148f Thermodynamically Consistent Adaptation of Scaled Particle Theory to an Arbitrary Equation of State: Hard Sphere Fluid Properties and a New Reference System for Solvation Theories

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The determination of the solvation free energy for a solute molecule added to a liquid is typically obtained by using a two step process. The first step is the creation of a molecular-sized cavity in the liquid and the second step is the activation of intermolecular potentials between the solute and liquid molecules. It is well known that the energy cost of forming the molecular-sized cavity is a non-trivial quantity in solvation theories. Hence, rigorous theoretical or semiempirical methods that provide values for the work of cavity formation are of constant interest for use in the prediction of solvation free energies. These methods are often developed by first choosing the hard sphere fluid as the ideal repulsive reference system and then applying an attractive perturbation.

Many theories for predicting the work of cavity formation stem from the Scaled Particle Theory (SPT) of Reiss et al. (J. Chem. Phys., 1959, 31, 369). SPT predicts the work of cavity formation in the hard sphere fluid exactly for cavities smaller than the hard sphere solvent particle and devises an interpolation that spans from small cavity radii to the limit of macroscopic size. The interpolation is based on a number of exact conditions imposed by geometry and thermodynamics and results in an equation of state (EOS). Accurate forms of SPT are achieved when many of the exact conditions are used, but the higher forms of SPT are numerically complex. Simple and relatively accurate methods for predicting the work of cavity formation have been developed by introducing interpolations based on the very accurate Carnahan-Starling EOS along with consistency conditions in a pseudo-SPT form (Matyushov and Ladanyi, J. Chem. Phys., 1997, 107, 5815 and Jiuxun, Chin. J. Chem. Phys., 1999, 12, 427). Neither of these methods, however, is truly thermodynamically consistent, resulting in a cavity function that suffers at small cavity size.

We therefore present a simple method of calculating the work of cavity formation in a SPT framework by adapting the interpolation method to an arbitrary EOS. In addition to incorporating several exact conditions of SPT, the interpolation utilizes both the pressure and chemical potential of the hard sphere fluid as provided by the particular EOS, and so is now thermodynamically consistent. This new interpolation method provides very accurate predictions for the work of cavity formation and hard sphere interfacial properties when any of the known accurate hard sphere equations of state are used. The recently obtained exact SPT conditions of Heying and Corti (J. Phys. Chem. B, 2004, 108, 19756) also enable our method to generate predictions of the slope and curvature of the hard sphere radial distribution function at contact. This structural information provides another test of the usefulness of future equations of state. The adaptation of SPT can also serve as a reference system for perturbation theories of solute dissolution. We explore the use of SPT in various perturbation theories that provide solvation free energies in square-well and Lennard-Jones liquids.