Crystal growth and nucleation at metal-organic framework / solution interfaces

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Abstract

Metal-organic frameworks (MOFs) represent an incredibly diverse class of materials with equally diverse applications in catalysis, separations, and gas storage. Despite the prevalence of MOF structures in the literature, in many cases the synthesis of pure, crystalline MOF materials remains a significant challenge, with failed syntheses often yielding mixed crystalline or non-porous amorphous products. Our recent work aims to enable targeted MOF synthesis by developing a comprehensive and predictive model of the fundamental processes occurring at the MOF-solution interface under synthetically-relevant conditions. Our recent accomplishments include: (i) development and implementation of a GPU-accelerated approach to simulation the nucleation of weak electrolytes, and the extension of these methods to large/complex solutes such as MOFs; and (ii) studies of the structure of ZIF interfaces under conditions relevant to crystal growth; and (iii) addressing important open questions in the mechanism of MOF solvent-assisted linker exchange (SALE), and important synthetic pathway for MOFs.

Nucleation of weak electrolytes. Predictive modeling of the nucleation of weak electrolytes presents fundamental challenges of widespread relevance in many domains (e.g. $CaCO_3$/biomineralization, oxalates/kidney stones, MOF growth). We recently developed a rigorous GPU-accelerated Grand Canonical Monte Carlo (GCMC)-based methodology that allows us to model the nucleation of low-solubility crystals in explicit solvent that are otherwise completely inaccessible to traditional molecular dynamics simulation. Our approach allows us to calculate the thermodynamic barriers governing the growth of small nucleates in solution, without relying on ad hoc "grafting" methods.

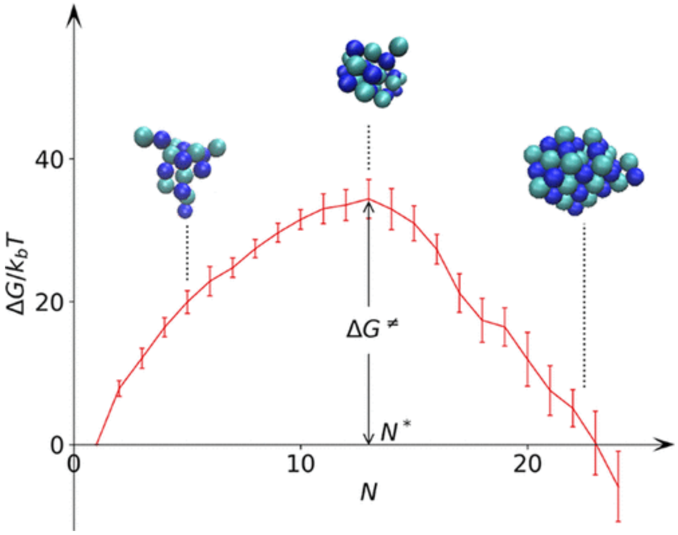

Figure 1. Free energy of salt cluster as a function of cluster, under modest supersaturation conditions.

We recently published a manuscript documenting this method and demonstrating its application in a low-solubility rock salt structure (e.g. LiF) in aqueous solution (see Figure 1). The elegance of this choice of model system is that it makes it possible to "benchmark" our method via comparison with large-scale (multi-μs) brute-force molecular dynamics of the same system. Crucially, we find good agreement between the molecular dynamics (which is infeasibly for most weak electrolytes) and our new method. Note that in addition to predicted free energies, we can also access structures of the evolving salt cluster during the course of nucleation, which provides additional mechanistic insight.

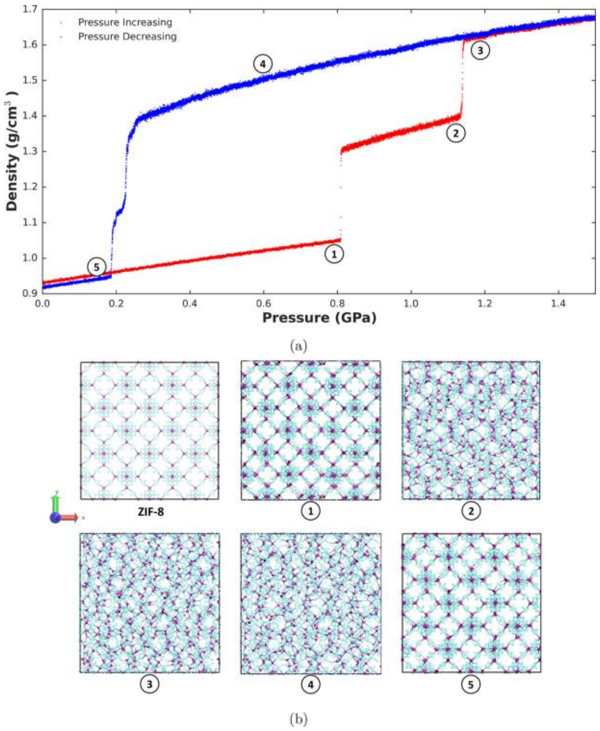

Figure 2. Density of ZIF-8 as a function of pressure during pressure-induced amorphization, modeled using ZIF-FF. The top panel shows density change with pressure, while the bottom panel shows representative structures at the marked time points.

More recently we have been working to extend this method to apply to larger and far more structurally complex solutes, such as $CaCO_3$ and MOFs. The presence of large, polyatomic cations/anions makes a simple GCMC-based approach more difficult to apply in such cases. As such, we have developed an elegant extension to the above protocol that utilizes a highly parallel "swarm" approach and GPU-accelerated thermodynamic integration to sequentially calculate the free energies on ensembles of increasing cluster size. We are currently benchmarking this method on a $CaCO_3$ system for ultimate applications to ZIFs.

