.*, **130**, 11813 (2008).
- [61] P. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghoufi, T. Devic, C. Serre, G. Dmitriev, G. Férey, G. L. Zhong, and G. Maurin, "Large breathing of the MOF MIL-47(V^{IV}) under mechanical pressure: a joint experimental-modelling exploration," *Chem. Sci.*, **3**, 1100 (2012).
- [62] E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren, and L. Brammer, "Solvent-switchable continuous-breathing behaviour in a diamondoid metal-organic framework and its influence on CO₂ versus CH₄ selectivity," *Nat. Chem.*, **9**, 882 (2017).
- [63] S. Horike, S. Shimomura, and S. Kitagawa, "Soft porous crystals," *Nat. Chem.*, **1**, 695 (2009).
- [64] C. A. Trickett, A. Helal, B. A. Al-Maythality, Z. H. Yamani, K. E. Cordova, and O. M. Yaghi, "The chemistry of metal-organic frameworks for CO₂ capture, regeneration and conversion," *Nat. Rev. Mater.*, **2**, 17045 (2017).
- [65] Y. He, F. Chen, B. Li, G. Qian, W. Zhou, and B. Chen, "Porous metal-organic frameworks for fuel storage," *Coord. Chem. Rev.*, **373**, 167 (2017).
- [66] H. Kim, S. Yang, S. R. Rao, S. Narayanan, E. A. Kapustin, H. Furukawa, A. S. Umans, O. M. Yaghi, and E. N. Wang, "Water harvesting from air with metal-organic frameworks powered by natural sunlight," *Science*, **356**, 430 (2017).
- [67] R. Zhao, Z. Liang, R. Zou, and Q. Xu, "Metal-organic frameworks for batteries," *Joule*, **2**, 2235 (2018).
- [68] L. E. Kreno, K. Leong, O. K. Farha, M. D. Allendorf, R. P. Van Duyne, and J. T. Hupp, "Metal-organic framework materials as chemical sensors," *Chem. Rev.*, **112**, 1105 (2012).

- [69] W. Danowski, T. van Leeuwen, S. Abdolazadeh, D. Roke, W. R. Browne, S. J. Wezenberg, and B. L. Feringa, "Unidirectional rotary motion in a metal-organic framework," *Nat. Nanotechnol.*, **14**, 488 (2019).
- [70] B. Li, X. Dong, H. Wang, D. Ma, K. Tan, S. Jensen, B. J. Deibert, J. Butler, J. Cure, Z. Shi, T. Thonhauser, Y. J. Chabal, Y. Han, and J. Li, "Capture of organic iodides from nuclear waste by metal-organic frameworks-based molecular traps," *Nat. Commun.*, **8**, 485 (2017).
- [71] J. E. Mondloch, M. J. Katz, W. C. Isley III, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp, and O. K. Farha, "Destruction of chemical warfare agents using metal-organic frameworks," *Nat. Mater.*, **14**, 512 (2015).
- [72] C. Zhang, B. Wang, W. Li, S. Huang, L. Kong, Z. Li, and L. Li, "Conversion of invisible metal-organic frameworks to luminescent perovskite nanocrystals for confidential information encryption and decryption," *Nat. Commun.*, **8**, 1138 (2017).
- [73] P.-L. Wang, L.-H. Xie, E. A. Joseph, J.-R. Li, X.-O. Su, and H.-C. Zhou, "Metal-organic frameworks for food safety," *Chem. Rev.*, **119**, 10638 (2019).
- [74] "NuMat Technologies, Inc." <https://www.numat-tech.com>.
- [75] "novomOF," <https://novomof.com>.
- [76] "MOF Technologies," <https://www.moftechnologies.com> ().
- [77] "MOFWORX," <https://www.mofworx.com> ().
- [78] Q.-L. Zhu and Q. Xu, "Metal-organic framework composites," *Chem. Soc. Rev.*, **43**, 5468 (2014).
- [79] B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, and J. Gascon, "Metal-organic framework based mixed matrix membranes: a solution for highly efficient CO₂ capture?" *Chem. Soc. Rev.*, **44**, 2421 (2015).
- [80] T. Tian, Z. Zeng, D. Vulpe, M. E. Casco, G. Divitini, P. A. Midgley, J. Silvestre-Albero, J.-C. Tan, P. Z. Moghadam, and D. Fairen-Jimenez, "A sol-gel monolithic metal-organic framework with enhanced methane uptake," *Nat. Mater.*, **17**, 174 (2018).

- [81] C. M. Simon, J. Kim, D. A. Gomez-Gualdron, J. S. Carno, Y. G. Chung, R. L. Martin, R. Mercado, M. W. Deem, D. Gunger, M. Haranczyk, D. S. Sholl, R. Q. Snurr, and B. Smit, "The materials genome in action: identifying the performance limits for methane storage," *Energy Environ. Sci.*, **8**, 1190 (2015).
- [82] S. M. J. Rogge, M. Waroquier, and V. Van Speybroeck, "Reliably modeling the mechanical stability of rigid and flexible metal-organic frameworks," *Acc. Chem. Res.*, **51**, 138 (2017).
- [83] J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi, and J. R. Long, "Methane storage in flexible metal-organic frameworks with intrinsic thermal management," *Nature*, **527**, 357 (2015).
- [84] R. B. Getman, Y.-S. Bae, C. E. Wilmer, and R. Q. Snurr, "Review and analysis of molecular simulations of methane, hydrogen, and acetylene storage in metal-organic frameworks," *Chem. Rev.*, **112**, 703 (2012).
- [85] Q. Yang, D. Liu, C. Zhong, and J.-R. Li, "Development of computational methodologies for metal-organic frameworks and their application in gas separations," *Chem. Rev.*, **113**, 8261 (2013).
- [86] S. O. Odoh, C. J. Cramer, D. G. Truhlar, and L. Gagliardi, "Quantum-chemical characterization of the properties and reactivities of metal-organic frameworks," *Chem. Rev.*, **115**, 6051 (2015).
- [87] F.-X. Coudert and A. H. Fuchs, "Computational characterization and prediction of metal-organic framework properties," *Coord. Chem. Rev.*, **307**, 211 (2016).
- [88] G. Fraux and F.-X. Coudert, "Recent advances in the computational chemistry of soft porous crystals," *Chem. Commun.*, **53**, 7211 (2017).
- [89] "MOFSIM2019," <https://mofsim.eu> ().
- [90] P. Z. Moghadam, T. Islamoglu, S. Goswami, J. Exley, M. Fantham, C. F. Kaminski, R. Q. Snurr, O. K. Farha, and D. Fairen-Jimenez, "Computer-aided discovery of a metal-organic framework with superior oxygen uptake," *Nat. Commun.*, **9**, 1378 (2018).
- [91] Y. J. Colón and R. Q. Snurr, "High-throughput computational screening of metal-organic frameworks," *Chem. Soc. Rev.*, **43**, 5735 (2014).

