diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

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

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Abstract

Size dependence of solute diffusivity has been investigated using molecular dynamics simulations for a range of solute radii in a binary mixture consisting of solute and solvent species. We demonstrate that the Stokes-Einstein relationship between self diffusivity and solute radius breaks down over a range of solute-solvent size ratios. This is a result of the previously known Levitation Effect. Three distinct regimes can be seen depending on the solute-solvent size ratio. Several properties have been computed to understand the nature of solute motion in the three regimes.

1. Introduction

Diffusion of solute in solution has been of interest for over a hundred years. Early studies by Brown and Einstein provided the required insight into the nature of diffusion of the solute within solution [1-2]. Einstein proposed the Theory of Brownian Motion based on kinetic theory and derived the following expression for self diffusivity [2-5]:

$$D = \frac{RT}{N_A}\frac{1}{6\pi\eta r_u} \tag{1}$$

where N_A is the Avogadro number, T is the temperature and η is the viscosity of the solution, r_u is the solute radius. Einstein assumed that the solute radius is larger than the solvent radius. The above expression has also been derived by Sutherland at about the same time as Einstein putting forth similar arguments [6]. More recently, Chandrasekar also derived the above expression by the application of Langevin equation to Brownian motion [7].

Over the past hundred years, extensive work by many different groups has attempted to understand more deeply the nature of diffusion in liquids. Number of experimental as well as theoretical work has been reported that attempts to understand many aspects of solute diffusion in solutions. A number of investigations have explored the validity of Stokes-Einstein expression, Eq. (1). A number of factors have been varied: among these is the viscosity, mass, density, size of the solute, nature of the interaction (hard sphere, soft sphere, Lennard-Jones, square well and others).

The validity of the reciprocal relation between D and η has been investigated extensively. van Gunsteren and coworkers found from molecular dynamics (MD) simulations, that the product of viscosity with diffusion coefficient of pure water is a function of the mass of water [8]. This suggests a deviation from Stokes-Einstein expression, Eq. 1 which predicts that the product is independent of mass. Alder et al. found that the inverse relationship between self diffusivity and viscosity is valid over a wide density range they studied for a hard sphere fluid [9].

In a detailed study, Kivelson investigated the validity of Stokes-Einstein relationship for solutes of lower mass and size [10]. Their study, however, restricts itself to solute mass (m_u) greater than or equal to solvent mass (m_v), $m_u \geq m_v$ and similarly the radius $r_u \geq r_v$. They find that SE relationship is valid under these conditions in agreement with experiments [11-14].

Alder et al. studied the binary mixture of hard sphere fluids at high densities [15]. They varied mass and size of the solute. They found deviations from Enskog theory for smaller solute sizes but found the results in agreement with experiment. Alder and Alley investigated a one-component fluid of hard disks by molecular dynamics [16]. Long-time correlations in the displacement distributions were found in these systems. Bernert and Kivelson found that the reciprocal relationship given by Stokes-Einstein expression (1) between D and η is valid over five orders of magnitude of variation of η [17]. Willeke reported MD simulation of binary Lennard-Jones mixtures and studied the validity of Stokes-Einstein relationship over a wide range of mass and size ratios of solute to solvent [18]. They found that the Stokes-Einstein relation is not valid for $\sigma_{uu}/\sigma_{vv} < 1$ and $1/16 < m_u/m_v < 50$ among other things.

Lamanna et al. have studied protein solutions and examined the validity of the reciprocal relationship between D and η given by Stokes-Einstein relation as a function of concentration of the solution [19]. Yamamoto and Onuki showed that the diffusivity is heterogeneous on time scales less than the stress relaxation time of a tagged particle [20]. Masters and Keyes investigated solute motion as a function of the size and mass ratio; an increase in the self diffusivity over and above the Stokes-Einstein value for light solutes when the solute size was about 1/4 of the solvent size was seen by them [21].

