

Existence of a Size-Dependent Diffusivity Maximum for Uncharged Solutes in Water and Its Implications

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Received: January 3, 2006; In Final Form: April 26, 2006

Recent studies suggest that there exists a size-dependent diffusivity maximum in binary mixtures interacting via Lennard-Jones potential when the size of one of the two components is varied (Ghorai, P. K.; Yashonath, S. *J. Phys. Chem.*, **2005**, 109, 5824). We discuss in the present paper the importance of the existence of a size-dependent maximum for an uncharged solute in liquid or amorphous solid water and its relation to the ionic conductivity maximum in water. We report molecular dynamics investigations into the size dependence of the self-diffusivity, D , of the uncharged solutes in water at low temperatures (30 K) with immobile as well as mobile water. We find that a maximum in self-diffusivity exists as a function of the size of solute diffusing within water at low temperatures but not at high temperatures. This is due to the relatively weak interactions between the solute and the water compared to the kinetic energy at room temperature. Previously, we have shown that a similar maximum exists for guests sorbed in zeolites and is known as the levitation effect (LE). Thus, it appears that the existence of a size-dependent maximum is universal and extends from zeolites to simple liquids to solvents of polyatomic species. We examine the implications of this for the size-dependent maximum in ionic conductivity in polar solvents known for over a hundred years. These results support the view that the size-dependent maximum seen for ions in water has its origin in the LE (see Ghorai, P. Kr.; Yashonath, S.; Lynden-Bell, R. M. *J. Phys. Chem.* **2005**, 109, 8120).

1. Introduction

A number of factors, such as temperature, concentration, size, and so forth, influence the diffusion of a species. Of these, the size dependence of the diffusion coefficient has attracted much attention in diverse systems. Hydrocarbon molecules diffusing within zeolitic void spaces exhibit significant size dependence. For example, branched hydrocarbons are known to typically diffuse more slowly than linear hydrocarbons in the same zeolite, with all other conditions being similar.^{1,2} Ions within polar solvents have been found to exhibit a pronounced dependence in conductivity arising from the dependence of diffusivity on size.^{3,4}

Earlier investigations into the size dependence of the diffusion coefficient of neutral spherical monatomic and polyatomic guest species in zeolites obtained from molecular dynamics (MD) simulations show an anomalous dependence on the size.^{5,6} The diffusion coefficient D initially decreases slowly with increase in the diameter σ_{gg} of the guest. Here it is seen that $D \propto 1/\sigma_{gg}^2$. This is termed the linear regime (LR). Subsequent increase in σ_{gg} shows a sharp increase in D , which is followed by a decrease with further increase in σ_{gg} . This is termed the anomalous regime (AR) (see Figure 1). This AR is seen when the size of the guest or diffusant is close to the size of the void through which it is diffusing. More precisely, the anomalous maximum is seen when the levitation parameter γ , defined as

$$\gamma = \frac{\sigma_{\text{opt}}}{\sigma_w}$$

approaches unity. Here, σ_{opt} is the distance at which the interaction is optimum between the guest or diffusant and the medium through which it is diffusing. For a system interacting via a purely Lennard-Jones potential, such as argon in a zeolite, $\sigma_{\text{opt}} = 2(2^{1/6}\sigma_{\text{so}})$, where σ_{so} is the Lennard-Jones potential parameter between the guest and the oxygen of the zeolite framework. The parameter σ_w is the neck or window diameter, which is essentially the diameter of the narrowest part of the void network. This unexpected maximum in D in the AR owes its origin to the minimum in force exerted by the zeolite on the guest. The force is a minimum because of the mutual cancellation of the forces exerted by the atoms of the zeolite surrounding the guest. Such a cancellation is due to the symmetry around the guest seen only when the size of the void and the size of the guest are similar. The cancellation leads to the guest experiencing a minimum in the force at the appropriate size. As a result of the reduced force, the diffusing species is weakly bound to the medium in which it is located. For this reason, this is termed the levitation effect (LE). Under these conditions, the interaction energy of a solute with the surrounding solvent species is also maximum or most favorable.

Recently, we reported studies on binary mixtures consisting of a large component and a smaller component.⁷ Such a binary mixture exhibits little or no resemblance to the guest–zeolite system discussed above. In the latter, the voids and the void connectivities are well defined and time independent. Further, the zeolite atoms perform only restricted vibrational motion around their equilibrium positions. As a consequence, only the guest can diffuse over large distances. In contrast, in the binary

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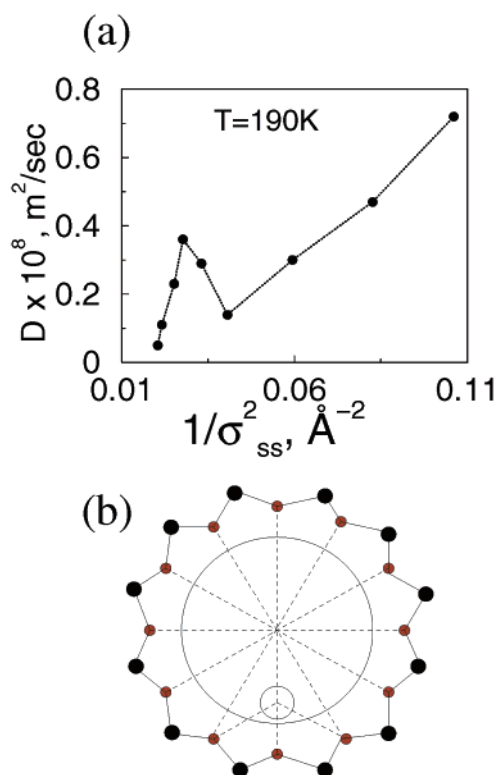