- [92] P. G. Boyd, Y. Lee, and B. Smit, "Computational development of the nanoporous materials genome," *Nat. Rev. Mater.*, **2**, 17037 (2017).
- [93] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, "Commentary: the Materials Project: a materials genome approach to accelerating materials innovation," *APL Mater.*, **1**, 011002 (2013).
- [94] International Human Genome Sequencing Consortium, "Finishing the euchromatic sequence of the human genome," *Nature*, **431**, 931 (2004).
- [95] Y. G. Chung, J. Camp, M. Haranczyk, B. J. Sikora, W. Bury, V. Krungeleviciute, T. Yildirim, O. K. Farha, D. S. Sholl, and R. Q. Snurr, "Computation-ready, experimental metal-organic frameworks: a tool to enable high-throughput screening of nanoporous crystals," *Chem. Mater.*, **26**, 6185 (2014).
- [96] F. Salles, A. Ghoufi, G. Maurin, R. G. Bell, C. Mellot-Draznieks, and G. Férey, "Molecular dynamics simulations of breathing MOFs: structural transformations of MIL-53(Cr) upon thermal activation and CO₂ adsorption," *Angew. Chem. Int. Ed.*, **47**, 8487 (2008).
- [97] J. S. Grosch and F. Paesani, "Molecular-level characterization of the breathing behavior of the jungle-gym-type DMOF-1 metal-organic framework," *J. Am. Chem. Soc.*, **134**, 4207 (2012).
- [98] A. U. Ortiz, A. Boutin, A. H. Fuchs, and F.-X. Coudert, "Anisotropic elastic properties of flexible metal-organic frameworks: How soft are soft porous crystals?" *Phys. Rev. Lett.*, **109**, 195502 (2012).
- [99] H. Wu, T. Yildirim, and W. Zhou, "Exceptional mechanical stability of highly porous zirconium metal-organic framework UiO-66 and its important implications," *J. Phys. Chem. Lett.*, **4**, 925 (2013).
- [100] M. R. Ryder, B. Civalieri, T. D. Bennett, S. Henke, S. Rudić, G. Cinque, F. Fernandez-Alonso, and J.-C. Tan, "Identifying the role of terahertz vibrations in metal-organic frameworks: from gate-opening phenomenon to shear-driven structural destabilization," *Phys. Rev. Lett.*, **113**, 215502 (2014).
- [101] A. W. Peters, A. J. Howarth, and O. K. Farha, "Experimentalists and theorists need to talk," *Nature*, **551**, 433 (2017).
- [102] T. Bogaerts, L. Vanduyfhuys, D. E. P. Vanpoucke, J. Wieme, M. Waroquier, P. Van Der Voort, and V. Van Speybroeck, "Fine-tuning the

- theoretically predicted structure of MIL-47(V) with the aid of powder X-ray diffraction,” *CrystEngComm*, **17**, 8612 (2015).
- [103] B. Bueken, F. Vermoortele, M. J. Cliffe, M. T. Wharmby, D. Foucher, J. Wieme, L. Vanduyfhuys, C. Martineau, N. Stock, F. Taulelle, V. Van Speybroeck, A. L. Goodwin, and D. De Vos, “A breathing zirconium metal-organic framework with reversible loss of crystallinity by correlated nanodomain formations,” *Chem. Eur. J.*, **22**, 3264 (2016).
- [104] G.-B. Wang, K. Leus, K. Hendrickx, J. Wieme, H. Depauw, Y.-Y. Liu, V. Van Speybroeck, and P. Van Der Voort, “A series of sulfonic acid functionalized mixed-linker DUT-4 analogues: synthesis, gas sorption properties and catalytic performance,” *Dalton Trans.*, **46**, 14356 (2017).
- [105] A. E. J. Hoffman, L. Vanduyfhuys, I. Nevjestic, J. Wieme, S. M. J. Rogge, H. Depauw, P. Van Der Voort, H. Vrielinck, and V. Van Speybroeck, “Elucidating the vibrational fingerprint of the flexible metal-organic framework MIL-53(Al) using a combined experimental/computational approach,” *J. Phys. Chem. C*, **122**, 2734 (2018).
- [106] J. Wieme, S. M. J. Rogge, P. G. Yot, L. Vanduyfhuys, S. K. Lee, J.-S. Chang, M. Waroquier, G. Maurin, and V. Van Speybroeck, “Pillared-layered metal-organic frameworks for mechanical energy storage applications,” *J. Mater. Chem. A*, **7**, 22663 (2019).
- [107] M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert, and A. L. Goodwin, “Correlated defect nanoregions in a metal-organic framework,” *Nat. Commun.*, **5**, 4176 (2014).
- [108] T. D. Bennett, A. K. Cheetham, A. H. Fuchs, and F.-X. Coudert, “Interplay between defects, disorder and flexibility in metal-organic frameworks,” *Nat. Chem.*, **9**, 11 (2017).
- [109] J. Hajek, C. Caratelli, R. Demuynck, K. De Wispelaere, L. Vanduyfhuys, M. Waroquier, and V. Van Speybroeck, “On the intrinsic dynamic nature of the rigid UiO-66 metal-organic framework,” *Chem. Sci.*, **9**, 2723 (2018).
- [110] S. M. J. Rogge, J. Wieme, L. Vanduyfhuys, T. Verstraelen, S. Vandenbrande, G. Maurin, M. Waroquier, and V. Van Speybroeck, “Thermodynamic insight in the high-pressure behavior of UiO-66: effect of linker defects and linker expansion,” *Chem. Mater.*, **28**, 5721 (2016).
- [111] J. P. Dürholt, R. Galvelis, and R. Schmid, “Coarse graining of force fields for metal-organic frameworks,” *Dalton Trans.*, **45**, 4370 (2016).

- [112] J. D. Evans and F.-X. Coudert, "Macroscopic simulation of deformation in soft microporous composites," *J. Phys. Chem. Lett.*, **8**, 1578 (2017).
- [113] J. Keupp and R. Schmid, "Molecular dynamics simulations of the "breathing" phase transformation of MOF nanocrystallites," *Adv. Theory Simul.*, 1900117 (2019).
- [114] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," *Ann. Phys.*, **389**, 457 (1927).
- [115] E. Schrödinger, "An undulatory theory of the mechanics of atoms and molecules," *Phys. Rev.*, **28**, 1049 (1926).
- [116] B. Vlaisavljevich, J. Huck, Z. Hulvey, K. Lee, J. A. Mason, J. B. Neaton, J. R. Long, C. M. Brown, D. Alfè, A. Michaelides, and B. Smit, "Performance of van der Waals corrected functionals for guest adsorption in the $M_2(\text{dobdc})$ metal-organic frameworks," *J. Phys. Chem. A*, **4139-4151**, 121 (2017).
- [117] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, **136**, B864 (1964).
- [118] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, **140**, A1133 (1965).
- [119] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, and K. A. Lyssenko, "Density functional theory is straying from the path toward the exact functional," *Science*, **355**, 49 (2017).
- [120] R. J. Maurer, C. Freysoldt, A. M. Reilly, J. G. Brandenburg, O. T. Hofmann, T. Björkman, S. Lebègue, and A. Tkatchenko, "Advances in density-functional calculations for materials modeling," *Annu. Rev. Mater. Res.*, **49** (2019).
- [121] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, **77**, 3865 (1996).
- [122] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, "Restoring the density-gradient expansion for exchange in solids and surfaces," *Phys. Rev. Lett.*, **100**, 136406 (2008).
- [123] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, "Higher-accuracy van der Waals density functional," *Phys. Rev. B*, **82**, 081101 (2010).

