160a Transferable Potentials Optimized for Mixed Site-Site Interactions

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A subtle problem arises when characterizing site-site potentials for molecules like primary alcohols, but it may not express itself until the potentials are applied to mixtures. For example, consider the disperse attraction energy between the CH2 and OH sites in a united atom model (UAM) of primary alkanols. This parameter would typically be estimated by something like Eij = sqrt(Eii*Ejj)*(1-Kij), where Eij is the depth of the potential well between sites i and j, and Kij is an adjustable parameter. In most cases, Kij is neglected during characterization of the pure component potentials. Unfortunately, the accuracy of phase equilibrium predictions with that approach is less than quantitative, necessitating application of Kij, or something similar, at the level of molecule-molecule interactions. But the UAM does not pertain to molecule-molecule interactions, it applies to site-site interactions. That is, a non-zero Kij between a CH2 site on octane and an OH site on butanol, must also apply to the interaction between a CH2 site on butanol and an OH site on butanol if the UAM is to be applied self-consistently. The mixture interactions are more sensitive to assumptions about Kij because the sites are not bound as in a pure fluid so there is no coupled interaction that would automatically be reduced to cancel the error in that assumption, as occurs in regressing potentials for pure fluids. When optimizing the pure fluid, the mixed site attractive interaction is confounded with other contributions to the UAM.

In this study, we address this confounded interaction problem by successively optimizing the site-site interactions while accounting for mixture observations as well as pure fluid vapor pressure and density. This successive approach is greatly facilitated by the perturbative approach of the Step Potentials for Equilibria And Dynamics (SPEAD) model. Because the attractive interactions can be treated as perturbations, both for the mixtures and the pure fluids, trial potentials can be rapidly evaluated without repeating the molecular simulations.

A related problem develops when treating hydrogen bonding interactions. In molecular models based on explicit treatment of hydrogen bonding interactions, like the SAFT model, SPEAD, and older versions of the CHARMM potential, it is necessary to approximate the solvation energy in a manner similar to the disperse interaction energy. Typically, it is assumed that Uij = (1-hij)*(Uii+Ujj)/2, where Uij is the hydrogen bonding energy and hij is the empirical correction factor. The fallacy of neglecting hij is demonstrated by treating mixtures of alcohols with amines, for which hij is significantly less than zero. The need for a non-zero value of hij shows up in phase behavior, heats of mixing, and in the spectroscopic studies that form the basis of the Kamelet-Taft parameters. In molecular models where hydrogen bonding interactions are implicit, like point charge models, anomalous solvation energies cannot be directly addressed. For amine-alcohol mixtures, this defect shows up as a large sign error in the predicted heat of mixing.