Quasichemical Theory and the Description of Associating Fluids Relative to a Reference

Artee Bansal, Yiwei Zhu, Yuchong Zhang, Walter Chapman and Dilip Asthagiri [C, S]
Chemical and Biomolecular Engineering, Rice University, Houston, TX, U.S.A.
dna6@rice.edu

The statistical associating fluid theory (SAFT) is a well-established framework for modeling associating fluids. SAFT and Wertheim's theory rest on using as a key ingredient information about two-particle or three-particle correlations in the reference. These approaches work well when the range of solute-solvent attraction is short and the sticky patches on particles are restricted to bond only once or at best twice. However, for problems such as those involving colloidal-solvent or ion-solvent association, acknowledging multiple bonding at a site, and multi-body effects in general, becomes essential. To develop insights into multi-body effects, here we study the association of a multi-bonding solute in a patchy solvent using quasichemical organization of the potential distribution theorem (QCT). We study a solute that can bond multiple times and a solvent that can bond only once. The fraction of times the solute is not associated with the solvent, the monomer fraction, is expressed in terms of the statistics of occupancy of the solvent around the solute in the reference fluid and the Widom factors that arise because of turning on solute-solvent association. Assuming pair-additivity, we expand the Widom factor into a product of Mayer f -functions and the resulting expression is rearranged to reveal a form of the monomer fraction that is analogous to that used within SAFT. The present formulation provides a fresh, more intuitive, perspective on Wertheim's theory and SAFT. Importantly, multi-body effects are transparently incorporated into the very foundations of the theory. QCT leads to the identification of the occupancy of a patch conditional on the total occupancy of the observation volume, all in the reference fluid, as an important quantity within the theory. We incorporate this information within SAFT and present results for self-assembly and phase equilibrium for a mixture of patchy colloid solvent and solutes ranging from one with a single bonding site, to a Janus particle, to a solute with isotropic attraction.