Figure 1. (a) Plot of self-diffusivity, D , vs $1/\sigma_{gg}^2$ in NaY, where σ_{gg} is the diameter of the guest. Figure reproduced with permission from Yashonath, S.; Santikary, P. *J. Chem. Phys.* **1994**, *100*, 4013, copyright 1994 American Institute of Physics; and Yashonath, S.; Santikary, P. *J. Phys. Chem.* **1994**, *98*, 6368, copyright 1994 American Chemical Society. (b) Explanation for panel a: the bottleneck for diffusion is the 12-membered ring or window in zeolite NaY, shown with Si and O atoms as filled circles. Guest atoms are shown as open circles. For the larger guest with a diameter comparable to that of the 12-membered ring, there is nearly a complete cancellation of forces on the guest due to the confining medium. This does not happen for the smaller guest, as it is closer to one part of the confining medium and relatively far away from other parts of the confining medium. This results in a diffusion maximum when the size of the guest is comparable to the neck diameter.

mixture, both the components perform diffusive motion over significant distances; therefore, it has little similarity with the guest–zeolite system. There is no component in the mixture that provides a stable, static, structural motif with voids within which the other component can diffuse. Instead, the void structure is constantly changing, and the guest diffuses within this time-varying void network. As a result, it appears to be unlikely that a size-dependent maximum in liquids will exist.

Previously, there have been investigations on the size dependence of diffusivity in a binary mixture.⁸ The study by Perera and Harrowell (PH) reports a maximum in diffusivity as a function of the size of the solute. However, there are several differences between this study and that by Pradip and Yashonath (PY).⁷ The most notable differences are (i) PH studied a two-dimensional liquid as opposed to the three-dimensional bulk mixture studied by PY. (ii) The diffusivity maximum is seen for a solute size that is greater than the solvent size in the case of PH, but PY found a maximum in the solute diffusivity for a solute radius that is lower than the solvent radius. (iii) Dispersion interaction is essential for the maximum seen under LE by PY; PH studied a system interacting with a purely soft repulsive term. (iv) An enhancement in the diffusivity of both solute and solvent was seen by PH; in contrast, PY observed an enhancement in solute diffusivity alone, with no accompanying en-

hancement in solvent diffusivity. Thus, clearly what we are discussing here is quite different from what PH reported.

We discuss here the maximum found by Pradip and Yashonath.⁷ A careful examination of LE and the binary mixture will show that the existence of LE is, in fact, not so surprising as it may appear at first. First, LE has been found to have its origin in the dispersion interaction between the guest and zeolite.^{5,6} It was found that, in the absence, of the dispersion interaction between the guest and the zeolite, the diffusivity maximum altogether disappeared. Upon introducing the dispersion interaction, the diffusivity maximum reappears. This demonstrates that there is a 1:1 correspondence between the dispersion interaction and the diffusivity maximum. The two are intimately related. Second, a close-packed solid such as a face-centered cubic (fcc) structure has a packing fraction of 0.74, suggesting that 26% of the total space consists of voids. Thus, in a liquid, the amount of void space is likely to be greater than 26%. The diameter of voids in a fcc solid is not small: it is 0.450R for a tetrahedral void and 0.828R for an octahedral void. These diameters are likely to be similar or probably even larger for a liquid. The void sizes, therefore, depend on the radius of the larger component in a binary mixture. Third, it has been found that LE exists in the presence of a significant amount of static disorder.⁹ Recent investigations have shown that, even in a binary liquid mixture, the diffusivity maximum or LE exists.⁷ This suggests that the LE may, in fact, be more universal than hitherto believed. The existence of LE in a simple binary liquid mixture suggests that the only essential condition for the existence of LE appears to be the dispersion interactions. The presence of a considerable degree of disorder seen in liquids or the dynamic nature of the void network does not seem to destroy the diffusivity maximum.

More recently, we proposed that LE provides an explanation for the observed maximum in the conductivity of ions in water.¹⁰ The computed properties of ion in water, such as activation energy, force on the ion, friction, and decay of the intermediate scattering function, appear to provide support to the fact that the conductivity maximum arises from the LE. However, more studies are required to verify that LE is indeed the theory that provides the explanation for the existence of the conductivity maximum. This work attempts to explore this conceptual basis further.

An important point to note with relation to LE is that the height or intensity of the diffusivity maximum is proportional to the strength of the interaction between the diffusant and the zeolite or, in the case of a liquid mixture, between the solute and the solvent.¹¹ More precisely, the height or the intensity of the diffusivity maximum is determined by the ratio of the strength of interaction to the kinetic energy or $-U_{gh}/k_B T$. Here, U_{gh} is the interaction energy between the diffusant and the medium in which it is placed. The previous study of Chitra and Yashonath¹¹ suggests that, as temperature increases, the diffusivity maximum decreases in intensity, and, at sufficiently high temperatures, it disappears altogether. For this reason, whenever U_{gh} is small, it is necessary to choose a temperature that is low enough to see the diffusivity maximum.

From previous studies and this discussion, it is clear that the diffusivity maximum must exist wherever there is solute–solvent attractive interactions. This nature of the interaction can be dispersion or electrostatic (Coulombic). It is not necessary that the electrostatic interactions are present. It is sufficient to have just the dispersion interactions. We assume in the present discussion that the repulsive interactions are always present. As we know, the dispersion interactions are always present in

TABLE 1: Water–Water Potential Parameters for the spc/e Model

spc/e	σ_{OO} (Å)	ϵ_{OO} (kJ/mol)	charge (q)
O (H ₂ O)	3.169	0.6502	−0.8476
H (H ₂ O)			+0.4238

any real system (there are no ideal gases in the real world). Therefore, it follows that the diffusivity maximum is also always present. This means that even an uncharged solute in a solvent should exhibit a diffusivity maximum, according to LE. None of the other existing theories, such as the solvent–berg model, continuum theories, or microscopic theories, suggest that a maximum should be seen for an uncharged solute. Thus, confirmation of the existence of a diffusivity maximum for an uncharged solute would provide strong support to LE as the correct theoretical framework or the right explanation for the ionic conductivity maximum seen in polar solvents. This has the added advantage of providing a unified theory for the size-dependent diffusivity maximum seen in diverse systems.

