Abstract

Reliable prediction of vapor-liquid phase equilibria with molecular simulation relies on efficient computational methods and well-parameterized force fields. Histogram reweighting (HR) is a standard approach for converting grand canonical Monte Carlo (GCMC) simulation output into vapor-liquid coexistence properties (saturated liquid density, $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, saturated vapor density, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, saturated vapor pressures, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and enthalpy of vaporization, ΔH_{v}). Due to the abundance of experimental vapor-liquid coexistence data and the sensitivity of such properties to both short- and long-range non-bonded interactions, numerous force fields have been parameterized using $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and/or ΔH_{v}. Unfortunately, computing $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and ΔH_{v} for each proposed non-bonded parameter set (e.g., the Lennard-Jones parameters ϵ and σ) requires a large amount of molecular simulations.

We demonstrate that histogram-free reweighting can alleviate the computational burden of force field parameterization. Specifically, the Multistate Bennett Acceptance Ratio (MBAR) reweights configurations sampled from GCMC simulations performed with an initial reference parameter set (θ_{ref}). While MBAR is similar to the traditional HR method for computing $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and ΔH_{v}, the primary advantage of MBAR is that this approach can estimate coexistence properties for a different "rerun" parameter set ($\theta_{\mathrm{rr}} \neq \theta_{\mathrm{ref}}$) without simulating θ_{rr} directly. MBAR thus greatly reduces the amount of GCMC simulations that are required for parameterizing the non-bonded potential.

Four different applications of GCMC-MBAR are presented in this study. First, we validate that GCMC-MBAR and GCMC-HR yield statistically indistinguishable results for $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and ΔH_{v} when $\theta_{\mathrm{rr}} = \theta_{\mathrm{ref}}$. Second, we utilize GCMC-MBAR to optimize an individualized (compound-specific) parameter (ψ) for 8 branched alkanes and 11 alkynes using the Mie Potentials for Phase Equilibria (MiPPE) force field. Third, we predict $\rho_{\mathrm{liq}}^{\mathrm{sat}}$, $\rho_{\mathrm{vap}}^{\mathrm{sat}}$, $P_{\mathrm{vap}}^{\mathrm{sat}}$, and ΔH_{v} for force field j by simulating force field i, where i and j are common force fields from the literature. In addition, we provide guidelines for determining the reliability of GCMC-MBAR predicted values when $\theta_{\mathrm{rr}} \napprox \theta_{\mathrm{ref}}$. Fourth, we develop an optimization scheme and report new MiPPE non-bonded parameters for cyclohexane ($\epsilon_{\mathrm{CH_2}}$, $\sigma_{\mathrm{CH_2}}$, and $\lambda_{\mathrm{CH_2}}$).