

Transferable Step Potentials for Amines, Primary Amides, Ketones, Thiophenes, Phosphates, and Chlorinated Hydrocarbons

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Abstract

Discontinuous molecular dynamics simulation (DMD) and thermodynamic perturbation theory (TPT) have been used to study thermodynamic and dynamic (transport) properties for a wide range of compounds.[1, 2] The fundamental basis of the method relies on a stepwise characterization of disperse interactions[3] and Wertheim potentials for hydrogen bonding.[4] Transferable step potentials are characterized based on vapor pressure and liquid density from available experimental data. An interaction site diameter and the depths of the inner and outer wells of the potential characterize the transferable multi-step potentials. Intermediate wells are interpolated reducing the number of adjustable parameters to three per site type. The combined use of step potentials for equilibrium and dynamic properties is referred to as the SPEAD model.

The present work focuses on the properties of amines, primary amides, acetates, ketones, chlorinated hydrocarbons, phosphates and thiophenes. Overall, the vapor pressures are correlated to within ~15% error and liquid densities to 4% error with reduced temperatures generally extending to 0.45. These deviations are consistent with recent results of naphthenic and aromatic compounds. The inclusion of these site types enables leveraging of minimal experimental data for toxic or noxious compounds. To illustrate, we predicted the properties for several compounds of prospective interest in current research. In some cases, alternatives to the DMD/TPT model are very limited for these site types.

We now have sufficient experience to make several broad generalizations with regard to the use of transferable potential models in predicting properties with the SPEAD model. First, the effective bonding volume for association sites tends to drop as the chain gets longer. We find it necessary to account for this effect to achieve

results for associating compounds that are comparable with results for non-associating compounds. Another general observation is that the availability of reliable experimental data becomes limited when the coverage of site types is extended beyond relatively simple compounds at an early stage. This problem was already encountered for the primary amides. Preliminary analysis of branched compounds shows substantially larger deviations than for non-branched compounds. The structural variability in isomers tends to undermine the assumption of transferability. In a preliminary attempt to adapt *ab initio* methods to infer isomer effects, we compare to predictions of the COSMO-Therm model when possible.

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