

Reweight molecular simulation configurations for rapid force field parameterization

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ABSTRACT

Molecular simulation is an efficient approach for predicting thermophysical properties, such as vapor-liquid equilibria (VLE), pressure-density-temperature behavior ($p\rho T$), and caloric properties. 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 (typically VLE) 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.

We demonstrate how to implement MBAR with NVT isothermal isochoric integration (ITIC) and Grand Canonical Monte Carlo (GCMC) to obtain vapor-liquid equilibria properties. The MBAR-ITIC and MBAR-GCMC algorithms require 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 when a linear relationship exists between the non-bonded energy (or force) and the non-bonded parameters. Implementing basis functions with MBAR-ITIC and MBAR-GCMC reduces the computational cost to parameterize the non-bonded potential by approximately three to five orders of magnitude relative to the traditional approach, where the reduction is greatest for larger molecules and systems.