

Clarifying the role of 3-body correlations for determining optimal coarse-grained pair potentials

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While providing a large degree of accuracy, fully atomistic molecular dynamics simulations are computationally expensive. Coarse-grained models represent multiple atoms with one bead, reducing the number of particles in the system as well as the number of degrees of freedom. Consequently, larger systems and longer timescales become accessible.

Accurate bottom-up coarse-grained models ideally reproduce all relevant properties of the underlying atomistic system, such as structure, thermodynamics and dynamics. Structure-based coarse-graining methods often determine optimal pair potentials for reproducing a given set of radial distribution functions. These procedures treat many-body correlations that arise in the condensed phase in various ways. Direct Boltzmann inversion, for example, assumes there are no correlations present in the system, resulting in potentials that tend to overcompensate for the missing correlations. Force matching, on the other hand, uses 3-body correlations from an underlying atomistic model to determine the optimal potentials. This can also result in inadequate potentials, since the coarse-grained model is often incapable of precisely reproducing the atomistic correlations.

In this work, we apply the generalized-Yvon-Born-Green integral equation framework to explore the interplay between 2- and 3-body contributions to the pair mean force in coarse-grained models of liquids. As a model system, we consider a one-site per molecule representation for liquid water with isotropic pair interactions. Prominent tetrahedral packing generates 3-body correlations that cannot be reproduced by the coarse-grained model. Our analysis suggests two complementary approaches for directly modifying the atomistic 3-body correlations to more accurately reflect the correlations generated by the coarse-grained models.