- [124] J. Sun, A. Ruzsinszky, and J. P. Perdew, “Strongly Constrained and Appropriately Normed semilocal density functional,” *Phys. Rev. Lett.*, **115**, 036402 (2015).
- [125] H. Peng, Z.-H. Yang, J. P. Perdew, and J. Sun, “Versatile van der Waals density functional based on a meta-generalized gradient approximation,” *Phys. Rev. X*, **6**, 041005 (2016).
- [126] Y. Zhao and D. G. Truhlar, “A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions,” *J. Chem. Phys.*, **125**, 194101 (2006).
- [127] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, “Influence of the exchange screening parameter on the performance of screened hybrid functionals,” *J. Chem. Phys.*, **125**, 224106 (2006).
- [128] A. D. Becke, “Density-functional exchange-energy approximation with correct asymptotic behavior,” *Phys. Rev. A*, **38**, 3098 (1988).
- [129] S. H. Vosko, L. Wilk, and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis,” *Can. J. Phys.*, **58**, 1200 (1980).
- [130] S. Kurth, J. P. Perdew, and P. Blaha, “Molecular and solid-state tests of density functional approximations: LSD, GGAs, and meta-GGAs,” *Int. J. Quantum Chem.*, **75**, 889 (1999).
- [131] F. Tran, J. Stelzl, and P. Blaha, “Rungs 1 to 4 of DFT Jacob’s ladder: extensive test on the lattice constant, bulk modulus, and cohesive energy of solids,” *J. Chem. Phys.*, **144**, 204120 (2016).
- [132] N. Mardirossian and M. Head-Gordon, “Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals,” *Mol. Phys.*, **115**, 2315 (2017).
- [133] J. Wieme, K. Lejaeghere, G. Kresse, and V. Van Speybroeck, “Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks,” *Nat. Commun.*, **9**, 4899 (2018).
- [134] A. E. J. Hoffman, J. Wieme, S. M. J. Rogge, M. Waroquier, and V. Van Speybroeck, “The impact of lattice vibrations on the macroscopic breathing behavior of MIL-53(Al),” *Z. Kristallogr. Cryst. Mater.*, **234**, 529 (2019).

- [135] L. Vanduyfhuys, S. Vandenbrande, J. Wieme, M. Waroquier, T. Verstraelen, and V. Van Speybroeck, "Extension of the QuickFF force field protocol for an improved accuracy of structural, vibrational, mechanical and thermal properties of metal-organic frameworks," *J. Comput. Chem.*, **39**, 999 (2018).
- [136] R. Demuynck, S. M. J. Rogge, L. Vanduyfhuys, J. Wieme, M. Waroquier, and V. Van Speybroeck, "Efficient construction of free energy profiles of breathing metal-organic frameworks using advanced molecular dynamics simulations," *J. Chem. Theory Comput.*, **13**, 5861 (2017).
- [137] R. Demuynck, J. Wieme, S. M. J. Rogge, K. D. Dedecker, L. Vanduyfhuys, M. Waroquier, and V. Van Speybroeck, "Protocol for identifying accurate collective variables in enhanced molecular dynamics simulations for the description of structural transformations in flexible metal-organic frameworks," *J. Chem. Theory Comput.*, **14**, 5511 (2018).
- [138] K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. de Gironcoli, T. Deutsch, J. K. Dewhurst, I. Di Marco, C. Draxl, M. Dufak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Grånäs, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iuşan, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepnik, E. Küçükbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordström, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G.-M. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunström, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. van Setten, V. Van Speybroeck, J. M. Wills, J. R. Yates, G.-X. Zhang, and S. Cottenier, "Reproducibility in density functional theory calculations of solids," *Science*, **351**, 1415 (2016).
- [139] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Phys. Rev. B*, **54**, 11169 (1996).
- [140] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Phys. Rev. B*, **59**, 1758 (1999).
- [141] A. M. Walker, B. Civalleri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Román-Pérez, J. M. Soler, and J. D. Gale, "Flexibility in a metal-organic framework material controlled by weak

- dispersion forces: the bistability of MIL-53(Al),” *Angew. Chem. Int. Ed.*, **41**, 7501 (2010).
- [142] F. London, “Über einige Eigenschaften und Anwendungen der Molekularkräfte,” *Z. Physik. Chem. B*, **11**, 222 (1930).
- [143] S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, “Dispersion-corrected mean-field electronic structure methods,” *Chem. Rev.*, **116**, 5105 (2016).
- [144] J. Hermann, R. A. DiStasio Jr., and A. Tkatchenko, “First-principles models for van der Waals interactions in molecules and materials: concepts, theory, and applications,” *Chem. Rev.*, **117**, 4714 (2017).
- [145] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 Elements H-Pu,” *J. Chem. Phys.*, **132**, 15104 (2010).
- [146] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, “Accurate and efficient method for many-body van der Waals interactions,” *Phys. Rev. Lett.*, **108**, 236402 (2012).
- [147] A. Ambrosetti, A. M. Reilly, R. A. DiStasio Jr., and A. Tkatchenko, “Long-range correlation energy calculated from coupled atomic response functions,” *J. Chem. Phys.*, **140**, 18A508 (2014).
- [148] A. Tkatchenko, “Current understanding of van der Waals effects in realistic materials,” *Adv. Funct. Mater.*, **25**, 2054 (2015).
- [149] L. M. Woods, D. A. R. Dalvit, A. Tkatchenko, P. Rodriguez-Lopez, A. W. Rodriguez, and R. Podgornik, “Materials perspective on Casimir and van der Waals interactions,” *Rev. Mod. Phys.*, **88**, 045003 (2016).
- [150] M. Stöhr, T. Van Voorhis, and A. Tkatchenko, “Theory and practice of modeling van der Waals interactions in electronic-structure calculations,” *Chem. Soc. Rev.*, **48**, 4118 (2019).
- [151] S. Grimme, S. Ehrlich, and L. Goerigk, “Effect of the damping function in dispersion corrected density functional theory,” *J. Comput. Chem.*, **32**, 1456 (2011).
- [152] H. B. G. Casimir and D. Polder, “The influence of retardation on the London-van der Waals forces,” *Phys. Rev.*, **73**, 360 (1948).