When electrostatic interactions are present, they play a very important role in that they increase the strength of the solute–solvent interactions (U_{gh}) because of their long range. Therefore, the ratio of $-U_{\text{gh}}/k_{\text{B}}T$ is large. As a result, the diffusivity maximum can be seen at relatively higher temperatures. Thus, for ions in water, the diffusivity maximum can be seen at room temperature. For an uncharged solute, this is not the case since (U_{gh}) is small, and therefore one needs to look for the maximum at rather low temperatures. In fact, this temperature may be so low that the solvent is frozen into an ordered crystalline solid or an amorphous solid.

In light of this, we examine the possible existence of a diffusivity maximum or LE for uncharged solutes in water, a typical polar solvent. We report MD simulations of the solutes in water at rather low temperatures (to be able to see the maximum as explained above) for different sizes of solute. We compute the self-diffusivity in immobile water as well as amorphous water. We show that, although the results here are in the quenched, frozen, metastable, amorphous state of water, the results and arguments that we give here are generic and therefore applicable to the study of ions in liquid water at room temperature. The LE is a highly generic, universal behavior, and therefore the observations at low temperatures are not only relevant but are of high value in the arguments put forth later.

2. Methodology

2.1. Intermolecular Potential. Water–Water. We employ the *extended simple point charge* (spc/e) model to simulate water.¹² In this model, a water molecule is represented by three sites positioned on the O and H atoms. The sites carry a mass similar to that of the respective atoms. The O–H bond length is taken to be 1.0 Å, and the HOH angle equals 109.47°. A charge of $+q$ is placed on H, and $-2q$ is placed on O. The short-range interaction is restricted to the oxygen through a Lennard-Jones potential. The pair potential between two water molecules has the form

$$\Phi_{\text{ww}} = 4\epsilon_{\text{OO}} \left[\left(\frac{\sigma_{\text{OO}}}{r_{\text{OO}}} \right)^{12} - \left(\frac{\sigma_{\text{OO}}}{r_{\text{OO}}} \right)^6 \right] + \sum_{i,j \in \text{w}, i \neq j} \frac{q_i q_j}{r_{ij}} \quad (1)$$

where ϵ_{OO} and σ_{OO} are the Lennard-Jones potential parameters between the oxygen of the two water molecules, and r_{OO} is the O–O distance. The term q_i is the charge at site i with three sites per molecule of water. The water–water interaction potential parameters are listed in Table 1.

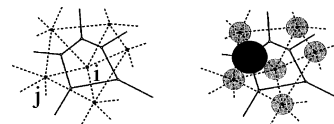


Figure 2. Two-dimensional illustration of the Voronoi–Delaunay dual construction. The central atom i is surrounded by atoms j . Figure was reproduced with permission from Corti, D. S.; Debenedetti, P. G.; Sastry, S.; Stillinger, F. H. *Phys. Rev. E* **1997**, 56, 5524. Copyright 1997 American Physical Society.

Solute–Water. Solute is represented as a spherical species through a short-range interaction site. It interacts with water through short-range interaction with the oxygen of water:

$$\Phi_{\text{sw}} = 4\epsilon_{\text{sO}} \left[\left(\frac{\sigma_{\text{sO}}}{r_{\text{sO}}} \right)^{12} - \left(\frac{\sigma_{\text{sO}}}{r_{\text{sO}}} \right)^6 \right] \quad (2)$$

where ϵ_{sO} and σ_{sO} are the Lennard-Jones potential parameters between the solute s and oxygen (O) of the water. The parameter r_{sO} is the solute–oxygen distance.

We varied the σ_{sO} , the Lennard-Jones parameter between the solute and the oxygen. We kept the interaction strength, ϵ_{sO} , constant at 1.5846 kJ/mol. The parameter σ_{sO} was varied between 0.7 and 2.1 Å.

Solute–Solute. Interaction between two solutes is through short-range Lennard-Jones (6–12) potential. The parameters are $\sigma_{\text{ss}} = 1.5$ Å and $\epsilon_{\text{ss}} = 0.2608$ kJ/mol. The parameter σ_{ss} for solute–solute interactions has not been varied. Thus, the solute–water cross interaction parameters do not obey the Lorentz–Berthelot combination rules. Calculations have been carried out for uncharged solute.

2.2. Voronoi Polyhedral Analysis. We use the Voronoi construction to characterize the structure of the “pore space” or “void space” in water. To characterize the structure of the void space in the host matrix, we use the Voronoi construction, which has been employed in similar studies of liquids^{13,14} and other disordered materials such as porous media and powders,^{15,16} resulting in valuable insight into the distribution of voids within these dense systems. In any specified configuration of equisized particles, the Voronoi polyhedron of a given particle i is the set (subvolume) of all points that are closer to i than to any other. The vertexes and edges of the Voronoi polyhedra are, by construction, equally far from the closest surrounding particles. Specifically, in disordered configurations, a Voronoi vertex is equidistant from four particles, and any point on a Voronoi edge is equidistant from three particles. Therefore, a natural and convenient description of the empty or void space can be given in terms of the network formed by the edges of the Voronoi polyhedra. Specifically, one can visualize the void space as being made of “pores”, each of a radius given by the distance of a Voronoi vertex to the surrounding particles *minus* the particle radius, and “channels” of radius given by the smallest lateral distance of a Voronoi edge and the surrounding particles *minus* the particle radius. We refer to the corresponding diameters as *void* and *neck* sizes, respectively. Figure 2 illustrates these for two dimensions. Diffusants of a given radius can find an interconnected path between voids if the intervening neck sizes are larger than the diffusant radius. However, the motion of the host atoms ensures that the void network is restructured dynamically. Thus, even a guest particle for which there is no interconnected path at a given time step manages to diffuse over a period of time.

