

## Transport Properties from Molecular Simulation with the SPEADMD Model

J. Richard Elliott<sup>C,S</sup>

*Department of Chemical and Biomolecular Engineering, University of Akron, Akron, OH, U.S.A.*

Z.Nevin Gerek

*Physics Department, Arizona State University, Tempe, AZ, U.S.A.*

Neil Gray

*Chemstations, Houston, TX, U.S.A.*

Molecular dynamics simulation holds the prospect of predicting both thermodynamic and transport properties through a single characterization of molecular interactions and liberal application of Newton's Laws of motion. The SPEADMD model (Step Potential Equilibria And Discontinuous Molecular Dynamics) has been developed based primarily on thermodynamic properties until now. This presentation illustrates how an analogous approach can form the basis for semi-empirical correlations of transport properties that can be applied at present. The key qualitative behavior is found to be dominated by the repulsive interactions, which are rigorously simulated in detail. Quantitative agreement with experimental data is obtained by correlating the effects of attractive forces in a semi-empirical manner. Results are presented for diffusivity and thermal conductivity.

When new molecules are synthesized, their target properties may be well known but their engineering properties may be completely unknown. For example, a small molecule drug candidate may be known to have high biological activity, but measuring its vapor pressure, bulk density, viscosity, and thermal conductivity would require gram quantities. Even the melting temperatures measured by millions of freshman chemistry students require purified quantities near 0.01g. Developing those quantities with that purity can be overwhelming for the large number of trial products that may be encountered in the early stages of development. The 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 like interpenetration of the interaction sites, 110° 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.[3,4] Unfortunately, there is no theory comparable to TPT when treating transport properties.[5] Most theories of transport properties rely on empirical variations of correlations for spherical reference fluids. Furthermore, existing correlations are typically specific to a given range of conditions: gas, dense gas, or liquid, for example. To overcome this situation, we must leverage the dynamics from the reference fluid simulations while accurately correlating and predicting experimental data. We show how to achieve this combination of rigorous fundamentals and empirical accuracy and compare to the accuracy of existing engineering correlations for diffusivity, thermal conductivity, and viscosity. The diffusivity analysis shows that previous correlations based on the hard sphere model are fundamentally flawed. When applying the conservation of volume principle, as is typical, the scaling in the low density limit deviates strongly from the Rouse scaling typically observed for unentangled polymer liquids. Our simulations show clearly that the Rouse scaling is the proper result in the low density limit for n-alkane chains. We derive a generalized correlation for any n-alkane based only on the molecular weight. For non-alkanes, we show how adapting an equivalent alkane perspective provides reasonable predictions and accurate correlations with fewer parameters than previously reported. The thermal conductivity shows that an asymptote is approached at high molecular weights when isotherms are correlated with respect to mass density. Once again, this deviates strongly from the currently popular hard sphere perspective.

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