

Transferable Potentials for Perfluorocarbons

J.R. Elliott^C and A.D. Sans

Chemical Engineering Dept., University of Akron, Akron, OH, U.S.A.
jelliott@uakron.edu

The Step Potential Equilibria and Discontinuous Molecular Dynamics (SPEADMD) model provides a basis for molecular modeling of thermodynamic and transport properties. It is based on Discontinuous Molecular Dynamics (DMD) and second order Thermodynamic Perturbation Theory (TPT). DMD simulation is applied to the repulsive part of the potential, complete with molecular details, such as interpenetration of the interaction sites, 110 degree bond angles, branching, and rings [1, 2]. The thermodynamic effects of disperse attractions and hydrogen bonding are treated by TPT. This approach accelerates the molecular simulations in general and the parameterization of the transferable potentials in particular. Transferable potentials have been developed and tested for over 200 components comprising 22 families. These families include thiophene, phosphate, fluorocarbon, alcohol, amine, aromatic, and ring compounds, to name just a few [3, 4].

One advantage of step potentials is that they offer the prospect of setting the step depths without preconceived notions regarding the shape of the potential. For example, the Lennard-Jones potential constrains the potential to reach a minimum at 1.112σ and to decay as r^{-6} with increasing radial distance, r , where σ represents the repulsive diameter. In the case of perfluorocarbons, we find that the minimum of the potential is reached at roughly 1.5σ , with the range from σ to 1.5σ acting as a soft "shoulder" region which is neither repulsive nor attractive. This shoulder region is necessary to explain the unusually high heat of vaporization of perfluorocarbons while maintaining relatively high vapor pressures.

Coincidentally, the zero shoulder also explains the weak mixture interactions between perfluorocarbons and n-alkanes. The potentials for n-alkanes have been found to follow trends more similar to the Lennard-Jones potential [2]. The explanation derives from assuming the Lorentz-Berthelot combining rule to describe site-site interactions between corresponding steps. This leads to $E_{ijk} \sim \text{SQRT}(E_{iik}E_{jjk})$, where E_{ijk} is the depth of the potential well between sites i and j in the k th step. For steps at short range, the alkane steps are at their deepest, but the perfluorocarbon interactions are zero, making the mixed interaction zero. For steps at long range, the perfluorocarbon steps are deep, but the alkane interactions are weak, making the mixed interaction weak.

The bases for these conclusions are presented, with extensive reference to molecular simulations of mixtures and experimental data for the vapor pressures of C2 - C8 perfluorocarbons and mixed phase vapor-liquid and liquid-liquid equilibria.

- [1] J. Cui and J.R. Elliott Jr., *J. Chem. Phys.* **114**, 7283 (2001).
- [2] O. Unlu, N.H. Gray, Z.N. Gerek, and J.R. Elliott, *Ind. Eng. Chem. Res.* **43**, 1788 (2004).
- [3] N.H. Gray, Z.N. Gerek, and J.R. Elliott, *Fluid Phase Eq.* **228-229C**, 147 (2005).
- [4] F.S. Baskaya, N.H. Gray, Z.N. Gerek, and J.R. Elliott, *Fluid Phase Eq.* **236**, 42 (2005).