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Insights into Capillary Condensation and Hysteresis in Nanoporous Materials from New Simulation Methods

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Capillary condensation and the related phenomenon of adsorption hysteresis can impact applications of porous materials such as gas storage, separations, and adsorption cooling. To better understand these phenomena, we have calculated the adsorption isotherms for methane, ethane, propane, and n-hexane from atomistic grand canonical Monte Carlo (GCMC) simulations in a metal-organic framework having both micropores and mesopores [1]. At low temperatures, the calculated isotherms exhibit sharp steps accompanied by hysteresis. As a complementary simulation method, canonical (NVT) ensemble simulations with Widom test particle insertions are demonstrated to provide additional information about these systems. The NVT+Widom simulations provide the full van der Waals loop associated with the sharp steps and hysteresis, including the locations of the spinodal points and points within the metastable and unstable regions that are inaccessible to GCMC simulations. The simulations provide molecular-level insight into pore filling and equilibria between high- and low-density states within individual pores. The effect of framework flexibility on adsorption hysteresis was also investigated for methane in IRMOF-1 [1].

We have also the adsorption and desorption isotherms for argon at 87 K in 1873 MOFs from the CoRE MOF database [2] and for short n-alkanes in selected MOFs. Analysis of the molecular configurations showed at least two different mechanisms and origins of hysteresis: one involving a transition in the pores similar to a liquid-to-solid transition and one more similar to a gas-to-liquid transition. The validity of an empirical relationship for the critical pore diameter for hysteresis was also tested using the calculated argon desorption isotherms. The simulations reveal some structures where isotherms exhibit two steps in the adsorption branch and only one step in the desorption branch. Hysteresis loops with a different number of adsorption and desorption steps are quite rare in the literature. To better understand why hysteresis is observed in the GCMC simulations, the concept of the transition probability, which describes the probability of observing a step in the adsorption isotherm at a given pressure in a GCMC simulation, is introduced. We used three different methods to calculate the transition probabilities, and we validated that the three methods yielded similar results. The transition probability can be used as a method to quantify and test the convergence of GCMC simulations in the metastable region of an adsorption process.

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