Thermodynamic perturbation theory: applications in coarse-graining and complex-fluid modelling

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The fundamental phase diagram of a pure substance exhibiting gas, liquid, and solid phases is reasonably well understood. As the pioneering work of van der Waals showed, the fluid phase behaviour of simple fluids can be understood in terms of the balance of spherical repulsive and attractive forces, and even the fluid-solid transition of such systems can be explained in terms of the freezing of a hard-sphere system. A challenge arises, however, when aiming to model accurately the properties and phase behaviour of complex molecules and mixtures such as surfactants, polymers, colloids, peptides, or proteins, which are commonly considered in modelling approaches now. Aiming to treat associating systems, in the thermodynamic perturbation of theory of Wertheim an anisotropic intermolecular potential that incorporates short-ranged attractive interactions to form associated aggregates and networks was proposed which greatly enhanced the capability of analytical methods and has, over the years, been extended provide a tool that can be used to study a plethora of complex fluids. I will discuss some of the recent advances in this area; especially the recasting of the free energy expression into a group contribution method, and the advantage of incorporation of generalised Lennard-Jonesium potentials to improve accuracy and predictive ability. Furthermore, with this framework in place, the theory can also be used to develop force-fields for use in computer simulation, and a link to coarse-grained force fields translatable over thermodynamic states and transferable over systems is possible.

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