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Size Dependence of Solute Diffusivity and Stokes-Einstein Relationship: Effect of van der Waals Interaction

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1. Introduction

Diffusion of solutes in solution was investigated by Einstein[1]. With the help of kinetic theory, he derived an expression for the self diffusivity, $D=RT/N_A6\pi\eta r_u$. The motion of the solute can be described by the random walk the solute performs due to collisions with the solvent molecules described by the Einstein's Theory of Brownian Motion and also reported by Sutherland[2] and more recently, Chandrasekhar[3].

Innumerable groups[4] have investigated the range of validity of the above expression. Dependence of D on viscosity, mass of the solute and interaction (hard sphere, square well, soft sphere, Lennard-Jones, etc) have been examined. This relationship has even been employed frequently to determine Avogadro number as well as radius of the solute. Willeke and several others[5-8] have reported higher diffusivities than what is predicted by the Stokes-Einstein expression given above.

Here we report molecular dynamics study of solute diffusion in solution, interacting via Lennard-Jones potential. The solute radius is varied to obtain the dependence of D on solute radius, r_u.

2. Methods

Molecular dynamics simulations have been carried out in the microcanonical ensemble using periodic boundary conditions. Both the solute and solvent interact via the Lennard-Jones interaction with: σ_{vv} =4.1Å; ε_{vv}=0.25 kJ/mol; σ_{uv}=1.0-4.7Å; ε_{uv}=1.5 kJ/mol; σ_{uu}=0.3-4.0Å; ε_{uu}=0.99 kJ/mol employed in this work. Solute-solvent interaction parameter $\sigma_{uv}= \sigma_{uu}+ 0.7$ and both σ_{uv} and σ_{uu} are varied. Note that $\sigma_{uu} = 2r_{uu}$.

All simulations have been carried out with 500 solvent and 50 solute particles at $\rho^* = 0.933$ and $T^* = 1.663$. Time step of 15fs was used for all solutes sizes with the exception of 0.3Å for which 10fs was employed. Energy conservation was better than 1×10^{-5}. Equilibration was for 2ns and production for 6ns. Properties were stored for analysis usually every 1ps with the exception of velocity autocorrelation functions and intermediate scattering function for which 100fs was the interval.

3. Results and Discussion

Figure 1 plots the variation of diffusivity with the ratio of the solvent Lennard-Jones diameter to the solute Lennard-Jones diameter, σ_{vv}/σ_{uu}, that is κ^{-1}, where $\kappa = \sigma_{uu}/\sigma_{vv}$. The variation of D with κ^{-1} should be a straight line if the Stokes-Einstein(SE) relationship is valid[9]. This is the case for large r_u. However, the deviation from SE is evident when κ^{-1}

is larger than 3. For $3 < \kappa^{-1} < 6$ *D*s are higher than predicted by SE. For $\kappa^{-1} > 6$, $D \sim 1/r_u^2$ dependence.

This surprising deviation from SE relation explains the enhanced diffusivity seen by several groups. Willeke et al as well as others[5-8] found in their study of Lennard-Jones binary mixture that the SE relation is not valid for $\kappa < 1$ as compared to deviations only for $\kappa < 0.33$ found here. There are several others who have found enhanced self diffusivity. For example, Noworyta et al. found higher *D* for small solutes in water than predicted by SE[8]. Bhattacharya and Bagchi found higher *D* for small solutes[7]. Ould-Kaddour and Barrat[10] found higher *D* for $0.066 < \kappa < 0.66$. We see here an enhanced *D* for $0.17 < \kappa < 0.48$.

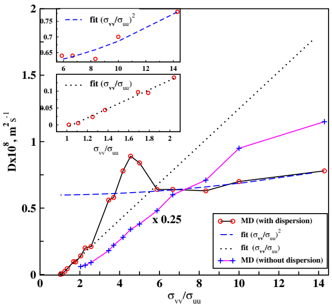

Figure 1 Plot of self diffusivity *D* as a function of the σ_{vv}/σ_{uu} with and without dispersion term.

Our results here indicate that deviation is a consequence of the existence of diffusivity maximum seen for solutes diffusing in porous solids or simple liquids and known as the Levitation Effect (LE). Diffusivity from simulations carried out without the dispersion term (that is with the purely soft repulsive term $1/r^{12}$ and no $1/r^6$ term) between the solute and the solvent show no such deviation for up to $\kappa^{-1} \approx 7$. The enhanced diffusion seen for intermediate sizes of the solute is therefore clearly shown to have its origin in the dispersion interaction.

3. Conclusion

Simulations reported suggest that the Stokes-Einstein relation between *D* breaks down for small solute sizes. It also suggests that this breakdown has its origin in the Levitation Effect or, equivalently, the presence of the dispersion interaction is responsible for the enhanced self diffusivity.

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