Voronoi and Delaunay tessellations were carried out using the algorithm by Tanemura et al.,¹⁷ as outlined in Sastry et al.¹⁴ The main purpose of Voronoi analysis is to obtain the

distribution of void and neck diameters. For diffusion within crystalline porous solids, the anomalous maximum in the self-diffusivity occurs when γ is close to unity. For diffusion within disordered systems,⁹ the maximum occurs at values of γ significantly less than unity when one uses the mean neck size to obtain σ_{neck} , which corresponds to σ_{window} or σ_{w} in crystalline solids such as zeolites.

In carrying out the Voronoi analysis, we made a simplifying assumption that water can be represented as a spherical species. Because of this, only σ_{OO} (3.169 Å) of the oxygen atom of the water molecule was utilized for generating the tessellation.¹⁷

2.3. MD Simulations. All simulations were carried out in a microcanonical ensemble by using the MD method. A slightly modified version of the DL-POLY program¹⁸ to simulate spc/e water was used. A fifth-order predictor–corrector algorithm was used to integrate the equations of motion. A cubic periodic boundary condition was employed throughout the calculation. We used the Ewald sum for the long-range Coulombic interactions. Rotational degrees of freedom were represented in terms of quaternions.

2.4. Computational Details. Runs were performed in a microcanonical ensemble. The solute radius σ_{SO} was varied over a wide range, as suggested by the Voronoi tessellation.

An integration time step of 1.5 fs was chosen. The density of water is $\rho^* = 0.792 \text{ gm/cm}^3$, which is somewhat lower than the density of ice. The simulation cell was a cube of length 26.0 Å with 466 water molecules. A cutoff radius of 13.0 Å was used. We took 64 solute particles. The solute mass was 18 amu, which is the same as that of the solvent. Calculations were carried out at 30 K for reasons already mentioned in the Introduction.

Properties were calculated from configurations stored at intervals of 100 integration steps. The equilibration period was 150 ps, during which the velocities were scaled to obtain the desired temperature, while the production runs were for 400 ps. We note that, if water is quenched sufficiently fast to low temperatures, it would result in an amorphous solid, even in a laboratory experiment. Such an amorphous solid is in fact a metastable nonergodic system, as all glasses are. Thus, the equilibration in the MD that we carried out was to obtain the “correct” configuration corresponding to that of the amorphous solid and not that of the crystalline forms of ice. Here we are dealing with amorphous solid and not the crystalline form of ice. Calculation of the void and neck distributions were carried out over 400 stored configurations.

Calculations were carried out at four different temperatures for a few selected sizes to obtain an estimate of the activation energy.

3. Results and Discussion

3.1. Structure. Three different sets of simulations were carried out. Set A consists of an MD simulation in which only the solute atoms were included in the MD integration. Water was cooled instantaneously from 300 to 30 K and equilibrated at this lower temperature. After this, MD integration was carried out only for the ions and not the water. In another set of simulations (set B), both the solute and water are permitted to move by including both of them in the MD integration. The third set (set C) is similar to set A, but a different initial configuration of water was chosen and held fixed throughout the simulation.

The radial distribution functions (rdf's) between solute–oxygen (s–O) and solute–hydrogen (s–H) for sets A and B are shown in Figures 3 and 4, respectively, for uncharged solutes

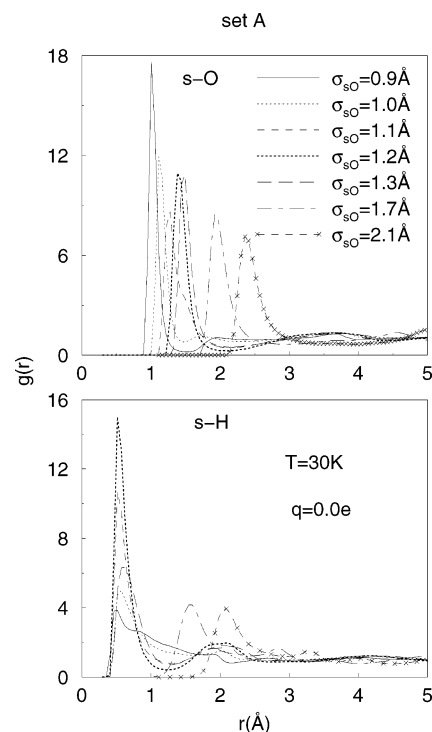


Figure 3. Solute (S)–H₂O (H, O) rdf's for set A (frozen or immobile amorphous H₂O) at 30 K with uncharged solute in amorphous H₂O.

