

Comments on “Monte Carlo Simulations for Water Adsorption in Porous Materials: Best Practices and New Insights” *

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To the Editor:

In Datar et al. [1], the authors present findings and best practices based on erroneous analysis of their simulations results, which affects their definition of average thermophysical properties, identification of vapor-liquid equilibrium conditions, and the existence of metastable states in grand-canonical Monte Carlo (GCMC) simulation. Fundamentally, these issues stem from the authors' analysis of the *macrostate probability distribution* (MPD), $\Pi(N; \mu, V, T)$, a quantity that they calculate using simulation and figures centrally in their work. At conditions where more than one phase can exist, the distribution is multimodal, where each peak or local maximum in Π may correspond to a metastable or stable phase. More specifically, in Ref. [1], the authors misuse their Eq. S1, which is intended for a unimodal distribution and thus not applicable at conditions near or corresponding to two-phase coexistence where Π is bimodal. The correct and more general form of their Eq. S1 *for phase* α is

$$\langle N \rangle_{\alpha}(\mu, V, T) = \frac{\sum_{N \in \alpha} N \cdot \Pi(N; \mu, V, T)}{\sum_{N \in \alpha} \Pi(N; \mu, V, T)}, \quad (1)$$

i.e., the summations are only taken over the macrostates that comprise phase α . Note that this requires segmenting Π into different phases [2, 3]. The same conceptual mistake is made in Ref. [4], and thus those results should be reconsidered in light of what is presented here.

One consequence of Eq. 1 is that properties of coexisting and metastable phases, as well as limits of stability, can be identified directly from the MPD and we point readers to Refs. [2, 3] for relevant discussion. This is in direct contradiction to the authors' statement, "An adequate sampling of the phase space should lead to a vapor liquid equilibrium curve with no hysteresis," as it implies that metastable states (the hysteretic states) are not accessible in a molecular simulation [5, 6]. Furthermore, this is contradicted by decades of literature that have used GCMC-based methods to study phase coexistence and metastability in bulk fluids and adsorption-desorption hysteresis in confined fluids [5, 7–16].

We must also comment on the authors' use of the fugacity (f) as a surrogate for pressure (p), by setting the fugacity coefficient $\phi = f/p = 1$. The authors overlook the fact that the absolute pressure can be easily obtained from the bulk MPD of the model fluid, which eliminates the need for the noted approximation. The pressure of phase α may be related

to the MPD [2, 3, 11, 16, 17] via

$$p_\alpha(\mu, V, T) = \frac{k_B T}{V} \left(\ln \Pi(0; \mu, V, T) - \ln \left[\sum_{N \in \alpha} \Pi(N; \mu, V, T) \right] \right) \quad (2)$$

where the summation is over all of the macrostates that belong to phase α , akin to Eq. 1. Additionally, Eq. 2 implies that a rigorous definition of equilibrium between phases α and ω is

$$\sum_{N \in \alpha} \Pi(N; \mu_{\text{sat}}, V, T) = \sum_{N \in \omega} \Pi(N; \mu_{\text{sat}}, V, T). \quad (3)$$

Stated simply, the probability of observing phase α (e.g., vapor) is equal to that of ω (e.g., liquid). There is no need to invent a heuristic for identifying vapor-liquid conditions, e.g., the authors’ “... the step pressure [the saturation pressure] is considered to be the point on the isotherm at which the loading is 50 % of the maximum loading,” which would also depend on how the maximum loading is actually determined. Combined with the aforementioned use of fugacity, their heuristic approach for identifying saturation conditions is not thermodynamically rigorous and only estimates the saturation pressure.

Ultimately, the authors’ use of their Eq. S1 [1] results in improper calculation of the properties of distinct phases, an inability to identify metastable phases, and imprecise identification of the saturation pressure. As a demonstration of the shortcomings of the authors’ work, we present some correct calculations of the properties of the SPC/E Water model at 300 K computed using the same method as Datar et al. Readers may consult the NIST Standard Reference Simulation Website [18], for reference properties of this water model. We note that we performed 1×10^6 Monte Carlo cycles at each value of N in our implementation of the simulations, which is significantly greater than what the authors claim to use in their work, to ensure the MPD has converged and matches results of other validated methods. Details of our simulations were included as the sixteenth tutorial in the flat-histogram plugin of FEASST v0.18 [19].