There have also been several studies attempting to understand the D-η relationship in supercooled liquids. Bagchi has shown that near the glass transition temperature the self diffusivity exhibits a change from the viscosity dependent, Stokes-Einstein to an activated, hopping motion [22]. The latter is nearly independent of viscosity. Subsequently, Tarjus and Kivelson showed that there is a decoupling of the translational motion from viscosity below the supercooled transition in a one-component system [23]. Bhattacharya and Bagchi have reported a similar study for a two component system in the supercooled regime [24]. In another study, Bhattacharyya and Bagchi have carried out mode coupling theory calculations of solute-solvent mixtures and found that small solutes have self diffusivities higher than that given by the Stokes-Einstein relationship [24]. They have also carried out studies with a range of solute sizes by choosing solute smaller as well as larger than the solvent size. Further, they studied dependence of diffusivity as a function of solute-solvent size ratio. Jung et al. investigated through MD simulation the decoupling and breakdown of Stokes-Einstein relation in supercooled liquids [25]. Srinivas et al. in a study based on computer simulation and mode coupling theory of the solute-solvent system, showed that varying the solute-solvent interaction from attractive to repulsive can change the diffusion coefficient of the solute nonlinearly [26]. Breakdown of the Stokes-Einstein relation for translational diffusion in supercooled liquids was studied by Viot, Tarjus and Kivelson at low temperatures [27]. In a density functional theoretical treatment of a tagged particle in a viscous liquid, Bagchi examined the validity of the inverse relationship between the orientational correlation time and the self-diffusivity of a tagged particle [28].

Experiments have also attempted to investigate the Stokes-Einstein relationship. Phillies et al. reported deviations from Stokes-Einstein dependence of self-diffusivity on viscosity in a light scattering study of hydroxypropylcellulose:water mixture [29]. Nigra and Evans have obtained the Stokes-Einstein relationship between the viscosity and the self diffusivity for a fluid interacting via modified square well potential [30].

Kaddour and Barrat and also Easteal and Woolf have carried out computer simulation investigations of solute-solvent mixtures to understand the variation of diffusion coefficient of the solute with size [31-32]. More recently, Noworyta et al. observed that small solutes in water also showed higher diffusivities than given by Stokes-Einstein expression [33]. Recently Sharma and Yashonath reported molecular dynamics studies of diffusion of solute particles in solvent [34]. These studies suggested existence of three regimes; in one of the regimes, it is seen that the solute exhibit diffusion coefficient that is higher than predicted by the Stokes-Einstein expression.

Here we report a systematic investigation of dependence of D on size of the solute in a binary mixture interacting via Lennard-Jones potential. The solute radius is varied over a reasonably wide range but is kept smaller than the solvent radius. We investigate in detail the nature of motion of the solute in the three regimes to bring out the differences between them.

2. Methods

2a. Intermolecular interactions

A binary mixture consisting of spherical solute and solvent atoms interacting via Lennard -Jones interaction potential (6-12) is studied. The total interaction energy has contributions from solute-solute (uu), solute-solvent (uv) and solvent-solvent (vv) terms:

$$\phi_{\alpha\beta} = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] \qquad \alpha, \beta = \mathrm{u, v} \qquad (2)$$

Simulations have been carried out with full Lennard-Jones (LJ) interaction potential between all the species (solute-solute, solute-solvent and solvent-solvent) and these are referred to as DISP. Further, simulations with the coefficient of the $1/r^6$ term in the

Lennard-Jones potential in equation (1) given above has been assumed as zero and in these simulations are referred to as SOFT. That is, the dispersion interaction is absent and only a soft repulsive interaction exists. The interaction for both solute-solute and solute-solvent interactions consist of only $1/r^{12}$ term; solvent-solvent interactions are always of full LJ (6-12) form in both DISP and SOFT.

Interaction between the solute and the solvent species are related through $\sigma_{uv} = 0.7 + \sigma_{uu}$ and the choice of ε are listed in Table 1 [35-36].

2b. Molecular Dynamics Simulations

All simulations have been carried out in the microcanonical ensemble with periodic boundary condition using DLPOLY package [37]. After equilibration, positions and its derivatives are stored for subsequent analysis. The atoms are integrated using Verlet Leapfrog algorithm.

