148g The Effects of Disperse Attractions on Transport Properties Using Step Potential Equilibria and Dynamics (Spead)

Zeynep N. Gerek, Neil H. Gray, and Richard Elliott

The Step Potential Equilibria And Dynamics (SPEAD) 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 like interpenetration of the interaction sites, 110,,a bond angles, branching, and rings.[Cui, and Elliott, 2001; Unlu et al., 2004] 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.

Unfortunately, there is no theory comparable to TPT when treating transport properties. Most theories of transport properties rely on empirical variations of correlations for spherical reference fluids. In the present work, we isolate the effects of disperse attractions by independently simulating transport properties for the reference potential and the full potential over a range of temperatures. These simulations are applied to n-alkanes from C4-C12 with packing fractions ranging from 0.2-0.5 and reduced temperatures ranging from 2.0 to 0.5. Diffusivity, shear viscosity, and thermal conductivity were simulated by equilibrium molecular dynamics using the Einstein relations.

Results show that attractive effects on all transport properties are negligible at reduced temperatures greater than 2.0. For diffusivity and thermal conductivity, the attractive effect is relatively mild and a single generalized correction can be formulated for all components based on reduced temperature and packing fraction. Viscosity is more sensitive to attractive effects, hindering any simple correction. As an alternative to simple correction, Quinones-Cisneros and coworkers have suggested the friction theory of viscosity.[Quinones-Cisneros et al., 2000] Friction theory is based on the assumption that shear is similar to two sliding surfaces with a constant friction coefficient and variable normal force. The normal force appears naturally in friction theory as separate contributions due to the repulsive pressure and the attractive pressure from the equation of state. In the present work, we apply only the correction resulting from the attractive pressure.

Comparing to experimental data is complicated by the influence of the softness of the potential. For diffusivity and thermal conductivity, the effects of softness and attraction tend to be mild and they tend to cancel each other, favoring reasonable accuracy with an empirical approach. For viscosity, softness strongly influences the behavior, necessitating a specific correction for the effective density before comparison with experiment is feasible.

Keywords: Physical properties, molecular simulation, diffusivity, thermal conductivity, viscosity.

References Cui, J.; Elliott, J.R.; J. Chem. Phys., 114:7283 (2001). Quinones-Cisneros, S.E.; Zeberg-Mikkelsen, C.K.; Stenby, E.H.; Fluid Phase Eq. 169:246 (2000). Unlu, O.; Gray, N.H.; Gerek, Z.N.; Elliott, J.R.; Ind Eng. Chem. Res., 43:1788 (2004).