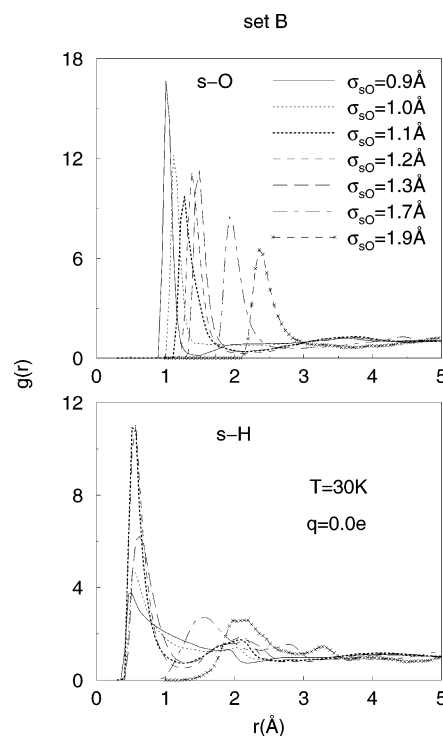


Figure 4. Solute (S)–H₂O (H, O) rdf's for set B (solute and mobile amorphous H₂O) at 30 K for uncharged solute in amorphous H₂O.

diffusing in liquid water. The s–O rdf exhibits a sharp first peak, which is followed by a very diffuse second peak. For large values of σ_{SO} (1.7 and 2.1 Å), it is seen that the position of the first peak shifts to larger distances. Note that these calculations were carried out at a rather low temperature of 30 K.

The void ($g(r_v)$) and the neck ($g(r_n)$) distributions for these three sets obtained from Voronoi tessellation are shown in Figure 5. The value of r_v , the void radius, extends over a reasonably

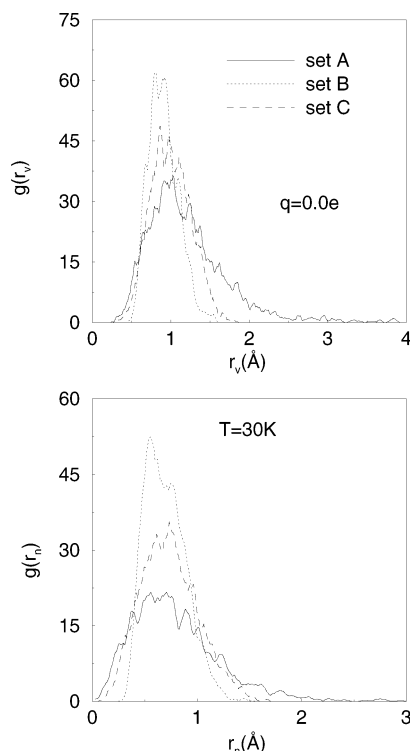


Figure 5. Void and neck distribution of all three sets (A, B, and C) at 30 K for spc/e amorphous H₂O with uncharged solutes.

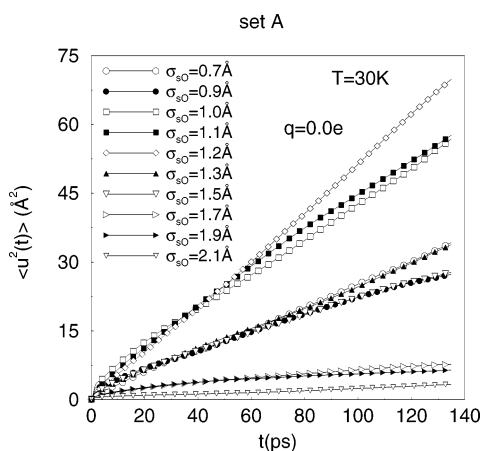


Figure 6. The msd of the uncharged solute for different sizes of the solute for set A at 30 K.

wide range from 0.3 to 3 or 4 Å, while the neck radius, r_n , extends from 0.1 to 2 or 3 Å. This suggests that the solute radius that can diffuse within water can vary over this rather wide range, even in the case of set A or set C (immobile water simulations). These simulations correspond to calculations in supercooled water. The void and neck distributions shown in Figure 5 provide us with a rough estimate of the size of solute that can diffuse through water.

3.2. Dynamics. Time evolution of mean square displacement (msd) for different values of σ_{so} for uncharged solute at 30 K are shown for sets A and B in Figures 6 and 7, respectively. Table 2 lists the self-diffusivity values for set A, set B, and set C obtained from MD trajectories by using the Einstein relation.¹⁹ Figure 8 shows a plot of self-diffusivity, D , as a function of $1/\sigma_{so}^2$. The plots for the three sets exhibit maxima for reasonably large sizes of σ_{so} . The maximum in D differs only slightly for the three sets and occurs between $\sigma_{so} = 1.1$ – 1.3 Å. The minimum for the three sets located between the LR and AR is in the range of $\sigma_{so} = 0.9$ – 1.0 Å.

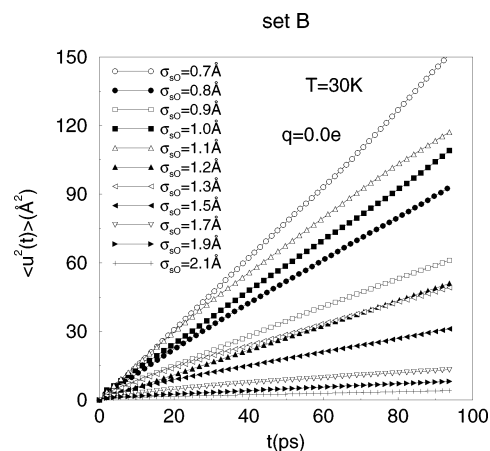


Figure 7. The msd of the uncharged solute for different sizes of the solute for set B at 30 K.

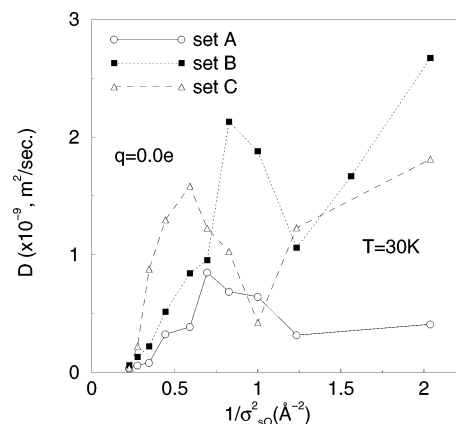


Figure 8. Self-diffusivity, D , as a function of $1/\sigma_{so}^2$ for set A, set B, and set C at 30 K. In sets A and C, amorphous H₂O is immobile, while, in set B, it is included in the MD integration.