- [153] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," *J. Comput. Chem.*, **27**, 1787 (2006).
- [154] J. Moellmann and S. Grimme, "DFT-D3 study of some molecular crystals," *J. Phys. Chem. C*, **118**, 7615 (2014).
- [155] B. M. Axilrod and E. Teller, "Interaction of the van der Waals type between three atoms," *J. Chem. Phys.*, **11**, 1943 (1943).
- [156] Y. Muto, "Force between nonpolar molecules," *Proc. Phys. Math. Soc. Jpn.*, **17**, 629 (1944).
- [157] A. Tkatchenko and M. Scheffler, "Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data," *Phys. Rev. Lett.*, **102**, 073005 (2009).
- [158] F. L. Hirshfeld, "Bonded-atom fragments for describing molecular charge densities," *Theor. Chem. Acc.*, **44**, 129 (1977).
- [159] A. G. Donchev, "Many-body effects of dispersion interaction," *J. Chem. Phys.*, **125**, 074713 (2006).
- [160] O. A. Vydrov and T. Van Voorhis, "Dispersion interactions from a local polarizability model," *Phys. Rev. A*, **81**, 062708 (2010).
- [161] T. Risthaus and S. Grimme, "Benchmarking of London dispersion-accounting density functional theory methods on very large molecular complexes," *J. Chem. Theory Comput.*, **9**, 1580 (2013).
- [162] A. M. Reilly and A. Tkatchenko, "Understanding the role of vibrations, exact exchange, and many-body van der Waals interactions in the cohesive properties of molecular crystals," *J. Chem. Phys.*, **139**, 024705 (2013).
- [163] A. M. Reilly and A. Tkatchenko, "van der Waals interactions in molecular materials: beyond pairwise additivity," *Chem. Sci.*, **6**, 3289 (2015).
- [164] H. Eshuis, J. E. Bates, and F. Furche, "Electron correlation methods based on the random phase approximation," *Theor. Chem. Acc.*, **131**, 1084 (2012).
- [165] J. Harl and G. Kresse, "Accurate bulk properties from approximate many-body techniques," *Phys. Rev. Lett.*, **103**, 056401 (2009).

- [166] X. Ren, P. Rinke, C. Joas, and M. Scheffler, "Random-phase approximation and its applications in computational chemistry and materials science," *J. Mater. Sci.*, **47**, 7447 (2012).
- [167] L. Schimka, R. Gaudoin, J. Klimeš, M. Marsman, and G. Kresse, "Lattice constants and cohesive energies of alkali, alkaline-earth, and transition metals: random phase approximation with singles correction," *Phys. Rev. B*, **87**, 094506 (2013).
- [168] O. Gunnarsson and B. I. Lundqvist, "Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism," *Phys. Rev. B*, **13**, 4274 (1976).
- [169] D. C. Langreth and J. P. Perdew, "Exchange-correlation energy of a metallic surface: wave-vector analysis," *Phys. Rev. B*, **15**, 2884 (1977).
- [170] M. Kaltak and J. Klimeš, "Low scaling algorithms for the random phase approximation: imaginary time and laplace transformations," *J. Chem. Theory Comput.*, **10**, 2498 (2014).
- [171] M. Kaltak, J. Klimeš, and G. Kresse, "Cubic scaling algorithm for the random phase approximation: self-interstitials and vacancies in Si," *Phys. Rev. B*, **90**, 054115 (2014).
- [172] B. Ramberger, T. Schäfer, and G. Kresse, "Analytic interatomic forces in the random phase approximation," *Phys. Rev. Lett.*, **118**, 106403 (2017).
- [173] J. Klimeš, M. Kaltak, E. Maggio, and G. Kresse, "Singles correlation energy contributions in solids," *J. Chem. Phys.*, **143**, 102816 (2015).
- [174] P. G. Boyd, S. M. Moosavi, M. Witman, and B. Smit, "Force-field prediction of materials properties in metal-organic frameworks," *J. Phys. Chem. Lett.*, **8**, 357 (2017).
- [175] J. Heinen and D. Dubbeldam, "On flexible force fields for metal-organic frameworks: Recent developments and future prospects," *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, **8**, e1363 (2018).
- [176] M. A. Addicoat, N. Vankova, I. F. Akter, and T. Heine, "Extension of the Universal Force Field to metal-organic frameworks," *J. Chem. Theory Comput.*, **10**, 880 (2014).
- [177] S. Bureekaew, S. Amirjalayer, M. Tafipolsky, C. Spickermann, T. K. Roy, and R. Schmid, "MOF-FF – A flexible first-principles derived force field for metal-organic frameworks," *Phys. Status Solidi B*, **250**, 1128 (2013).

- [178] L. Vanduyfhuys, S. Vandenbrande, T. Verstraelen, R. Schmid, M. Waroquier, and V. Van Speybroeck, "QuickFF: a program for a quick and easy derivation of force fields for metal-organic frameworks from ab initio input," *J. Comput. Chem.*, **36**, 1015 (2015).
- [179] J. Chen and T. J. Martínez, "QTPIE: charge transfer with polarization current equalization. A fluctuating charge model with correct asymptotics," *Chem. Phys. Lett.*, **438**, 315 (2007).
- [180] T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Speybroeck, M. Waroquier, and P. W. Ayers, "Minimal Basis Iterative Stockholder: atoms in molecules for force-field development," *J. Chem. Theory Comput.*, **12**, 3894 (2016).
- [181] J. H. Lii and N. L. Allinger, "Molecular mechanics. The MM3 force field for hydrocarbons. 3. The van der Waals potentials and crystal data for aliphatic and aromatic hydrocarbons," *J. Am. Chem. Soc.*, **111**, 8576 (1989).
- [182] N. L. Allinger, X. Zhou, and J. Bergsma, "Molecular mechanics parameters," *J. Mol. Struct.-THEOCHEM*, **312**, 69 (1994).
- [183] H. Sun, "COMPASS: an ab initio force-field optimized for condensed-phase applications - overview with details on alkane and benzene compounds," *J. Phys. Chem. B*, **102**, 7338 (1998).
- [184] J. Wieme, L. Vanduyfhuys, S. M. J. Rogge, M. Waroquier, and V. Van Speybroeck, "Exploring the flexibility of MIL-47(V)-type materials using force field molecular dynamics," *J. Phys. Chem. C*, **120**, 14934 (2016).
- [185] A. Lemaire, J. Wieme, S. M. J. Rogge, M. Waroquier, and V. Van Speybroeck, "On the importance of anharmonicities and nuclear quantum effects in modelling the structural properties and thermal expansion in MOF-5," *J. Chem. Phys.*, **150**, 094503 (2019).
- [186] V. Kapil, J. Wieme, S. Vandenbrande, A. Lemaire, V. Van Speybroeck, and M. Ceriotti, "Modeling the structural and thermal properties of loaded metal-organic frameworks. An interplay of quantum and anharmonic fluctuations," *J. Chem. Theory Comput.*, **15**, 3237 (2019).
- [187] J. Wieme, S. Vandenbrande, A. Lemaire, V. Kapil, L. Vanduyfhuys, and V. Van Speybroeck, "Thermal engineering of metal-organic frameworks for adsorption applications: a molecular simulations perspective," *ACS Appl. Mater. Inter.*, **11**, 38697 (2019).