2c. Computational Details

The system consists of 50 solute and 500 solvent atoms. The length of the simulation cell is 33.3Å for a reduced density (ρ^*) of 0.933 which is higher than the triple point reduced density, 0.7. The reduced temperature (T^*) of the system is 1.663 (50K). The solute mass (200amu) is heavier as compared to the solvent mass (80amu). The time step for integrating the Newton's equations of motion is 5fs and the system is equilibrated for 2ns. The relative standard deviation in total energy is better than 5 x 10^{-5}. The position coordinates and their derivatives are stored at an interval of 100fs for a run length of 700ps to compute different autocorrelation functions. Further, a production run of 6ns with a storage interval of 1ps to store the position coordinates has been made to calculate the mean square displacement.

Table 1 Interaction Parameters

Type of interaction	σ, Å	ε, kJ/mol
vv	4.1	0.25
uv	1.0 – 4.7	1.5
uu	0.3 – 4.0	0.99

3. Results ar

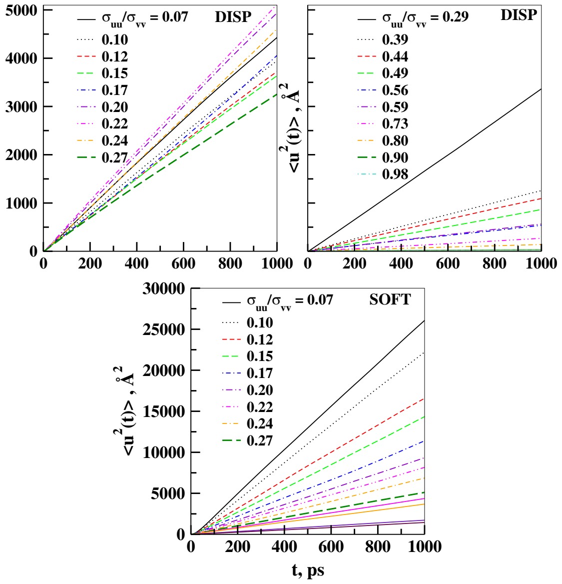


Figure 1 Time Evaluation of mean square displacement with (DISP) and without (SOFT) dispersion interaction

The mean square displacements of solute atoms as a function of time is evaluated for systems with and without dispersion interaction (see Figure 1). The time evolution of the mean squared displacement over 1ns shows that the statistics are adequate; there are no deviations from the straight line behaviour suggesting that all solute are exhibiting diffusive behaviour. The data can be fitted well to straight line. The dependence of the slope of the mean square displacement on the size of the solute is different in simulations with dispersion and without dispersion interaction as we will see.

We define the solute-solvent size ratio; $\kappa = \sigma_{uu}/\sigma_{vv}$. Figure 2 shows the variation of diffusivity of the solute with κ^{-1}. *D* is seen to exhibit a monotonic increase with κ^{-1} for the simulations without dispersion interaction (SOFT). For simulations with full LJ potential, we see that the in the limit of small κ^{-1}, the increase in κ^{-1} leads to an increase in *D*. This is the behaviour expected from the SE equation (1). This is seen for $\kappa^{-1} < 2.56$. This is the regime I where SE is perfectly valid. In the range $2.56 < \kappa^{-1} < 5.88$, we see that the self diffusivity *D* is higher than the value predicted by Stokes-Einstein relationship, .i.e. the *D* values are higher than the Stokes-Einstein value obtained from Eq. (1). This is what we call as regime II. This deviation has not been noted previously, although several groups (as discussed in the introduction) have reported enhanced diffusivities when the solute diameter is approximately 1/4 to 1/3 of the solvent diameter. For example, Masters and Keyes who studied light solutes found that for solute sizes about 0.25 times the solvent size, self diffusion is higher than the SE value [21].

Similarly, Ould-Kaddour and Barrat as well as Easteal and Woolf also reported such enhanced diffusivity [31-32]. More recently, Noworyta have reported higher D for Li^0 in water [33]. Bhattacharya and Bagchi have reported mode-coupling calculations in which they found self diffusivity values higher than the Stokes-Einstein value for small solutes in solvent [24]. Thus, present simulations results are consistent with previous studies reporting higher D for smaller solutes.