TABLE 2: Self-Diffusivity Values for Sets A, B, and C at 30 K

σ_{so} (Å)	$D \times 10^9$ (m ² /s)		
	set A	set B	set C
0.7	0.41	2.67	1.81
0.9	0.32	1.67	1.23
1.0	0.64	1.88	0.42
1.1	0.69	2.13	1.02
1.2	0.85	0.95	1.22
1.3	0.39	0.84	1.58
1.5	0.32	0.52	1.29
1.7	0.08	0.22	0.87
1.9	0.06	0.13	0.22
2.1	0.03	0.06	0.04

The differences in the $D - 1/\sigma_{so}^2$ plot for sets A and C are not statistically significant, and therefore we shall not attempt to interpret these minor differences. Further, even a laboratory experiment shows properties that depend on the rate of cooling and on initial conditions. In fact, ideally, an average over many quenched configurations of amorphous H₂O should be employed. However, the principal objective of this work is to demonstrate the existence of a size-dependent diffusivity maximum for solutes in water. (Unfortunately, the temperature at which the maximum exists is so low that water is frozen into an amorphous solid.) Figure 8 and Table 2, however, demonstrate, beyond any doubt, the existence of a size-dependent maximum for an uncharged solute in water. The idea of using three different quenched configurations or sets was to

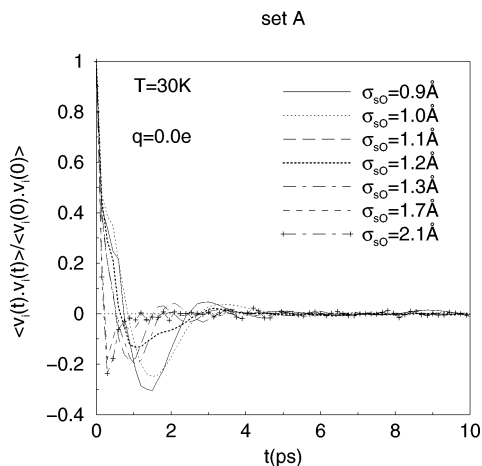


Figure 9. The vacf for different sizes of the uncharged solute in amorphous H₂O for set A at 30 K.

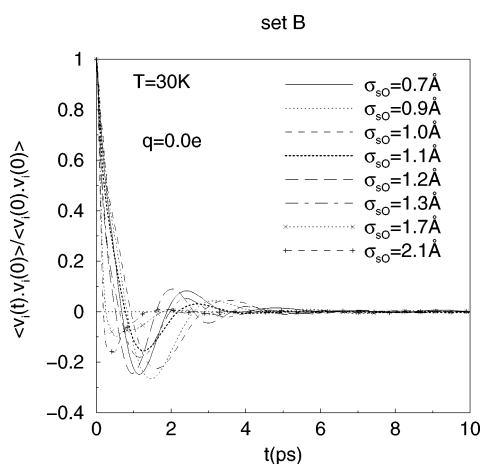


Figure 10. The vacf for uncharged solute in amorphous H₂O for set B at 30 K.

demonstrate that the maximum is, in fact, independent of the initial conditions.

For guests in zeolites, it is seen that, at higher temperatures, the maximum disappears, leading to monotonic change in D with σ_{SO} (or $1/\sigma_{\text{SO}}^2$).²⁰ The movement of water in the case of set B effectively reduces the void and the neck radius. This leads to a diffusion maximum at a rather high value of $1/\sigma_{\text{SO}}^2$ (low value of σ_{SO}). This is consistent with previous simulation results in which it was found that an increase in static disorder in the window diameters of zeolite in guest–zeolite systems leads to a shift of the diffusion maximum to a smaller value of σ_{SO} .⁹ In the present case, the increase in disorder is not static but dynamic. However, its effect on LE appears to be the same. We do not report the rdf and other properties for set C, as they are similar to those of set A.

The velocity autocorrelation functions (vacf's) for sets A and B are shown in Figures 9 and 10, respectively, for different sizes (σ_{SO}) of the solute. For values of $\sigma_{\text{SO}} = 0.9$ Å, near the diffusion minimum, the vacf shows a pronounced foray into the negative region. In contrast to this, for values of $\sigma_{\text{SO}} = 1.1$ Å, corresponding to the diffusion maximum, only a relatively shallow minima is seen in the vacf. Previous studies of guests in zeolites suggest that this behavior of the diffusion maximum and the minimum are respectively associated with the relatively flat and highly undulating potential energy landscape reported previously for these two cases.²⁰ It was found that, for a particle in the LR, the potential energy landscape is highly undulating, but, for a particle in the AR, the potential energy landscape is

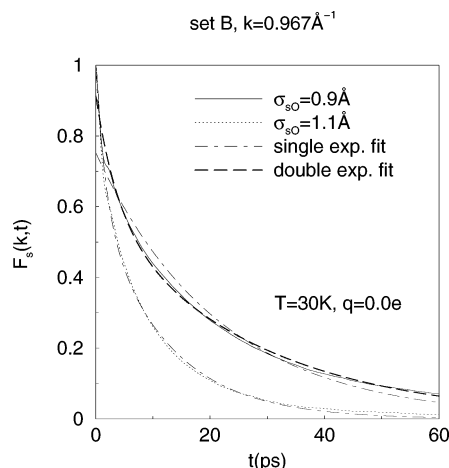


Figure 11. The decay of the intermediate scattering function, $F_s(k, t)$, for set B, for a particle from linear ($\sigma_{\text{SO}} = 0.9$ Å) and anomalous ($\sigma_{\text{SO}} = 0.9$ Å) regimes.

