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Flat-histogram Simulations of Water in MOFs: Advanced Strategies for Overcoming Sampling Challenges

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Adsorption of water by porous materials has recently reemerged as an area of interest due to its possible application as a platform for harvesting water from humid air. Combined with the widespread application of computational screening of adsorbent materials for various applications, molecular simulations of water in confinement are once again an area of ongoing investigation. However, the key challenge of water simulations in porous materials remains unchanged: due to strong water-water hydrogen bonding, adsorption of water occurs primarily at high relative humidity or low temperature and typically over a narrow pressure range [1], akin to Type V isotherms in the standard IUPAC classification scheme. Hydrogen bonding networks also encourage coalescence of water in pores rather than monolayer formation [2,3]. These challenges are exacerbated in hydrophobic metal-organic frameworks (MOFs) with cage-like pores, where adsorption occurs non-sequentially, but via abrupt steps in which one cage (cavity) fills with a single cluster of water in each step [1]. These simulation challenges are manifested by slow equilibration, inefficient sampling, and large uncertainties in ensemble averages [1]. The introduction of so-called superhydrophobic materials only amplifies these simulation challenges. Recent work has explored strategies to overcome the sampling challenges by using energy look-up tables, insertion (deletion) biases, and continuous-fractional component Monte Carlo [1].

We approach the problematic sampling of water adsorption in hydrophobic materials through a similar suite of simulation tools, starting with flat-histogram Monte Carlo (MC) and adding advanced MC moves, and then parallel simulations, all focuses on improving the efficiency with which the statistical phase space is sampled. In particular, we introduce configurational-bias MC operations that are tuned for adsorption in crystalline materials and specialized MC moves that address the proclivity of water to form clusters. We implement flat-histogram MC using Wang-Landau and Transition-matrix biases, which additionally allows us to examine water cluster formation via the macrostate probability distribution, such as through identification of free-energy barriers between individual clusters. However, the water-clustering effect necessitates the introduction of new analysis tools for converting the macrostate probability distribution to ensemble averages including the adsorption isotherm. These advanced strategies are implemented using the FEASST Monte Carlo toolkit [4], which provides modularity and is accessible to other researchers. The end effect is to both present simulation results for specific materials that highlight the challenges of water adsorption and use these prototype systems to suggest specific strategies for other researchers that simulate water adsorption.

References:

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