We note that the self diffusivity increases with increase in κ^{-1} and is higher than the SE value above $\kappa^{-1} = 2.56$. This deviation from the reciprocal relationship given by Stokes-Einstein expression reaches a maximum at around $\kappa^{-1} = 4.55$. As κ^{-1} increases further above 4.55, it is seen that the deviation from SE value decreases. By $\kappa^{-1} = 5.88$, the enhancement in the value of D ceases to exist. Thus, it is only over a small region of $2.56 < \kappa^{-1} < 5.88$ where the deviation leading to enhancement is seen. This behaviour has been previously seen in widely differing systems. Guests in zeolites exhibit a maximum in self diffusivity when the size of the guest is comparable to the neck diameter. Zeolites have pores through which the guests can diffuse; the pores at some points are narrower and these are referred to as neck or bottleneck [38-39]. Recently similar size dependent diffusivity maximum has been seen in binary liquid mixtures [40]. The maximum occurs due to the mutual cancellation of forces exerted on the diffusant (guest or solute) by the surrounding media and is known as Levitation effect.

We further note that this regime II does not exist in SOFT simulations where the dispersion term is absent. Thus, the presence of the attractive dispersion term is responsible for the deviation in D from the Stokes-Einstein value between $5.88 < \kappa^{-1} < 2.56$. In the absence of the $1/r^6$ term, which is long-ranged, the absence of the retarding effect of this attractive potential leads to higher diffusivity values. Thus, we see that the D values are higher for SOFT simulations as compared to DISP simulations almost over the entire range of κ. However, the enhancement in D arises from the presence of mutual cancellation of forces that occurs because of symmetry and has relevance only in the presence of the dispersion term. When $\kappa^{-1} = 4.55$, the solute behaves as though is not confined to the pores of the medium in which it exists although it is still diffusing within the medium. In the absence of the dispersion interaction, the potential is short-ranged and there is no attractive term and therefore such a cancellation does not significantly reduce the forces (for $\kappa^{-1} = 4.55$ in comparison to other sizes) exerted on the solute by the solvent. For more detailed discussion please see other references.

For κ^{-1} greater than 5.88, we see that the solute diffusivity increases more rapidly with increase in κ^{-1}. The dependence of D is $1/\sigma^2_{uu}$. This is expected from kinetic theory whenever the diffusant is significantly smaller than the voids through which it is diffusing. This fit is also shown in Figure 2. This is regime III.

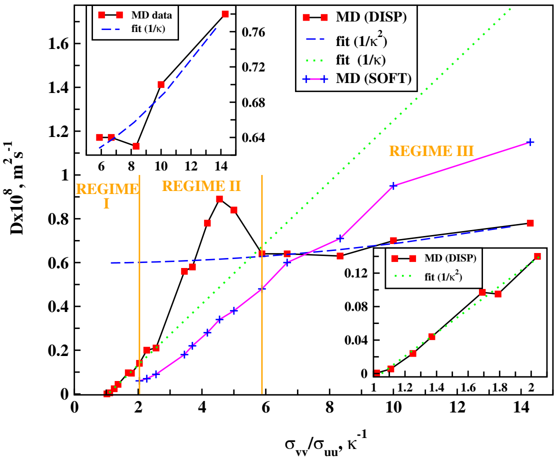


Figure 2 Self diffusivity D is plotted against the solute-solvent size ratio κ for (a) with dispersion interaction (DISP) and (b) without dispersion interaction (SOFT). Continuous lines shown are only a guide to the eye. Also shown are fits 1/κ in the limit of large κ and $1/\kappa^2$ in the limit of small κ to MD data of DISP simulations in the

Figure 3 shows the mean square force averaged over all times and solutes. This is the force exerted on the solute by the surrounding solvent atoms. We see that the force on the solute decreases with decrease in solute radius or κ upto κ = 0.22. As κ decreases below this value, the average mean square force actually increases. Thus, the average force is *lowest* for κ = 0.22. Thus, both a larger solute as well as a smaller solute will encounter a higher force. This peculiarity arises from the existence of Levitation Effect. According to this, when the size of the solute is similar to the size of the neck or void in which it exists, then there is mutual cancellation of force leading to a lower net force on the solute. Thus, the diffusivity is higher for κ = 0.22 in comparison to any solute larger than this size. For sizes smaller than this size, other factors play a role which is discussed below. The plot of the average force shown in Figure 3 clearly demonstrates that the mutual cancellation of forces indeed is the reason for higher diffusivity.