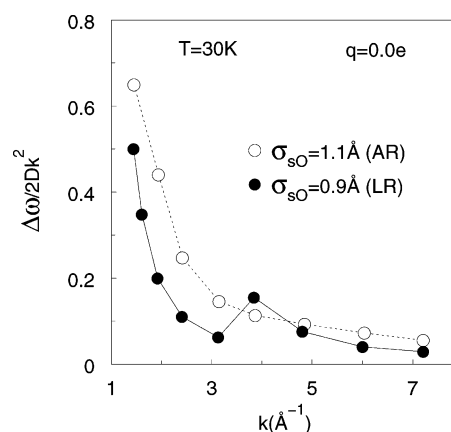


Figure 12. Variation of $\Delta\omega(k)/2Dk^2$ as a function of k for set B at 30 K. Note the oscillations for the particle from LR and the smooth decay with k for a particle from AR.

rather flat. A comparison with the vacf for a guest–zeolite system for the size corresponding to the diffusion maximum shows that the negative values of the vacf are more pronounced in the case of disordered water compared to those of highly ordered, crystalline zeolites.

3.3. k Dependence of Diffusion Properties. As discussed in the Introduction, the AR and the LR exhibit different behaviors.^{5,6,21} One such difference is the behavior of the intermediate scattering function $F_s(k, t)$ at small k corresponding to motion at large distances. Here we report results for set B only. Figure 11 shows the decay of $F_s(k, t)$ at $k = 0.967$ Å⁻¹ for $\sigma_{\text{SO}} = 0.9$ Å (solute from LR) and 1.1 Å (solute from AR) along with single- (e^{-t/τ_1}) and double-exponential ($e^{-t/\tau_1} + e^{-t/\tau_2}$) fits to $F_s(k, t)$ obtained from MD. A single-exponential function provides a good fit to $\sigma_{\text{SO}} = 1.1$ Å, but not to $\sigma_{\text{SO}} = 0.9$ Å. The value of τ_1 for a $\sigma_{\text{SO}} = 1.1$ Å particle is 9.26 ps, and τ_1 and τ_2 for the $\sigma_{\text{SO}} = 0.9$ Å particle are 4.78 and 28.01 ps, respectively.

We now investigate the dependence of the diffusion properties on wavenumber, k , for intermediate k values. In the hydrodynamic limit ($k \rightarrow 0$, $\omega \rightarrow 0$), the simple diffusion model is valid and the full width at half-maximum (fwhm), $\Delta\omega$, of the dynamic structure factor $S_s(k, \omega)$ is proportional to $2Dk^2$. Figure 12 shows the variation of $\Delta\omega(k)/2Dk^2$ as a function of k for set B (water and solute both mobile) at 30 K. For $\sigma_{\text{SO}} = 0.9$ Å, a minimum in the variation of $\Delta\omega(k)/2Dk^2$ is observed. In contrast, for a larger solute ($\sigma_{\text{SO}} = 1.1$ Å), we see a smooth decay of $\Delta\omega(k)/2Dk^2$.

Similar trends have been seen in the case of a binary liquid mixture of Lennard-Jones spheres (ref 7). The reasons for these surprising trends have been discussed therein. The results of earlier studies on diffusion in a single-component fluid, namely, liquid argon, by Nijboer and Rahman²² and Levesque and Verlet²³ as well as the discussion of Boon and Yip²⁴ are also useful. Here, we only briefly recollect the main arguments, and the interested reader can see the work on binary liquid mixtures in ref 7. The slow down or decrease (i.e., the minimum) in $\Delta\omega(k)/2Dk^2$ seen for 0.9 Å solute for intermediate k values arises from the difficulty encountered by the solute during its passage through or past the first shell of neighbors of solvent. No such barrier is encountered by the *larger* solute of 1.1 Å. This counterintuitive result arises from the fact that the opening in the first shell of solvent (through which the solute has to pass to get past the first shell) is comparable to the size of the 1.1 Å solute particle. When this is the case, according to the LE, the energy barrier encountered is lower for the *larger* solute if the size of the solute is comparable to the opening. This is the case for 1.1 Å solute. The 0.9 Å solute is smaller than the opening and therefore encounters a significant energy barrier. This is the molecular interpretation of the reason for the existence of a diffusivity maximum as well as the nonmonotonic decay of $\Delta\omega(k)/2Dk^2$. Similar results have also been observed for guest diffusivity in porous solids such as zeolite (as well as in dense liquid mixtures).^{5–7,10,21}

3.4. Comparison with Previous Studies. Previously, Rasaiah and co-workers reported room-temperature MD simulations of ions as well as uncharged solutes in water.²⁵ The species they studied were alkali and halide ions, charged as well as uncharged. They found no maximum in diffusivity or no minimum in friction for uncharged solutes as a function of the solute size. The friction was evaluated through the integration of a force–force autocorrelation function.

More recently, Chandra and co-workers²⁶ also reported diffusion coefficients of neutral or uncharged solutes in water and methanol. They carried out simulations at room temperature (298 K) and at a lower temperature (258 K) for solutes with radii between 0.7 and 2.5 Å. They found that the self-diffusivity decreased monotonically in this range in both water and methanol and at both temperatures. Further, they carried out a study of neutral solutes in a water–dimethyl sulfoxide (DMSO) mixture,²⁷ although here they did not investigate the size dependence of self-diffusivity.

