Abstract

Histogram reweighting (HR) is a standard approach for converting grand canonical Monte Carlo (GCMC) simulation output into vapor-liquid coexistence properties (saturated liquid density, $\rho_{\text{liq}}^{\text{sat}}$, saturated vapor density, $\rho_{\text{vap}}^{\text{sat}}$, saturated vapor pressures, $P_{\text{vap}}^{\text{sat}}$, and enthalpy of vaporization, ΔH_{v}). We demonstrate that a histogram-free reweighting approach, namely, the Multistate Bennett Acceptance Ratio (MBAR), is similar to the traditional HR method for computing $\rho_{\text{liq}}^{\text{sat}}$, $\rho_{\text{vap}}^{\text{sat}}$, $P_{\text{vap}}^{\text{sat}}$, and ΔH_{v}. The primary advantage of MBAR is the ability to predict phase equilibria properties for an arbitrary force field parameter set that has not been simulated directly. Thus, MBAR can greatly reduce the number of GCMC simulations that are required to parameterize a force field with phase equilibria data.

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 $\rho_{\text{liq}}^{\text{sat}}$, $\rho_{\text{vap}}^{\text{sat}}$, $P_{\text{vap}}^{\text{sat}}$, and ΔH_{v} in a limiting test case. 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 $\rho_{\text{liq}}^{\text{sat}}$, $\rho_{\text{vap}}^{\text{sat}}$, $P_{\text{vap}}^{\text{sat}}$, 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. Fourth, we develop and apply a post-simulation optimization scheme to obtain new MiPPE non-bonded parameters for cyclohexane (ϵ_{CH_2}, σ_{CH_2}, and λ_{CH_2}).