

Reweighting molecular simulation configurations for rapid prediction of vapor-liquid equilibria, $p\rho T$, and caloric properties

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ABSTRACT

The reliability of molecular simulation results depends primarily on the force field, with the non-bonded interactions playing a key role. Unfortunately, non-bonded potentials that are empirically parameterized with thermophysical properties traditionally use iterative brute-force methods that require large amounts of molecular simulation.

A more efficient approach than simulating each proposed non-bonded parameter set is to reuse the information gained from nearby parameter sets. This study demonstrates how to utilize Multistate Bennett Acceptance Ratio (MBAR) for this purpose. Specifically, MBAR reweights configurations that are sampled using a few reference parameter sets to predict the internal energy and pressure for other non-bonded parameter sets, without performing additional direct simulations.

The MBAR algorithm requires that the energies and forces are recomputed for the sampled configurations using the new non-bonded parameter set. Basis functions are shown to be a computationally efficient method for recomputing these quantities. Basis functions eliminate the need for looping through non-bonded interactions by providing a linear relationship between the total non-bonded energy and the non-bonded parameters.

We demonstrate how to implement MBAR with NVT isothermal isochoric integration (ITIC) and Grand Canonical Monte Carlo (GCMC) to obtain vapor-liquid equilibria properties. MBAR with basis functions reduces the computational cost by approximately three to five orders of magnitude relative to direct simulation of VLE, where the reduction is greatest for larger molecules and systems. With this significant computational speed-up, we use a robust, high-dimensional, Bayesian optimization routine to simultaneously parameterize a Mie n -6 potential for several interaction sites.