- [188] X.-L. Lv, M. Tong, H. Huang, B. Wang, L. Gan, Q. Yang, C. Zhong, and J.-R. Li, "A high surface Zr(IV)-based metal-organic framework showing stepwise gas adsorption and selective dye uptake," *J. Solid State Chem.*, **223**, 104 (2015).
- [189] F. Niekel, M. Ackermann, P. Guerrier, and N. Stock, "Aluminum-1,4-cyclohexanedicarboxylates: high-throughput and temperature-dependent in situ EDXRD studies," *Inorg. Chem.*, **52**, 8699 (2013).
- [190] H. J. Choi, M. Dincă, and J. R. Long, "Broadly hysteretic H₂ adsorption in the microporous metal-organic framework Co(1,4-benzendipyrzolate)," *J. Am. Chem. Soc.*, **130**, 7848 (2008).
- [191] D. N. Dybtsev, H. Chun, and K. Kim, "Rigid and flexible: a highly porous metal-organic framework with unusual guest-dependent dynamic behavior," *Angew. Chem. Int. Ed.*, **43**, 5033 (2004).
- [192] U. Stoeck, S. Krause, V. Bon, I. Senkovska, and S. Kaskel, "A highly porous metal-organic framework, constructed from a cuboctahedral super-molecular building block, with exceptionally high methane uptake," *Chem. Commun.*, **48**, 10841 (2012).
- [193] L. Vanduyfhuys and V. Van Speybroeck, "Unraveling the thermodynamic conditions for negative gas adsorption in soft porous crystals," *Commun. Phys.*, **2**, 102 (2019).
- [194] L. Liu, X. Wang, and A. J. Jacobson, "AlF · 1,4-benzenedicarboxylate: synthesis and absorption properties," *Dalton Trans.*, **39**, 1722 (2010).
- [195] M. Gaabg, N. Trukhan, S. Maurer, R. Gummaraju, and U. Müller, "The progression of Al-based metal-organic frameworks – From academic research to industrial production and applications," *Micropor. Mesopor. Mater.*, **157**, 131 (2012).
- [196] G. Chaplais, A. Simon-Masseron, F. Porcher, C. Lecomte, D. Bazer-Bachi, N. Bats, and J. Patarin, "IM-19: a new flexible microporous gallium based-MOF framework with pressure- and temperature-dependent openings," *Phys. Chem. Chem. Phys.*, **11**, 5241 (2009).
- [197] S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang, and M. Schröder, "Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host," *Nat. Chem.*, **4**, 887 (2012).

- [198] D. A. Gomez-Gualdron, O. V. Gutov, V. Krungleviciute, B. Borah, J. E. Mondloch, J. T. Hupp, T. Yildirim, O. K. Farha, and R. Q. Snurr, "Computational design of metal-organic frameworks based on stable zirconium building units for storage and delivery of methane," *Chem. Mater.*, **26**, 5632 (2014).
- [199] L. Stewart, W. Lu, Z.-. Wei, D. Ila, C. Padilla, and H.-C. Zhou, "A zirconium metal-organic framework with an exceptionally high volumetric surface area," *Dalton Trans.*, **46**, 14270 (2017).
- [200] D. E. P. Vanpoucke, K. Lejaeghere, V. Van Speybroeck, M. Waroquier, and A. Ghysels, "Mechanical properties from periodic plane wave quantum mechanical codes: the challenge of the flexible nanoporous MIL-47(V) framework," *J. Phys. Chem. C*, **119**, 23752 (2015).
- [201] J. Hoja, A. M. Reilly, and A. Tkatchenko, "First-principles modeling of molecular crystals: structures and stabilities, temperature and pressure," *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, **7**, e1294 (2017).
- [202] A. Togo and I. Tanaka, "First principles phonon calculations in materials science," *Scr. Mater.*, **108**, 1 (2015).
- [203] A. Ghysels, T. Verstraelen, K. Hemelsoet, M. Waroquier, and V. Van Speybroeck, "TAMkin: a versatile package for vibrational analysis and chemical kinetics," *J. Chem. Inf. Model.*, **50**, 1736 (2010).
- [204] S. M. J. Rogge, L. Vanduyfhuys, A. Ghysels, M. Waroquier, T. Verstraelen, G. Maurin, and V. Van Speybroeck, "A comparison of barostats for the mechanical characterization of metal-organic frameworks," *J. Chem. Theory Comput.*, **11**, 5583 (2015).
- [205] T. Verstraelen, L. Vanduyfhuys, S. Vandenbrande, and S. M. J. Rogge, "Yaff 1.4.2," (2017).
- [206] S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *J. Comput. Phys.*, **117**, 1 (1995).
- [207] D. Frenkel and B. Smit, *Understanding Molecular Simulations* (Academic Press, 2002).
- [208] A. Einstein, "Die Plancksche Theorie der Strahlung und die Theorie der Spezifischen Wärme," *Ann. Phys.*, **327**, 180 (1907).
- [209] P.-L. Dulong and A. T. Petit, "Recherches sur quelques points importants de la théorie de la chaleur," *Ann. Chim. Phys.*, **10**, 395 (1819).

- [210] M. Parrinello and A. Rahman, "Study of an F center in molten KCl," *J. Chem. Phys.*, **80**, 860 (1984).
- [211] R. P. Feynman, "Space-time approach to non-relativistic quantum mechanics," *Rev. Mod. Phys.*, **20**, 367 (1948).
- [212] J. P. Neirotti and D. L. Freeman, "A heat capacity estimator for Fourier path integral simulations," *J. Chem. Phys.*, **112**, 3990 (2000).
- [213] K. R. Glaesemann and L. E. Fried, "Improved heat capacity estimator for path integral simulations," *J. Chem. Phys.*, **117**, 3020 (2002).
- [214] C. Predescu, D. Sabo, J. D. Doll, and D. L. Freeman, "Heat capacity estimators for random series path-integral methods by finite-difference schemes," *J. Chem. Phys.*, **119**, 12119 (2003).
- [215] M. Shiga and W. Shinoda, "Calculation of heat capacities of light and heavy water by path-integral molecular dynamics," *J. Chem. Phys.*, **123**, 134502 (2005).
- [216] W. Shinoda and M. Shiga, "Quantum simulation of the heat capacity of water," *Phys. Rev. E*, **71**, 041204 (2005).
- [217] T. M. Yamamoto, "Path-integral virial estimator based on the scaling of fluctuation coordinates: application to quantum clusters with fourth-order propagators," *J. Chem. Phys.*, **123**, 104101 (2005).
- [218] I. Poltavsky and A. Tkatchenko, "Modeling quantum nuclei with perturbed path integral molecular dynamics," *Chem. Sci.*, **7**, 1368 (2016).
- [219] S. Jang, S. Jang, and G. A. Voth, "Applications of higher order composite factorization schemes in imaginary time path integral simulations," *J. Chem. Phys.*, **115**, 7832 (2001).
- [220] T. E. Markland and D. E. Manolopoulos, "A refined ring polymer contraction scheme for systems with electrostatic interactions," *Chem. Phys. Lett.*, **464**, 256 (2008).
- [221] M. Ceriotti and D. E. Manolopoulos, "Efficient first-principles calculation of the quantum kinetic energy and momentum distribution of nuclei," *Phys. Rev. Lett.*, **109**, 100604 (2012).
- [222] V. Kapil, J. VandeVondele, and M. Ceriotti, "Accurate molecular dynamics and nuclear quantum effects at low cost by multiple steps in real and imaginary time: using density functional theory to accelerate wavefunction methods," *J. Chem. Phys.*, **144**, 054111 (2016).

