Overview
Iterative Boltzmann inversion (IBI) has become a popular method to derive coarse-grained (CG) potentials due to its straightforward nature and general applicability. The method optimizes a potential to match target properties from an atomistic simulation mapped to the CG level. For non-bonded potentials, target data is structural, taking the form of the radial distribution function (RDF). Though widely used, the potentials derived with IBI:

- Are generally non-unique.
- Often highly state-dependent.
- May include artifacts from intermediate and long-range structural correlations.

Here, we propose an extension to the IBI method to include target data from multiple states, adding constraints to the potential optimization process. We show that adding these constraints results in potentials that are less state-dependent and more representative of the underlying potential and therefore applicable over a wider range of state points.

Coarse-Grained Models
CG models reduce the number of degrees of freedom in a system by reducing the number interaction sites, resulting in a model that is computationally less expensive than the equivalent fully atomistic model.

Effective bond and angle potentials are typically derived from the bond and angle distortions in an atomic trajectory. E.g., for a bond length distribution $p_b(r)$, a Gaussian curve is fitted:

$$p_b(r) = \frac{1}{r_0 \sqrt{2\pi \sigma^2}} \exp \left( -\frac{(r-r_0)^2}{2\sigma^2} \right)$$

from which a harmonic potential is derived through a Boltzmann inversion:

$$V(r) = -k_B T \ln p_b(r) = k \left( r - r_0 \right)^2,$$

where the sum is taken over all states, and the "$s$" script denotes the property at state $s$. The scaling factor $a(s)$ is now a weighting factor for state $s$, allowing more or less emphasis to be put on this state in the potential update. The parameter $a$ is set to be a linear function of $s$ such that the potential smoothly approaches zero at the cutoff.

Iterative Boltzmann Inversion

Multi-state extension
Single-state IBI does not guarantee a unique solution, but rather a solution from the region of potential phase space that encompasses solution potentials, i.e., those that result in an RDF that matches the target. Different thermodynamic states have different regions of phase space that contain solution potentials. In multi-state IBI, we perform an "A" state (bottom) IBI. Each point on the x-y plane represents a perfect match between the united atom and CG simulations.

Applications

Propane
A CG model was developed for propane using a united atom model as the target data. The resulting model is a single-site model which can be compared to the LJ system mapped to have the same critical point as propane.

Good agreement between the derived and target structural data is seen at all states, with the derived potential demonstrating similar behavior to the published LJ propane model of Pu et al.

Lipid bilayers
Using tail potentials from fatty acid simulations and a water potential from previous work, the headgroup bead potentials for 2-tailed skin lipid using fluid and crystals. Varying the weighting factors, $a(s)$, used in the potential derivation alters the bilayer properties, e.g., area per lipid (A PL), enabling the model to be tuned to match properties beyond the RDF.

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Conclusion
We extend the IBI method to yield less state-dependent potentials by including target data from multiple states. We show the multi-state extension is able to recover a known potential where the single-state method cannot. A potential is derived for a single-site model of propane, showing good agreement with a Lennard-Jones particle mapped to the critical point. Structural properties of n-dodecane are better estimated with potentials derived using the multi-state extension than the single-state method. Finally, adjusting relative weighting factors of the states used can alter a system’s properties, allowing dynamic adjustment of the weighting factors to match bulk properties of a system of interest.