Towards modeling spatiotemporal processes in metal-organic frameworks

Sander Vandenhaute, Center for Molecular Modeling, Ghent University, Belgium
Veronique Van Speybroeck, Center for Molecular Modeling, Ghent University, Belgium

Metal-organic frameworks (MOFs) have the ability to respond in a unique dynamic way upon exposure to external stimuli, which may critically depend on the presence of defects and crystal size.[1, 2] Modeling has greatly contributed to understanding the thermodynamics of flexible behavior in MOFs, however the simulation of kinetic phenomena including the appearance of metastable states is very challenging. To realistically simulate the dynamic response of MOFs under operating conditions, it is essential to model realistic crystals with spatial heterogeneities varying from the subnanometer to the micrometer scale on real crystallites with a given morphology. This leads to the terminology spatiotemporal evolution of a MOF, referring to the entanglement between the dynamics of the material and its spatial heterogeneities.[3] Modeling spatiotemporal processes in realistic MOFs at length and time scales comparable to experimental observations is extremely challenging.

Within this contribution, I will illustrate some of the recent efforts to reach this goal. In the contribution of Rogge et al., we have performed mesoscale simulations on a series of MOFs, having dimensions up to 10–20 nm and containing up to a few tens of thousands of atoms, which showed that phase transformations is accompanied by the creation of an interfacial defect where the two phases temporarily coexist.[4] This proof of concept shows the necessity of including spatial heterogeneity in the models. More recently Vandenhaute et al. pushed the limits of current simulations even further, by performing the first classical force field based simulation on MIL-53(Al) containing more than a million atoms. To this end, we exploited the massive parallelism of state-of-the-art GPUs using the OpenMM software package. A new pressure control algorithm was implemented in order to allow for anisotropic cell fluctuations.[5] It was shown that the mechanism of the phase transformation is critically dependent on the size of the systems and the conditions in which the material is brought. Previous simulations were all performed at the classical force field level.

To proceed further in this field and effectively capture dynamic rearrangements of bonds, one needs a more accurate description of the potential energy surface and the

interatomic forces. Density Functional Theory (DFT) simulations are typically used to simulate nanostructured materials with quantum accuracy, however their applicability is limited to nanometer-sized structural models due to their computational cost, even on state-of-the-art computing infrastructure. To bridge the gap towards larger length and time scales, one needs fundamentally new methods which combine the accuracy of DFT with the computational efficiency of classical force fields. The rapidly developing field of Machine Learning Potentials (MLPs) may offer such a hybrid alternative, whereby energies and forces are learned from underlying training data obtained with quantum accuracy and the resulting MLPs may be used to drastically increase accessible length and time scales while keeping the quantum accuracy. So far the usage of MLPs within the MOF community is rather limited. Eckhart and Behler trained a high dimensional neural network potential for MOF-5.[6] Properly trained MLPs typically rely on large training dataset containing tens of thousands of reference configurations, which all need to be calculated at the DFT level. We recently succeeded in developing an MLPs for both rigid and flexible MOFs, based on NequIP, a message passing neural network that requires a drastically lower amount of input data due to its use of rotationally equivariant feature representations.[7] The obtained MLPs are transferable to a wide range of thermodynamic conditions and allow to simulate phase transformations in MOFs with an accuracy mimicking the underlying DFT data. In summary, within this contribution some of our recent contributions towards simulating larger spatiotemporal simulation windows are shown, with the ambition to close the length-time scale gap between theory and experiment.

References

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