- [223] V. Kapil, J. Behler, and M. Ceriotti, "High order path integrals made easy," *J. Chem. Phys.*, **145**, 234103 (2016).
- [224] T. E. Markland and M. Ceriotti, "Nuclear quantum effects enter the mainstream," *Nat. Rev. Chem.*, **2**, 0109 (2018).
- [225] M. Suzuki, "Hybrid exponential product formulas for unbounded operators with possible applications to Monte Carlo simulations," *Phys. Lett. A*, **201**, 425 (1995).
- [226] S. A. Chin, "Symplectic integrators from composite operator factorizations," *Phys. Lett. A*, **226**, 344 (1997).
- [227] G. Bussi, T. Zykova-Timan, and M. Parrinello, "Isothermal-isobaric molecular dynamics using stochastic velocity rescaling," *J. Chem. Phys.*, **130**, 074101 (2009).
- [228] M. Ceriotti, J. More, and D. E. Manolopoulos, "i-PI: A Python interface for ab initio path integral molecular dynamics simulations," *Comp. Phys. Commun.*, **185**, 1019 (2014).
- [229] V. Kapil, M. Rossi, O. Marsalek, R. Petraglia, Y. Litman, T. Spura, B. Cheng, A. Cuzzocrea, R. H. Meißner, D. M. Wilkins, P. Juda, S. P. Bienvenue, W. Fang, J. Kessler, I. Poltavsky, S. Vandenbrande, J. Wieme, C. Corminboeuf, T. D. Kühne, D. E. Manolopoulos, T. E. Markland, J. O. Richardson, A. Tkatchenko, G. A. Tribello, V. V. Speybroeck, and M. Ceriotti, "i-PI 2.0: A universal force engine for advanced molecular simulations," *Comput. Phys. Commun.*, **236**, 214 (2019).
- [230] M. Tuckerman, B. J. Berne, and G. J. Martyna, "Reversible multiple time scale molecular dynamics," *J. Chem. Phys.*, **97**, 1990 (1992).
- [231] B. Leimkuhler and C. Matthews, "Robust and efficient configurational molecular sampling via Langevin dynamics," *J. Chem. Phys.*, **138**, 174102 (2013).
- [232] B. Mu and K. S. Walton, "Thermal analysis and heat capacity study of metal-organic frameworks," *J. Phys. Chem. C*, **115**, 22748 (2011).
- [233] F. A. Kloutse, R. Zacharia, D. Cossement, and R. Chahine, "Specific heat capacities of MOF-5, Cu-BTC, Fe-BTC, MOF-177 and MIL-53(Al) over wide temperature ranges: measurements and application of empirical group contribution method," *Microporous Mesoporous Mater.*, **217**, 1 (2015).

- [234] D. Dubbeldam, K. S. Walton, D. E. Ellis, and R. Q. Snurr, "Exceptional negative thermal expansion in isorecticular metal-organic frameworks," *Angew. Chem. Int. Ed.*, **46**, 4496 (2007).
- [235] S. S. Han and W. A. Goddard, "Metal-organic frameworks provide large negative thermal expansion behavior," *J. Phys. Chem. C*, **111**, 15185 (2007).
- [236] J. A. Greathouse and M. D. Allendorf, "Force field validation for molecular dynamics simulations of IRMOF-1 and other isorecticular zinc carboxylate coordination polymers," *J. Phys. Chem. C*, **112**, 5795 (2008).
- [237] M. Tafipolsky and R. Schmid, "Systematic first principles parameterization of force fields for metal-organic frameworks using a genetic algorithm approach," *J. Phys. Chem. B*, **113**, 1341 (2009).
- [238] M. Tafipolsky, S. Amirjalayer, and R. Schmid, "First-principles-derived force field for copper paddle-wheel-based metal-organic frameworks," *J. Phys. Chem. C*, **114**, 14402 (2010).
- [239] W. Zhou, H. Wu, T. Yildirim, J. R. Simpson, and A. R. Hight Walker, "Origin of the exceptional negative thermal expansion in metal-organic framework-5 $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$," *Phys. Rev. B*, **78**, 054114 (2008).
- [240] S. R. G. Balestra, R. Bueno-Perez, S. Hamad, D. Dubbeldam, A. R. Ruiz-Salvador, and S. Calero, "Controlling thermal expansion: a metal-organic frameworks route," *Chem. Mater.*, **28**, 8296 (2016).
- [241] N. Lock, Y. Wu, M. Christensen, L. J. Cameron, V. K. Peterson, A. J. Bridgeman, C. J. Kepert, and B. B. Iversen, "Elucidating negative thermal expansion in MOF-5," *J. Phys. Chem. C*, **114**, 16181 (2010).
- [242] Y. Wu, A. Kobayashi, G. J. Halder, V. K. Peterson, K. W. Chapman, N. Lock, P. D. Southon, and C. J. Kepert, "Negative thermal expansion in the metal-organic framework material $\text{Cu}_3(\text{1,3,5-benzenetricarboxylate})_2$," *Angew. Chem. Int. Ed.*, **47**, 8929 (2008).
- [243] M. Ceriotti, G. Bussi, and M. Parrinello, "Colored-noise thermostats à la carte," *J. Chem. Theory Comput.*, **6**, 1170 (2010).
- [244] R. E. Peierls, "Zur kinetischen Theorie der Wärmeleitung in Kristallen," *Ann. Phys. Lpz.*, **395**, 1055 (1929).
- [245] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, "ShengBTE: A solver of the Boltzmann transport equation for phonons," *Comp. Phys. Comm.*, **185**, 1747 (2014).