Both of the above results, which were carried out at room temperature or close to room temperature, suggest that neutral species do not exhibit any size-dependent maximum in self-diffusivity. The present results obtained at 30 K suggest that such a maximum indeed exists at low temperatures. It is not difficult to reconcile these two, somewhat contradictory, results if we understand the nature of the diffusivity maximum and the characteristics of the LE.

Previous studies have shown that the LE is sensitive to temperature. The height of the diffusivity maximum or the magnitude of the change in self-diffusivity with solute or diffusant radius depends on the temperature.^{11,28} At low temperatures, the maximum in D in the $D - 1/\sigma_{\text{SO}}$ plot is very pronounced. As temperature increases, the maximum is less pronounced, as was shown for guests in zeolites. When the kinetic energy $k_{\text{B}}T$ is comparable to the intermolecular interaction energy, the anomalous maximum altogether disappears. As already discussed, the dispersion interaction is essential to observe LE.^{5,6} The greater the strength of the dispersion interaction, the greater the intensity or height of the diffusivity

maximum (although the magnitude of the diffusivity decreases with increase in dispersion interaction). These results explain why the room-temperature simulations of Koneshan et al.²⁵ and Chandra and co-workers²⁶ did not observe the diffusivity maximum: the ratio of $U_{\text{gh}}/k_{\text{B}}T$ is small in their studies. The typical interaction strength is around 0.6502 kJ/mol between the solute and O of H₂O, which is much smaller than the kinetic energy at room temperature. At 30 K, the kinetic energy is lower than U_{gh} . This leads to the existence of a maximum.

In addition, simulations with immobile water reported here suggest that the motion of water is *not essential* to the observation of the maximum. This situation is akin to the guest–zeolite system where the zeolite was immobile. This clearly points to the fact that the observed maximum in D is a consequence of LE where the interaction plays a predominant role. The question that naturally arises then is Why do the ion-in-polar solvents exhibit anomalous conductivity even at room temperature? This is because the presence of Coulombic or electrostatic interactions in these systems lead to considerable increase in the interaction strength, which leads to significant increase in $U_{\text{gh}}/k_{\text{B}}T$. This is responsible for the existence of a diffusivity maximum, even at room temperatures. Note that here $U_{\text{gh}} = U_{\text{disp}} + U_{\text{el}}$, where the total interaction strength consists of two parts: the dispersion term (ϵ_{disp}) and the electrostatic term (ϵ_{el}).

3.5. Existing Theories and the Maximum in D for Uncharged Solute. Now we consider the existing theories in an attempt to account for the maximum seen here in the self-diffusivity for the uncharged solute in water.

The solvent–berg model^{29–31} suggests that, for ions of small radii, the charge density (i.e., the density per unit volume) is high, which is responsible for the increased or strong polarization or electrostatic interaction between the ion and the molecules of the first shell of the solvent surrounding the ion. As a result, there is an increase in the kinetic diameter of the smaller ion, which results in a decrease in conductivity of that ion. However, in the absence of a charge on the solute, there is no reason for the solvent molecule to be so associated with the solute. Therefore, the solvent–berg model does not seem to account for the observed maximum in diffusivity as a function of the size of the uncharged solute seen here.

Continuum theories^{32–36} suggest that the maximum in conductivity arises from the interaction between the electric field associated with the ion and the polarization of the surrounding solvent molecules. In the absence of a charge on the solute, such interactions are altogether absent. Consequently, this leads to zero dielectric friction. The maximum in diffusivity arises from the different r (distance) dependence of the dielectric friction and friction due to viscous drag. Since, for an uncharged solute, there is no dielectric friction, the maximum in diffusivity cannot be accounted for by any of the continuum-based theories, such as, for example, the Hubbard and Onsager theory.³⁷

Microscopic theories^{3,4,38–41} attempt to explain the observed anomalous behavior in terms of the relaxation behavior, which takes into account the molecularity of the solute and the solvent. These may be able to offer a suitable explanation for the observed maximum in diffusivity when both the solvent and the solute are mobile. However, it is clear that simulations in which the water is immobile produce results that even these microscopic theories may find difficult to explain since there will be no relaxation associated with the solvent.

It appears that the mutual cancellation of forces that the LE suggests arising out of the symmetry around the diffusant or solute is, in fact, a generic explanation of the observed size-

dependent diffusivity maximum for the case of neutral or uncharged solute in water.

4. Conclusions

Our results here demonstrate that a size-dependent maximum exists for uncharged solutes in water, similar to the maximum seen (experimentally as well as theoretically and computationally) for ions in polar solvents. Previously, the maximum for ions in polar solvents had been explained in terms of theories such as the solvent–berg model or continuum or molecular theories. Here we consider each of these models or theories and whether they can account for the existence of the maximum for uncharged solute in water. In a forthcoming communication, we investigate the size dependence of self-diffusivity in binary liquid mixtures over a wide range of solute diameters and show that the Stokes–Einstein relationship breaks down for smaller solute diameters.⁴² Further, we shall also present in another communication the detailed results on the size-dependent conductivity maximum for ions in water along with a thorough analysis of MD results as well as experimental results, which suggest that LE indeed provides the right theoretical framework to understand the maximum.

LE suggests that the maximum occurs because of the symmetry around the solute at the bottleneck. Such a symmetry exists only for the size of the solute that is comparable to the neck diameter. This leads to a lowering of the force on the solute due to the solvent, which is responsible for the maximum. This can account for the maximum in the self-diffusivity of both uncharged and charged solutes or ions in polar solvents. This, in fact, also explains the observed maximum in guest–host systems as well as liquid mixtures.^{5,6,10} Such a unified general treatment is desirable to invoking different theories for different systems.

Acknowledgment. We wish to gratefully acknowledge financial support from the Department of Science and Technology, New Delhi. The authors thank the referees for their input, which resulted in considerable improvement in the presentation of this work.

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