

PRF# 56782-DNI6
Project Title: Guiding nucleation and growth of metal-organic frameworks
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Overview

Metal-organic frameworks (MOFs) are nanoporous crystals consisting of metal ions that are connected by organic molecules. Because of their high porosity, MOFs are outstanding potential platforms for gas storage, catalysis, separations, optoelectronic devices, and charge storage. However, specific applications require MOFs with fine-tuned properties including pore size, crystal structure, thermal stability, and linker chemistry. While synthesized MOFs display a large variety of these properties, only few general guiding principles exist that allow the synthesis of a MOF with pre-programmed physical and chemical properties – in fact, the discovery of new MOFs often proceeds through time consuming and inefficient trial-and-error strategies. These synthetic challenges are rooted in our limited understanding of the microscopic processes that occur during the nucleation and growth of MOFs. In this PRF project, we address this problem with a computer simulation study of porous framework formation. We use simple and efficient computational models of prototypical MOFs to identify the microscopic mechanisms underlying framework nucleation and growth, as well as their susceptibility to changes in experimental control parameters. The overarching goal of this project is to provide experimenters with firm guiding principles that enable the targeted synthesis of porous framework materials with desired structure, porosity, and chemical composition.

Results

Classical vs. non-classical crystal nucleation. We have chosen zeolitic-imidazolate frameworks (ZIFs), a prototypical family of MOFs, as our platform for studying MOF formation. ZIFs have simple chemical composition (zinc ions and imidazole linkers) but display many intriguing features found in chemically more complicated MOFs, including pronounced polymorphism and complex nucleation kinetics. Several recent experimental publications have probed the early stages of ZIF formation, with seemingly contradictory results. While some studies report the initial formation of amorphous clusters that crystallize in a second step, other authors find evidence of direct, classical nucleation of ZIFs from the supersaturated solution. To shed light on the mechanism of ZIF nucleation, we have developed a coarse-grained model of the molecular constituents of ZIF-8 (*i.e.*, zinc ions and methyl-imidazolate linkers, $\text{Zn}(\text{mIm})_2$). The model treats solvent effects implicitly and is able to access the long time-scale of ZIF-8 nucleation in straightforward molecular dynamics computer (MD) simulations. Our simulations show a surprising sensitivity of the nucleation mechanism on model parameters and experimental conditions. Figure 1 shows time series of snapshots from MD simulations at two different temperatures. In both cases, ZIF-8 does not form directly from solution, but we observe phase-separation of the system into a dilute solution and a dense amorphous phase. Depending on temperature, this amorphous phase either has liquid-like character (Fig. 1b) or forms a solid with short-ranged order characteristic of a gyroid structure (Fig. 1f), reminiscent of a recently observed gyroidal MOF (FIR-30) with ZIF-like composition. The time evolution of these two amorphous phases is strikingly different. While the liquid-like amorphous phase is observed to nucleate a well-ordered ZIF-8 crystal on the simulation time scale (Fig. 1c), gyroidal clusters are metastable on much longer time scales. The phase diagram of our model, evaluated via direct simulations of phase coexistence, confirms that both the liquid-like and gyroid-like amorphous phases are metastable with respect to ZIF-8 and thus constitute different kinetic products that will transform into ZIF-8 on long time scales.

Our simulations furthermore point to a marked sensitivity of ZIF nucleation mechanisms to solvation environments. Our implicit-solvent model enables us to simulate the effects of different zinc coordination environments on ZIF-8

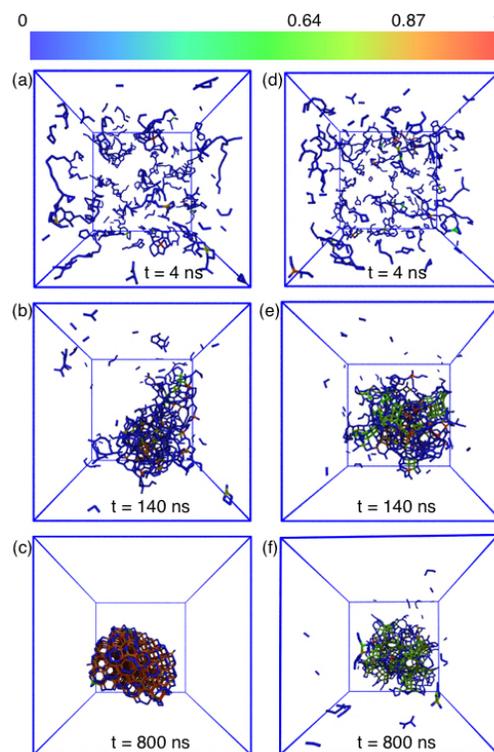


Figure 1. Snapshots from MD simulations of a solution of ZIF-8 components at $T = 260$ K (a)-(c), and $T = 255$ K (d)-(f). Bonds are shown between Zn ion connected by linkers; colors indicate the degree of tetrahedrality of 4-coordinated zincs: Liquid-like environments are indicated in blue, ZIF-8-like binding geometry is indicated by orange, square-planar geometry is shown in green and is indicative of gyroid-like clusters, as described in the text.