In Fig. 1, we provide a plot of $\ln \Pi(N; \mu, V, T)$ at different conditions and a plot of density versus fugacity for both the liquid and vapor phases of SPC/E Water, at 300 K. The traces of $\ln \Pi$ at other values of μ were generated by applying histogram reweighting to the MPD determined by simulation at μ_{sim} . The three $\ln \Pi$ traces shown in panel (a) all contain two local extrema: a vapor maximum (which is at $N = 0$ in these cases, though not necessarily in general) and a liquid maximum. The value of N that segments each trace into liquid and

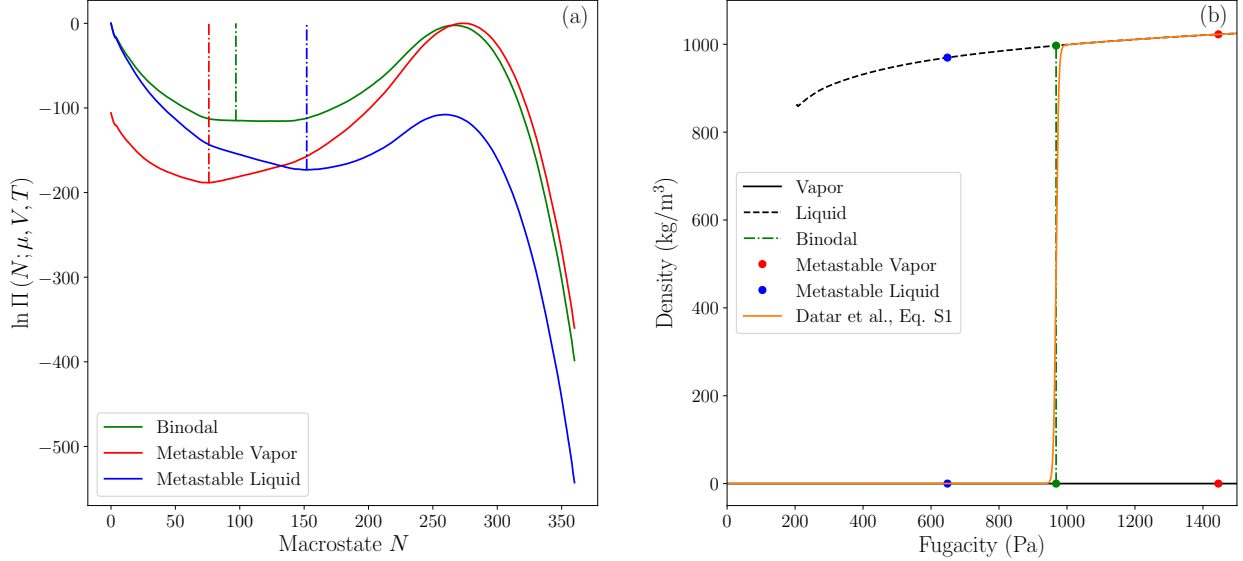


FIG. 1: Simulation results of SPC/E at 300 K. (a) Plots of the MPD versus particle number (solid lines) at chemical potentials corresponding to three bimodal states. The dash-dot lines identify the N value where the MPD is divided into vapor and liquid phases. (b) Plot of density versus fugacity, computed using Eq. 1, including vapor and liquid branches. The binodal fugacity is identified by the vertical green dash-dot line. Discrete points correspond to the states shown in (a). Use of Datar et al’s Eq. S1 yields the continuous orange isotherm.