We have also calculated the activation energy of different solutes in the three regimes from the Arrhenius relationship:

$$D = D_0 \exp\left(\frac{-E_{act}}{RT}\right) \tag{3}$$

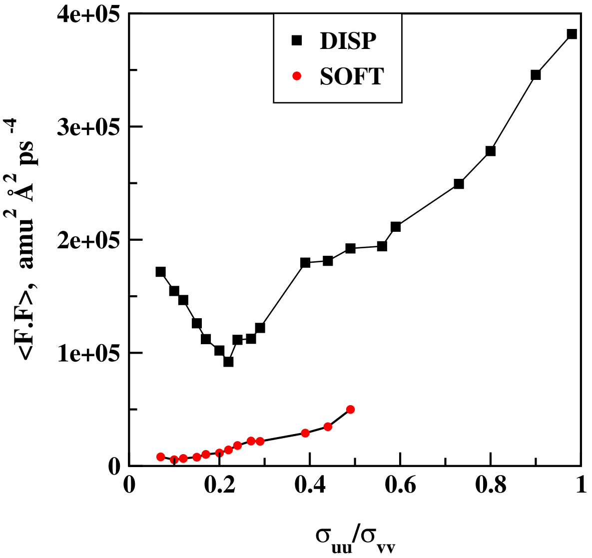
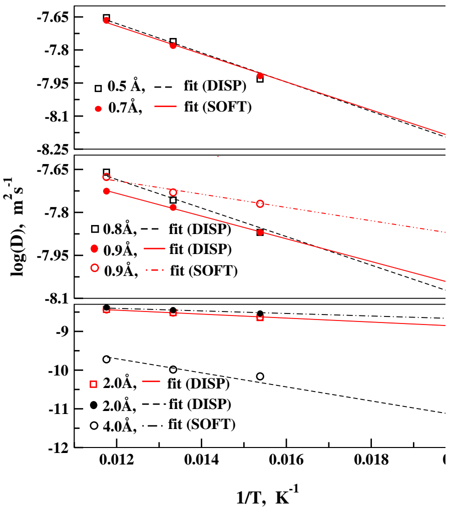


Figure 3 Average mean square force is shown for different solute-solvent size ratios (κ), in the presence (DISP) and absence of (SOFT) dispersion interaction.

The self diffusivity of solutes at four different temperatures obtained from MD simulations show the expected Arrhenius behaviour. Figure 4 shows the Arrhenius plot for the solutes with and without dispersion interaction. Figure 5 shows the variation of the activation energy, E_{act} and pre-exponential factor D_o with κ, calculated from the slope and intercept respectively of the Arrhenius plot. Results are shown for the solutes in the three different regimes in the presence and the absence of dispersion interaction.

The results show interesting variation of E_{act} and D_o for the three regimes. We confirm that although we have shown results for only one or two solute sizes in each regime, other solute sizes in a given regime exhibit values similar to the solutes shown here. Therefore, the trend seen here is the correct trend. In regime III, E_{act} is large as compared to regime II but less than what is obtained for regime I. Thus we see the trend E_{act}(II) < E_{act}(III) < E_{act}(I). The pre-exponential factor D_o for regime III is large and for regime II it is somewhat less. For regime I, D_o is smallest among the three regimes. Within regime I, we see that D_o increases slightly with increase in size of the solute as expected. Thus, we see the trend D_o(I) < D_o(II) < D_o(III). Thus, for regime II, while activation energy is lowest and the pre-exponential factor is intermediate in value as compared to the other two regimes. Since, the predominant influence on self diffusivity is that of the activation energy, we see that the overall diffusivity of solutes for regime II is maximum and those of regime I and regime III is lower than that of solutes in regime II.