formation by restricting bond-angle fluctuations between linker molecules bound to zinc ions in solution. For solvent species that coordinate only loosely to zinc ions, the fluctuations will be determined mainly by interactions between linker molecules. Results shown in Fig. 1 were obtained under these conditions. If ZIF formation occurs in a strongly coordinating solvent, however, linker fluctuations will be severely restricted and bond angles mostly tetrahedral. Under such conditions, we do not observe the intermittent formation of amorphous phases, but ZIF-8 nucleates directly from solution via a "classical" mechanism. In conclusion, these results rationalize seemingly contradictory experimental observations of pre-nucleation clusters with different structure and suggest routes for controlling the nucleation mechanism of ZIF-8 in experiments.

ZIF polymorphism. Our results for ZIF-8 suggest the intriguing possibility of synthesizing a new gyroidal polymorph of $\text{Zn}(\text{mIm})_2$ with large bi-continuous pores. To better understand the microscopic mechanisms of polymorph selection on ZIFs, we have turned to systems of unsubstituted imidazolate linkers, which are known to form a large number of different framework topologies, depending on small changes to synthetic conditions including temperature, monomer concentrations, and solvent composition. We hypothesize that solvent fluctuations, including fluctuations in local density and their commensurability with the different pore sizes of ZIF polymorphs, play a major role in polymorph selection. To probe the role of explicit solvent, we have developed a coarse-grained model that treats imidazolate linkers as effective beads and reproduces the relative enthalpies of different ZIFs measured in experiment, as well as amorphous and glassy phases of ZIFs. To accurately describe energetic differences between these frameworks, the model includes three-body interactions that mimic biases for particular bonding geometries that arise from the molecular shape of imidazole molecules. This new three-body potential is generally applicable to the study of MOFs and other porous framework materials. Using methods of metadynamics, we are currently mapping out the free energy of nucleation of different ZIF polymorphs in different solvents to determine the mechanism of polymorph selection.

Defect dynamics. Our ZIF-8 model not only allows the study of framework formation, but enables us to study the dynamics of defects in the final solid. In fact, we observe the spontaneous formation of linker vacancies during the simulated nucleation of ZIF-8. These and other types of defects, including metal ion vacancies and interstitial species, can markedly alter the physical and chemical properties of MOFs and can play an important role in the diffusion of other molecular species through the framework. Little is known, however, about the dynamics and effective interactions of these defects. We have started a computational study of defect motion in ZIF-8 crystals, focusing on the diffusion and interactions of linker vacancies, most common type of defect. Using efficient algorithms to identify and track vacancy positions in the ZIF-8 lattice, our preliminary results show that defect motion is highly anisotropic, proceeding with substantially enhanced rates along particular directions of the lattice (Fig. 2a). Furthermore, interactions between nearby vacancies can be either repulsive or attractive, depending on the relative position of two vacancies with respect to the host crystal (Fig. 2b). We expect that our continuing studies of MOF formation and defect dynamics will result in key mechanistic insights that pave the way for enhanced experimental control of the properties of MOFs.

Impact

This PRF project has had clear and tangible impact on the careers of the PI and the students who participated in the project. The grant has allowed the PI to employ two graduate students as full-time researchers on a new research direction very early in his career as an independent researcher. The models and insight generated within this grant will result in several highly visible publications and form the basis for a broad research program focused on understanding the self-assembly and dynamics of porous framework materials. The students who worked on this project have benefitted substantially from the grant. They have received broad training in computer simulation methods, data analysis, and the physical chemistry of crystallization and porous framework materials. They have presented their results at several conferences and workshops, and received training in the preparation of talks and manuscript. The results achieved in this project will constitute substantial parts of their doctoral theses and prepare them for successful careers as researchers in academia and industry.

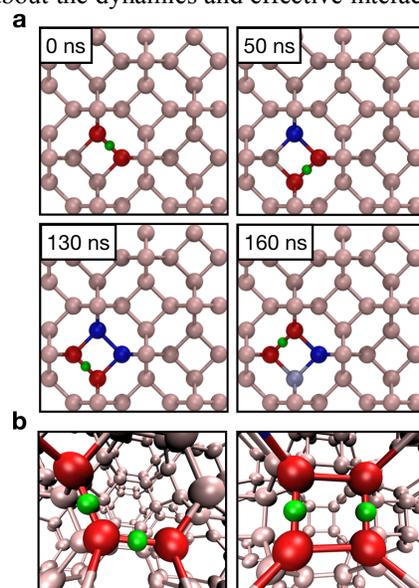


Figure 2. (a) Schematic representation of the dynamics of a linker vacancy (green) in ZIF-8, showing preferential diffusion of defects along square motifs in the lattice. Red color indicates zinc ions with missing linker, blue indicates previous vacancy positions. (b) A pair of linker vacancies (green) in two configurations. While the left configuration is highly unfavored, the configuration on the right has a long lifetime in simulations.