vapor phases is noted with the dash-dot line. For the two metastable phases, one of the peaks is at noticeably lower $\ln \Pi$ than the other, which corresponds to the metastable phase in contrast to the higher $\ln \Pi$ of the stable phase at that μ . Panel (b) plots the density-fugacity relationship for the vapor and liquid phases, where the density was computed using $\langle N \rangle$ from Eq. 1; discrete points are averages corresponding to traces in (a). We first note that, by use of Eq. 1, metastable vapor and liquid states are shown for above and below the saturation fugacity. Second, we point out that the tie line connecting the vapor and liquid branches of the density-fugacity plot at the binodal is perfectly vertical. Use of Datar et al.’s Eq. S1 erroneously results in the orange trace in Fig. 1(b), where the density smoothly and rapidly increases from the vapor branch to the liquid branch near the saturation fugacity, which would contradict the well-known fact that this is a first-order phase transition [6]. In Ref. [1], these issues can be seen in Figs. 1 and 2, where the authors’ results are given by continuous traces, indicating that stable homogeneous states exist between the coexisting phases, with non-vertical phase-coexistence lines and no metastable branches. The apparent implication

Model	p_{sat} (Pa)	f_{sat} (Pa)	$\phi_{\text{sat}} = f_{\text{sat}}/p_{\text{sat}}$
SPC/E	1017(5)	978(3)	0.962
TIP3P	5123(12)	4892(14)	0.955
TIP4P	5137(16)	4978(16)	0.963
TIP4P/2005	802(2)	773(2)	0.964

TABLE I: Pressure (p_{sat}), fugacity (f_{sat}), and the fugacity coefficient ϕ_{sat} of vapor-liquid coexistence at 300 K for four models of water, based on flat-histogram simulation data in Ref. [18]. Numbers in parenthesis are the 95 % uncertainty interval, based on three replicate simulations.

that this is not a first-order transition is a consequence of computing the average $\langle N \rangle$ over the entire range of macrostates without segmenting $\ln \Pi$ into phases. Ultimately, our results show that proper analysis of the MPD rigorously identifies vapor-liquid coexistence and yields properties of metastable states. In Table I, we reprint the saturation pressures at 300 K given in Ref. [18] for four of the models, along with the saturation fugacity that was recalculated from the original Grand-Canonical Transition-Matrix Monte Carlo data and the fugacity coefficient at saturation (ϕ_{sat}). We note that ϕ_{sat} is approximately 0.96 in all cases, indicating that fugacity underpredicts the saturation pressure. This and the heuristic approach to identifying p_{sat} contribute to the authors’ reported 5 % discrepancies with the saturation pressures in Ref. [18].

Our comment has thus far focused on the bulk-water simulations in Ref. [1], but the concerns we raise are equally applicable to confined-fluid simulations such as water adsorbed in a MOF. A failure to use Eq. 1 when the MPD is bimodal will result in an erroneous adsorption isotherm that lacks metastable states and improperly identifies the pressure at which low- and high-density adsorbed phases coexist [16]. In the authors’ previous work [4], we are certain that this mistake was made as the reported MPDs are bimodal but the associated isotherms show no hysteresis (cf. Fig. 5 therein). The same mistake was likely made in Ref. [1], as the isotherms in Fig. 3 show nearly vertical rises, but no metastable branches of the isotherms; we cannot be certain because MPDs of the water-MOF simulations are not provided. However, the authors’ reference to “step” pressure in their description is a strong indication that the MPDs are bimodal.

In summary, we recommend the following: (1) computation of thermophysical properties

from the MPD must respect the existence of multiple phases, *a la* Eq. 1 (2) fugacity should not be misleadingly substituted for pressure and (3) pressure should be computed rigorously from the MPD using Eq. 2. We agree with Datar et al. on an important point, which is worth reiterating here: p_{sat} for the model fluid should be used for analysis of water simulations in adsorbents, not that from experimental measurements or an engineering EOS. In fact, for self-consistency, we recommend that the fluid pressure itself be obtained from simulation-based data of the fluid model, and we urge caution when using an engineering EOS intended to model the real fluid to obtain the pressure of the model fluid.

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