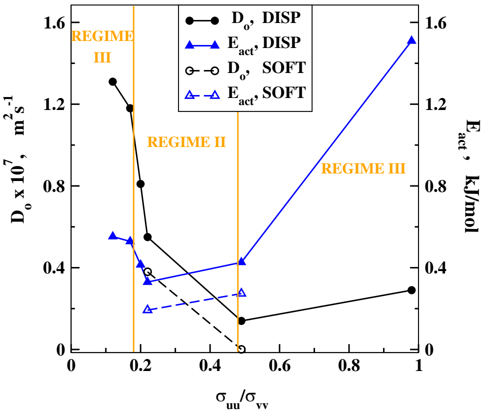
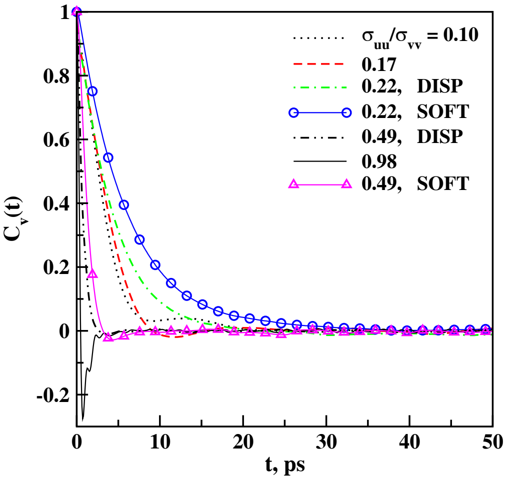


Figure 4 Arrhenius plot for solutes in the three regimes, with and without dispersion interaction

In Figure 6 we show velocity autocorrelatio function (vacf) for several κ. We note tha for regime I and II, the vacf exhibit little c no backscattering. For regime III, th intercept of the curve with *x*-axis occurs a large time leading to large diffusivity However, note that in spite of the larg diffusivity for regime III, the activatio energy barrier is higher for regime III a compared to regime II. This is mainl because of the significant increase in th pre-exponential factor, D_o. The curve for κ 0.22 from regime II is seen to exhib smooth decay in comparison to a solut from either regime I or III. A solute fro regime I (large κ) exhibits larg backscattering and has low diffusivity. I absence of dispersion interaction, solute has higher diffusivity than with dispersion interaction as seen for κ = 0.22 and 0.49.



for solutes in the three regimes, with and without dispersion interaction.

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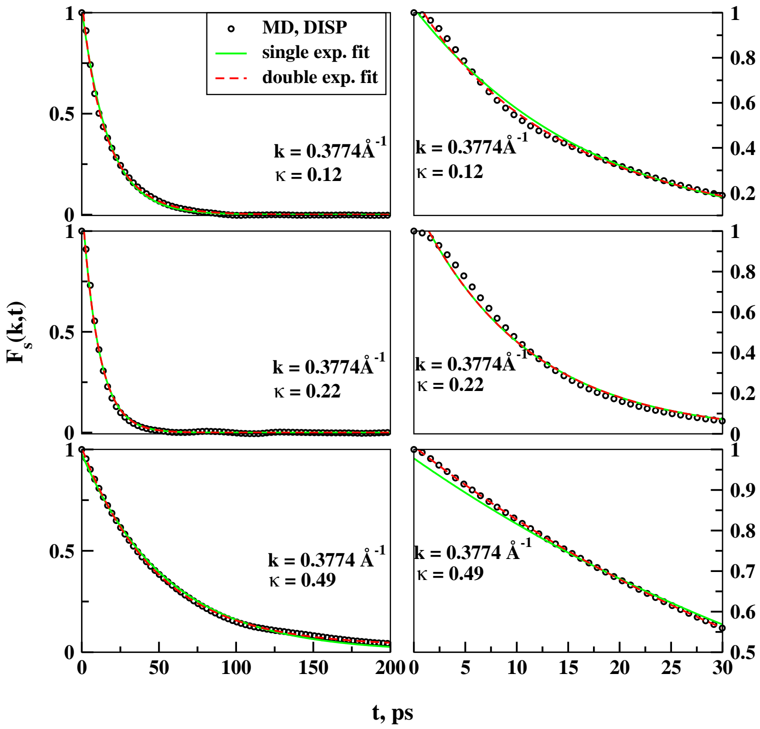

Figure 7 Intermediate scattering functions for solutes at small *k*. Left figure shows the decay over the whole duration while the right figure shows, on an expanded scale, the decay during the first few picoseconds. Results are shown for the system with dispersion interaction.

