

Use of the Transition Matrix Monte Carlo Simulation Method to Compute Fluid Properties and Identify Capillary Phase Transitions in Gas Adsorption Processes

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In light gas adsorption in porous materials, an understanding of the key features of the adsorption isotherm and engineering exploitation of those features is often reliant on identification of the stable and metastable parts of the phase diagram. For example, in the quintessential gas adsorption process where capillary phase transitions are present in the adsorption isotherm, pore-filling occurs at a limit of stability and pore-evacuation occurs at a stable coexistence state point. Identification of these stability limits and the location of phase transitions is problematic in molecular simulation since it requires simulation of state points at metastable conditions. More sophisticated techniques are needed to effectively probe such parts of the phase diagram. Recently, the Transition Matrix Monte Carlo (TMMC) technique has come to prominence as a method for simulating fluids and identifying phase equilibria. TMMC differs from normal Monte Carlo simulation by utilizing information from all attempted transitions between microstates to construct the probability distribution for an entire set of macrostates. In the grand canonical ensemble, TMMC provides the probability of observing a certain macrostate (i.e., molecule count) at a given temperature and chemical potential. From this probability distribution, one can compute various properties of the thermodynamic state and identify stable and metastable states. Using histogram reweighting, one can reconstruct an entire density-pressure isotherm from a single TMMC macrostate distribution function. We apply TMMC to light gas adsorption in porous materials and, in doing so, demonstrate the usefulness of the technique in the computation of adsorption isotherms and the identification of limits of stability, metastable regions, and the equilibrium phase transition for the confined fluid. Additionally, we use TMMC to straightforwardly compute the isotropic enthalpy of adsorption. Overall, we aim to introduce TMMC as a useful tool for studying fluid behavior in porous materials.