- [246] J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, "Predicting phonon properties and thermal conductivity from anharmonic lattice dynamics calculations and molecular dynamics simulations," *Phys. Rev. B*, **79**, 064301 (2009).
- [247] B. L. Huang, Z. Ni, A. Millward, A. J. H. McGaughey, C. Uher, M. Kaviani, and O. M. Yaghi, "Thermal conductivity of a metal-organic framework (MOF-5): Part II. Measurement," *Int. J. Heat Mass Transf.*, **50**, 405 (2007).
- [248] P. K. Schelling, S. R. Phillpot, and P. Keblinski, "Comparison of atomic-level simulation methods for computing thermal conductivity," *Phys. Rev. B*, **65**, 144306 (2002).
- [249] D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, "Size effects in molecular dynamics thermal conductivity predictions," *Phys. Rev. B*, **81**, 214305 (2010).
- [250] H. Babaei, A. J. H. McGaughey, and C. E. Wilmer, "Effect of pore size and shape on the thermal conductivity of metal-organic frameworks," *Chem. Sci.*, **8**, 583 (2017).
- [251] C. Carbogno, R. Ramprasad, and M. Scheffler, "Ab initio Green-Kubo approach for the thermal conductivity of solids," *Phys. Rev. Lett.*, **118**, 175901 (2017).
- [252] L. Han, M. Budge, and A. P. Greaney, "Relationship between thermal conductivity and framework architecture," *Comp. Mat. Sci.*, **94**, 292 (2014).
- [253] B. L. Huang, A. J. H. McGaughey, and M. Kaviani, "Thermal conductivity of metal-organic framework 5 (MOF-5): Part I. Molecular dynamics simulations," *Int. J. Heat Mass Transf.*, **50**, 393 (2007).
- [254] H. Babaei and C. E. Wilmer, "Mechanisms of heat transfer in porous crystals containing adsorbed gases: applications to metal-organic frameworks," *Phys. Rev. Lett.*, **116**, 025902 (2016).
- [255] M. S. Green, "Markoff random processes and the statistical mechanics of time-dependent phenomena. II. Irreversible processes in fluids," *J. Chem. Phys.*, **22**, 398 (1954).
- [256] R. Kubo, "Statistical-mechanical theory of irreversible processes. I. General theory and simple applications to magnetic and conduction problems," *J. Phys. Soc. Jpn.*, **12**, 570 (1957).

- [257] Z. Fan, L. F. C. Pereira, H.-Q. Wang, J.-C. Zheng, D. Donadio, and A. Harju, "Force and heat current formulas for many-body potentials in molecular dynamics simulations with applications to thermal conductivity calculations," *Phys. Rev. B*, **92**, 094301 (2015).
- [258] J. E. Turney, A. J. H. McGaughey, and C. H. Amon, "Assessing the applicability of quantum corrections to classical thermal conductivity predictions," *Phys. Rev. B*, **79**, 224305 (2009).
- [259] J. Li, L. Porter, and S. Yip, "Atomistic modeling of finite-temperature properties of crystalline β -SiC. II. Thermal conductivity and effects of point defects," *J. Nucl. Mater.*, **255**, 139 (1998).
- [260] J. Chen, G. Zhang, and B. Li, "How to improve the accuracy of equilibrium dynamics for computation of thermal conductivity?" *Phys. Lett. A*, **374**, 2392 (2010).
- [261] A. J. H. McGaughey and M. Kaviani, "Thermal conductivity decomposition and analysis using molecular dynamics simulations Part II. Complex silica structures," *Int. J. Heat Mass Transf.*, **47**, 1799 (2004).
- [262] J. Klimeš, "Lattice energies of molecular solids from the random phase approximation with singles corrections," *J. Chem. Phys.*, **145**, 094506 (2016).
- [263] T. Gould, S. Lebégue, J. G. Ángyán, and T. Bučko, "A fractionally ionic approach to polarizability and van der Waals many-body dispersion calculations," *J. Chem. Theory Comput.*, **12** (2016).
- [264] W. P. I. Mounfield and K. S. Walton, "Effect of synthesis solvent on the breathing behavior of MIL-53(Al)," *J. Colloid Interface Sci.*, **447**, 33 (2015).
- [265] M. Fischer, J. Schwegler, C. Paula, P. S. Schulz, and M. Hartmann, "Direct synthesis of non-breathing MIL-53(Al)(ht) from a terephthalate-based ionic liquid as linker precursor," *Dalton Trans.*, **45**, 18443 (2016).
- [266] H. Depauw, I. Nevjestic, G. Wang, K. Leus, F. Callens, E. De Canck, K. De Buysser, H. Vrielinck, and P. Van Der Voort, "Discovery of a novel, large pore phase in a bimetallic Al/V metal-organic framework," *J. Mater. Chem. A*, **5**, 24580 (2017).
- [267] L. Vanduyfhuys, T. Verstraelen, M. Vandichel, M. Waroquier, and V. Van Speybroeck, "Ab initio parametrized force field for the flexible metal-organic framework MIL-53(Al)," *J. Chem. Theory Comput.*, **8**, 3217 (2012).

- [268] C. Serre, F. Millange, C. Thouvenot, M. Nogués, G. Marsolier, D. Louër, and G. Férey, "Very large breathing effect in the first nanoporous chromium(III)-based solids: MIL-53 or $\text{Cr}^{\text{III}}(\text{OH}) \cdot \text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2 \cdot \text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}_x \cdot \text{H}_2\text{O}_y$," *J. Am. Chem. Soc.*, **124**, 13519 (2002).
- [269] I. Beurroies, M. Boulhout, P. L. Llewellyn, B. Kuchta, G. Férey, C. Serre, and R. Denoyel, "Using pressure to provoke the structural transition of metal-organic frameworks," *Angew. Chem. Int. Ed.*, **49**, 7526 (2010).
- [270] P. G. Yot, Z. Boudene, J. Macia, D. Granier, L. Vanduyfhuys, T. Verstraelen, V. Van Speybroeck, T. Devic, C. Serre, G. Férey, N. Stock, and G. Maurin, "Metal-organic frameworks as potential shock absorbers: the case of the highly flexible MIL-53(Al)," *Chem. Commun.*, **50**, 9462 (2014).
- [271] J. Rodriguez, I. Beurroies, T. Loiseau, R. Denoyel, and P. L. Llewellyn, "The direct heat measurement of mechanical energy storage metal-organic frameworks," *Angew. Chem. Int. Ed.*, **54**, 4626 (2015).
- [272] P. G. Yot, L. Vanduyfhuys, E. Alvarez, J. Rodriguez, J.-P. Itié, P. Fabry, N. Guillou, T. Devic, I. Beurroies, P. L. Llewellyn, V. Van Speybroeck, C. Serre, and G. Maurin, "Mechanical energy storage performance of an aluminum fumarate metal-organic framework," *Chem. Sci.*, **7**, 446 (2016).
- [273] M. Wahiduzzaman, N. Reimer, J.-P. Itié, N. Stock, G. Maurin, and P. G. Yot, "Mechanical-pressure induced response of the MOF Al-MIL-53-TDC," *Polyhedron*, **155**, 144 (2018).
- [274] T. Loiseau, C. Mellot-Draznieks, H. Muguerra, G. Férey, M. Haouas, and F. Taulelle, "Hydrothermal synthesis and crystal structure of a new three-dimensional aluminum-organic framework MIL-69 with 2,6 naphthalenedicarboxylate (ndc), $\text{Al}(\text{OH})(\text{ndc}) \cdot \text{H}_2\text{O}$," *C. R. Chimie*, **8**, 765 (2005).
- [275] A. Boutin, D. Bousquet, A. U. Ortiz, F.-X. Coudert, A. H. Fuchs, A. Balandras, G. Weber, I. Bezverkhyy, J.-P. Bellat, G. Ortiz, G. Chaplais, J.-L. Paillaud, C. Marichal, H. Nouali, and J. Patarin, "Temperature-Induced Structural Transitions in the Gallium-Based MIL-53 Metal-Organic Framework," *J. Phys. Chem. C*, **117**, 8180 (2013).
- [276] X.-L. Luo, Z. Yin, and M. Kurmoo, "The construction, structures, and functions of pillared layer metal-organic frameworks," *Inorg. Chem. Front.*, **3**, 1208 (2016).