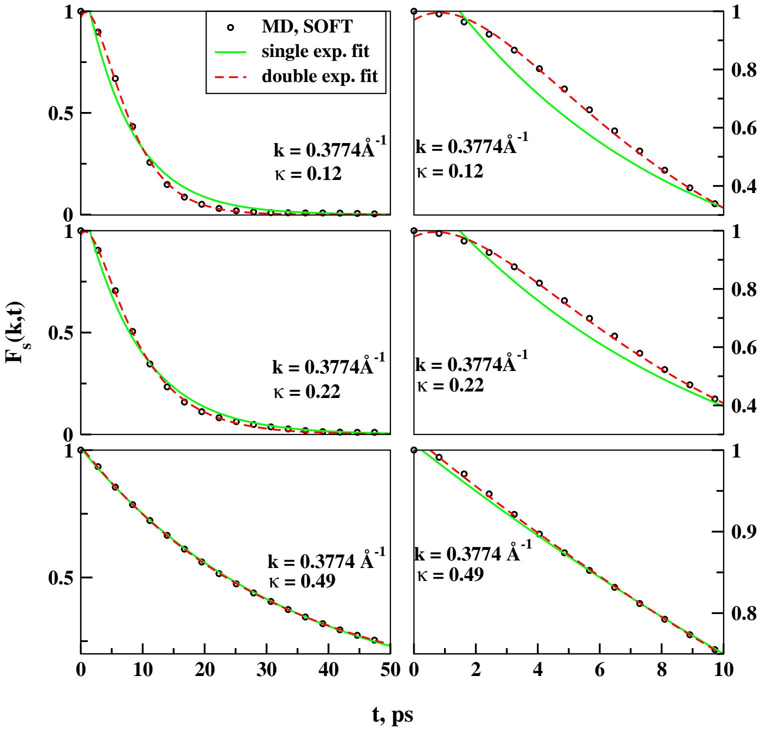

Figure 8 Intermediate scattering functions for solutes at small *k*. Left figure shows the decay over the whole duration while the right figure shows, on an expanded scale, the decay during the first few picoseconds. Results are shown for the system without dispersion interaction.

Figure 7 shows the intermediate scattering function as a function of time for solutes in the three regimes in the presence and in the absence of dispersion interaction. For solutes in regime I and III, double exponential gives a better fit as compared to single exponential fit for both with and without dispersion interaction. The single exponential fit to $F_s(k,t)$ for $\kappa = 0.12$ is not good near 15 and 50 ps (other than initial times (< 2ps) where even bi-exponential fit provides poor agreement with $F_s(k,t)$). At times less than 2ps, the decay is mainly in the ballistic regime and therefore not of relevance to diffusive behaviour which we are discussing here. The better agreement of bi-exponential fit

$$f(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \tag{5}$$

to MD derived $F_s(k,t)$ suggests that the solute perceives the liquid or solution as consisting of two distinct regimes. In contrast to this, for the slightly larger solute (κ =

0.22), the $F_s(k,t)$ from MD fit well to a single-exponential fit (except for the ballistic regime). We see that for still larger size of the solute (e.g., κ = 0.49), the single exponential still provides a good fit to $F_s(k,t)$.

Figure 8 shows the $F_s(k,t)$ for a few solute sizes for the case without the dispersion interaction. The results suggest that for κ = 0.22, the single exponential does not provide a good fit at all. In the case of the larger solute (κ = 0.49), although the bi-exponential provides a better fit, the single exponential also seems to fit reasonably well.

In order to understand these results, we have computed the *k*-dependence of width of the self part of the dynamic structure factor, $\Delta\omega/2Dk^2$. Figure 9 shows the behaviour of $\Delta\omega/2Dk^2$ for four different sizes of the solute. For κ = 0.12, this function exhibits a minimum at some intermediate value of *k*. For the larger sized solute κ = 0.22, such a behaviour is not seen; a smooth decrease with *k* is seen. For still larger sizes, κ = 0.49 and 0.73, pronounced minimum exist at some intermediate values of *k*.

