Combining Molecular Simulation with Residual Entropy Scaling to Correlate Self-Diffusivity

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A recent evaluation[1] of self-diffusivity correlation and prediction methods recommended the correlation of Silva et al. (1998)[2] for most applications. The Silva method is based on a correlation of molecular dynamics simulations for the Lennard-Jones (LJ) fluid and equating all modeled fluids to "effective" LJ fluids. Many sources of LJ simulations have appeared in the literature since 1998.[3] This work re-examines the Silva method in light of these data and finds significant shortcomings. Bell et al.[3] have compiled a database of LJ simulations for transport properties and identified three primary sources of self-diffusivity data.[4–6] Bell et al. have also examined the entropy scaling of the LJ fluid's transport properties with particular attention to the low-density limit.[3] This work incorporates the work of Bell et al. for the LJ fluid and extends it to non-spherical fluids. Gerek and Elliott[7] analyzed self-diffusivity with particular attention to molecular simulations and experimental data for long chain *n*-alkanes like *n*-triacontane and *n*-hexacontane. They found fundamental deficiencies in treating *n*-alkanes with carbon number greater than 16 as spherical molecules like the LJ fluid. This work revisits the work of Gerek and Elliott, first making it thoroughly consistent with the primary sources of the LJ fluid for spherical molecules then providing a fundamentally sound extension to non-spherical molecules. The work of Gerek and Elliott did not incorporate residual entropy scaling. Instead, it applied a correction for attractive effects that was first order in temperature. Residual entropy scaling suggests that the attractive correction should be second order in temperature. This work evaluates both entropy scaling and a second-order correction to recommend the optimal choice. Finally, Gerek and Elliott posted an open-source database of experimental self-diffusivity data compiled from the literature. This work re-evaluates that database with help from the TDE compilation,[8] identifying several inconsistencies that required revision.

References:

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