On Adsorption Hysteresis in Closed-end Pores: Isotherm Reconstruction and Free Energy Analysis via Flat-histogram Monte Carlo Simulation

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In studies of the thermodynamics of fluids confined in porous materials, a particularly interesting observed effect is that of adsorption-desorption hysteresis at subcritical temperature. This effect was observed and remarked upon nearly a century ago[1] and has been a point of discussion and, occasionally, contention ever since. An early explanation of hysteresis based on macroscopic thermodynamics, the Kelvin-Cohan relationship, proposed that the effect resulted from the formation of different gas-liquid menisci during the respective adsorption and desorption processes[2]. Later investigations linked hysteresis to fluid metastability and confirmed this argument via statistical mechanical means. Based on the Kelvin-Cohan relationship, it was long assumed that hysteresis would not occur in a closed-end pore because the meniscus would be identically structured in the adsorption and desorption processes[2]. Some molecular simulations suggested the existence of hysteresis in a closed-end pore, but the uncertainty in the data precluded a firm conclusion[3]. More recent work by Do and coworkers has more confidently revealed the existence of hysteresis in closed-end pores of various shapes[4] via molecular simulations. Despite these results, disagreement over the existence of hysteresis in closed-end pores still persists in the field. In the present work, we examine adsorption-desorption hysteresis in closed-end pores using flat-histogram Monte Carlo methods, in particular hybrid Wang-Landau/Transition-matrix Monte Carlo simulation. As we demonstrated recently[5], TMMC can easily and accurately compute adsorption isotherms exhibiting hysteresis including identification of the metastable regions, with high confidence. We now apply this method to adsorption in closed-end pores with the intention of verifying the results of Do and coworkers, as well as examining the purported metastable regions via ensemble macrostate probability distributions and free energy analyses.

References

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