Let us now see what is known about this quantity. This quantity has been previously computed from MD simulations by several groups. Levesque and Verlet [41] computed this quantity for argon fluid at low density and high temperature (ρ^*= 0.65 and T^* = 1.872). They found that $\Delta\omega/2Dk^2$ exhibits only a monotonic decrease with increase in *k*. Nijboer and Rahman [42] studied a high density argon fluid at low temperature and found that ((ρ^*= 0.8442 and T^* = 0.722). They found that $\Delta\omega/2Dk^2$ exhibits a pronounced minimum at an intermediate value of *k*. This value of *k* corresponds to the near neighbour shells. No understanding of why the two different behaviours of this quantity are seen for two different densities and two different temperatures is available in the literature.

We now provide a qualitative explanation for the observed behaviour of $F_s(k,t)$ as well as $\Delta\omega/2Dk^2$ as a function of the size of the diffusant. We have seen previously that the when the solute is small (κ = 0.12), the activation energy is large. Let us try to understand from where this activation energy arises. The radial distribution function provides the structure of a liquid; from the radial distribution function, it is evident that the maximum density occurs at or near the first solvent shell. A solute that diffuses through the liquid has to pass through this shell. It need not pass through it only in the case when it moves carrying with it such a solvent shell. This latter possibility is ruled out since this will mean movement of the whole shell which is likely to be only slower and since the solute-solvent interaction is not too strong, this is unlikely. For the solute to escape the first solvent shell then would provide the most difficult step in the passage of a solute. We note that the first solvent shell is a sphere. For the solute to get past the solvent shell there has to be an opening on the surface of the first solvent shell that is large enough for the solute to pass through.

At this point it is relevant to recollect the past findings with regard to what is now known as Levitation Effect. A guest inside a zeolite cage (can be approximately considered to be spherical in shape) goes out of the cage through a narrow window located on the sphere. Such a passage through the window or neck is found to be associated with a higher energy barrier if the guest is significantly smaller than the window diameter. If the guest is similar to the window size, then it encounters little or no energetic barrier and it goes past the cage without difficulty.

We use this knowledge here in the present context of solute motion. We suggest that the smaller solute (κ = 0.12) is smaller than the average opening that is seen on the surface of the first solvent shell. As a result, it encounters larger activation energy. This is what we saw earlier. The larger solute (κ = 0.22), is of a size that is comparable to the opening in the first solvent shell and therefore has a lower activation energy (as suggested by the Levitation Effect). Thus, the results we obtain for solute-solvent systems with dispersion interaction are understandable. The bi-exponential decay of the intermediate
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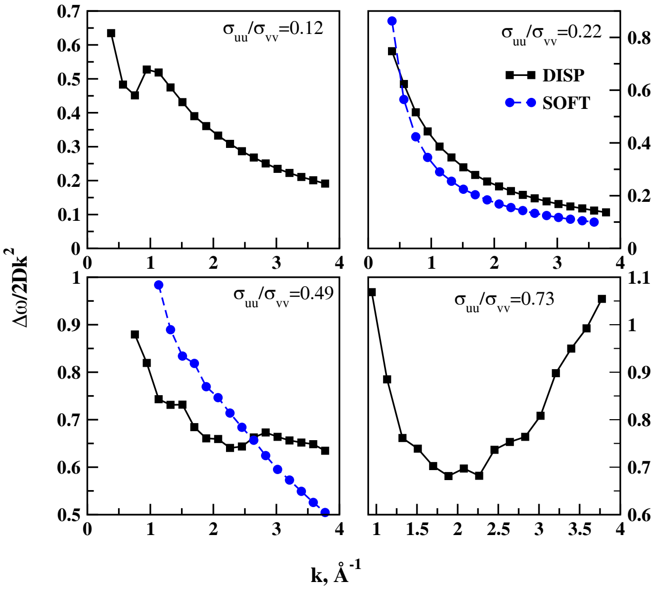

Figure 9 Wavevector dependence of solutes in the three regimes, with and without solute-solvent dispersion interaction.

4. Conclusion

We have shown that the reciprocal dependence suggested by the Stokes-Einstein expression breaks down over a narrow range of solute-solvent size ratio, κ. We have discussed the range over which this deviation occurs and the reasons for the same. Further, we demonstrate that the solutes in this range called the Levitating regime is associated with different (a lower) activation energies, different behaviour of $F_s(k,t)$ and also $\Delta\omega/2Dk^2$. We also propose a microscopic picture that is consistent with all these properties. This picture or scenario needs to be verified by direct calculation of the additional quantities or properties.

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