- [277] N. C. Burtch and K. S. Walton, "Modulating adsorption and stability properties in pillared metal-organic frameworks: a model system for understanding ligand effects," *Acc. Chem. Res.*, **48**, 2850 (2015).
- [278] S. Henke, A. Schneemann, A. Wütscher, and R. A. Fischer, "Directing the breathing behavior of pillared-layered metal-organic frameworks via a systematic library of functionalized linkers bearing flexible substituents," *J. Am. Chem. Soc.*, **134**, 9464 (2012).
- [279] S. Henke, A. Schneemann, and R. A. Fischer, "Massive anisotropic thermal expansion and thermo-responsive breathing in metal-organic frameworks modulated by linker functionalization," *Adv. Funct. Mater.*, **23**, 5990 (2013).
- [280] S. Henke, W. Li, and A. K. Cheetham, "Guest-dependent mechanical anisotropy in pillared-layered soft porous crystals - a nanoindentation study," *Chem. Sci.*, **5**, 2392 (2014).
- [281] K. Uemura, Y. Yamasaki, Y. Komagawa, K. Tanaka, and H. Kita, "Two-step adsorption/desorption on a jungle-gym-type porous coordination polymer," *Angew. Chem. Int. Ed.*, **46**, 6662 (2007).
- [282] K. Uemura, Y. Yamasaki, F. Onishi, H. Kita, and M. Ebihara, "Two-Step adsorption on jungle-gym-type porous coordination polymers: dependence on hydrogen-bonding capability of adsorbates, ligand-substituent effect, and temperature," *Inorg. Chem.*, **49**, 10133 (2010).
- [283] Y. Kim, R. Haldar, H. Kim, J. Koo, and K. Kim, "The guest-dependent thermal response of the flexible MOF $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$," *Dalton Trans.*, **45**, 4187 (2016).
- [284] K. Seki, S. Takamizawa, and W. Mori, "Design and gas adsorption property of a three-dimensional coordination polymer with a stable and highly porous framework," *Chem. Lett.*, **30**, 332 (2001).
- [285] H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li, and H.-C. Zhou, "Recent advances in gas storage and separation using metal-organic frameworks," *Mater. Today*, **21**, 108 (2018).
- [286] Y. Ming, J. Purewal, D. Liu, A. Sudik, C. Xu, J. Yang, M. Veenstra, K. Rhodes, R. Soltis, J. Warner, M. Gaab, U. Müller, and D. J. Siegel, "Thermophysical properties of MOF-5 powders," *Microporous Mesoporous Mater.*, **185**, 235 (2014).

- [287] T. F. Willems, C. H. Rycroft, M. Kazi, J. C. Meza, and M. Haranczyk, "Algorithms and tools for high-throughput geometry-based analysis of crystalline porous materials," *Micropor. Mesopor. Mater.*, **149**, 134 (2012).
- [288] J.-C. Tan and A. K. Cheetham, "Mechanical properties of hybrid inorganic-organic framework materials: establishing fundamental structure-property relationships," *Chem. Soc. Rev.*, **40**, 1059 (2011).
- [289] C. S. Coates and A. Goodwin, "How to quantify isotropic negative thermal expansion: magnitude, range, or both?" *Mater. Hor.*, **6**, 211 (2019).
- [290] B. Cui, C. O. Audu, Y. Liao, S. T. Nguyen, O. K. Farha, J. T. Hupp, and M. Grayson, "Thermal conductivity of ZIF-8 thin-film under ambient gas pressure," *ACS Appl. Mater. Interfaces*, **9**, 28139 (2017).
- [291] H. Wu, W. Zhou, and T. Yildirim, "Methane sorption in nanoporous metal-organic frameworks and first-order phase transition of confined methane," *J. Phys. Chem. C*, **113**, 3029 (2009).
- [292] D. Dubbeldam, S. Calero, D. E. Ellis, and R. Q. Snurr, "RASPA: molecular simulation software for adsorption and diffusion in flexible nanoporous materials," *Mol. Simul.*, **42**, 81 (2016).
- [293] H. Babaei, A. J. H. McGaughey, and C. E. Wilmer, "Transient mass and thermal transport during methane adsorption into the metal-organic framework HKUST-1," *ACS Appl. Mater. Interfaces*, **10**, 2400 (2018).
- [294] M. Beckner and A. Dailly, "A pilot study of activated carbon and metal-organic frameworks for methane storage," *Appl. Energy*, **162**, 506 (2016).
- [295] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi,

- C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian16 Revision D.01," (2013), Gaussian Inc. Wallingford CT.
- [296] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian16 Revision A.03," (2016), Gaussian Inc. Wallingford CT.
- [297] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, "Real-space grid implementation of the projector augmented wave method," *Phys. Rev. B*, **71**, 035109 (2005).
- [298] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsarlis, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen, and K. W. Jacobsen, "Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method," *J. Phys.: Condens. Matter*, **22**, 253202 (2010).
- [299] A. Togo and I. Tanaka, "First principles phonon calculations in materials science," *Scr. Mater.*, **108**, 1 (2015).
- [300] T. Verstraelen, V. Van Speybroeck, and M. Waroquier, "ZEOBUILDER: a GUI toolkit for the construction of complex molecular structures on the nanoscale with building blocks," *J. Chem. Inf. Model.*, **48**, 1530 (2008).



This research was supported by the Research Foundation Flanders (FWO) through a personal mandate.



Funding was also received from the European Union's Horizon 2020 research and innovation programme under the European Research Council consolidator grant agreement no. 647755 (project acronym: DYNPOR).



The computational resources (Stevin Supercomputer Infrastructure) and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, FWO, and the Flemish Government – department EWI.