Transferable force fields for ZIFs. We recently published a manuscript documenting a highly transferable set of intra-molecular force fields for ZIFs. The resulting force fields can describe a huge number of different ZIF topologies using a single set of parameters. Crucially, the force fields reproduce the relative stability of these ZIF phases (as calculated form DFT) and thus are amenable for use in simulations of ZIF nucleation and growth. A fascinating application of these force fields to the pressure-induced amorphization of ZIF-8 is shown in Figure 2. Within the simulation, we observe a pressure-induced amorphization that exhibits hysteresis (due to a pressure ramp that is rapid on the experimental time scale), with the experimental amorphization pressure (~0.3 GPa) lying within the hysteresis "loop". The predicted amorphous structure is also in excellent agreement with the experimentally observed structure factor (not shown). This result is particularly impressive in that the force fields were not parameterized for the amorphous.

Structure of ZIF-solution interfaces. Over the last year, we also used a combination of DFT calculations and our previously developed ZIF force fields to predict the structure and surface termination of ZIF interfaces under both gas-phase "post-synthetic" and solution-phase conditions. In the case of gas-phase, we find that ZIF surfaces are almost inevitably terminated primarily by imidazole-related species, rather than residual adsorbed solvent. This termination remains stable even under high relative humidity and extremely low imidazole (Hmim) partial pressure, and thus we expect that it would be altered only via prolonged heating under vacuum (to remove any desorbed Hmim).

In the case of solution, the situation is more complex. Under high solute-phase imidazole concentrations, a fully imidazole terminated surface remains quite stable. However, at low pH, where the free (unprotonated) Hmim concentrations becomes low, partial and even total

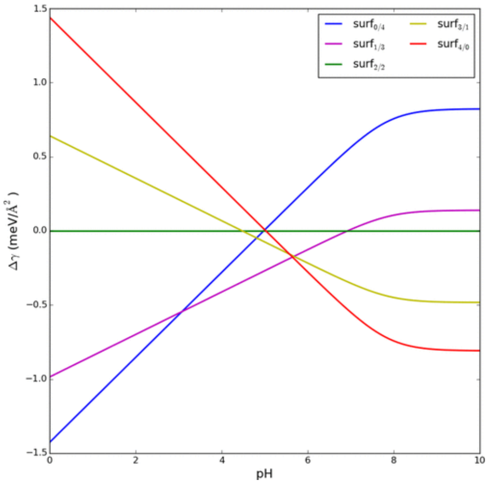

Figure 3. ZIF-8 surface phase diagram at 298K in aqueous solution vs pH; favored surface exhibits lowest surface energy.

solvent incorporation may occur (see Figure 3), where we use the notation "surf$_{n/m}$" to denote surface terminations with n imidazole species and m water (H_2O, OH^-) species. These predictions are consistent with prior experimental observations of ZIF evolution under acid exposure, which was shown to result in water/hydroxyl incorporation as detected via both IR and XPS. Small free Hmim concentrations can also arise from the use of stoichiometric Zn:Hmim ratios, e.g., as is common in solvothermal synthesis, cases where in situ AFM has also shown evidence for surface solvent incorporation, consistent with our phase diagram predictions. We anticipate that these diagrams may provide a useful predictive tool in understanding how ZIF surface structure may be altered/controlled as a function of both synthetic and postsynthetic conditions, with associated impacts on ZIF interfacial properties, including those governing surface mass transport barriers.

Mechanism of solvent-assisted linker exchange is ZIFs. Very recently, we have also begun to examine another important process of relevant to MOF/ZIF synthesis: solvent-assisted linker exchange (SALE). In SALE, MOFs are exposed to concentrated solutions of alternative organic linkers, resulting in the slow exchange with the original linking groups. This SALE process is a vital tool in accessing MOFs in specific topologies for which often no direct synthetic route is possible. Our work is focusing on resolving significant open question in the mechanism in SALE, including the role of spontaneous or solvent-induced defects, associative vs. dissociate pathways, and/or the role of solvent in catalyzing the SALE process. We are utilizing plane-wave DFT calculations (and ultimately QM/MM approaches) in ZIFs to model the SALE process and its inherent barriers both tin the presence and absence of additional solvent, making comparison against existing experimental data. We are also directly evaluating various proposed mechanisms for SALE. We anticipate that the resulting insights into the SALE mechanism will aid in the overcoming current challenges in the "targeted" synthesis of MOFs, including those identified by various ongoing high-throughput computational screenings.

Integration of computational and time-resolved experimental data on MOF nucleation and growth. Extremely recent experimental time resolved and/or in situ experimental studies provide unique insights into the nucleation and growth of MOFs and key benchmarks for ongoing computational studies. To this end, we recently published a comprehensive Chemical Review article that summarize the state-of-the-art with regard to such experimental studies. Our review focuses specially on time resolved and/or in situ methods, since such methods can provide direct methods into the early stages of MOF nucleation. Crucially, the review highlights not only "ripe" opportunities for both future experimental and computational studies, but also several important general conclusions that can be extracted from the totality of the associated literature.

Grant Numbers and Grant Titles

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Student(s): Tingting Weng; Kai Cui; Xinyi Li

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

1. Weng, T.; Schmidt, J. R., Structure and Thermodynamic Stability of Zeolitic Imidazolate Framework Surfaces. *J. Phys. Chem. C* **2020,** 124, 1458.
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