

Size-Dependent Maximum in Ion Conductivity: The Levitation Effect Provides an Alternative Explanation

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We propose an alternative explanation of the size-dependent maximum in ion mobility in water in terms of the levitation effect, which accounts for the observed size-dependent maximum in the mobility of guest diffusion in porous media. In this explanation, the size at which the maximum occurs is related to the structure of the void space of the water; at the mobility maximum, the diffusant passes smoothly through necks connecting voids, and its potential energy shows minimum fluctuations. Molecular dynamics simulations of charged spheres of varying sizes are used to support this hypothesis. As in the levitation effect, the friction coefficient, the potential energy fluctuations, and the activation energy are found to be minima for particles with maximum self diffusivities similar to the guest diffusion in zeolites. Wavelength-dependent self diffusivities indicate a monotonic and oscillatory dependence, respectively, on wavenumber k for anomalous (AR) and linear regimes (LR). These are associated with single and biexponential decay of the incoherent intermediate scattering function.

1. Introduction

Ionic mobility in electrolyte solutions has been of considerable interest for more than 100 years.^{1–3} Walden's rule combined with Stokes' law states that the product of Λ_0 , the ionic conductivity at infinite dilution, and the solvent viscosity, η_0 , is inversely proportional to the ion radius, r_{ion} ($\Lambda_0\eta_0 = \text{constant}/r_{\text{ion}}$). However, ions in polar solvents do not obey this relation because the product, $\Lambda_0\eta_0$, is found to increase to a maximum and then decrease as the ion radius increases. Such nonmonotonic dependence has been observed for positively charged (e.g., Li^+ , Na^+ , etc.) as well as negatively charged ions (e.g., F^- , Cl^- , etc.) and in *all polar solvents*, such as methanol, ethanol, acetonitrile, and so forth, suggesting that this nonmonotonic dependence is *universal*.

Several theories have been put forward to explain this unexpected behavior.^{4,5} One of the early theories is the solventberg model. According to this model, the deviation arises from an increase in the effective size of small ions due to a strongly bound solvent shell. Because the solvent shell is less strongly bound for larger ions, the effective size may not be much different from that of the bare ion.^{2,3,6} An alternative explanation is in terms of dielectric friction. The central idea here is that the ionic motion alters the equilibrium polarization of the solvent, and the friction on the ion is due to the decay of polarization mode.^{7–10} In this class of model, the total friction $\zeta_{\text{total}} = \zeta_{\text{bare}} + \zeta_{\text{DF}}$, where ζ_{bare} is the friction arising from Stokes' law due to shear viscosity (η_0) of the solvent and ζ_{DF} is the dielectric friction from the solvent polarization.⁵ Using a continuum theory, Zwanzig was successful in predicting a size-

dependent maximum in ionic conductivity. However, the actual values of Λ_0 that were predicted were significantly lower than the experimental values. A microscopic theory was proposed subsequently by Wolynes and co-workers.¹¹ This overcame some of the limitations of the continuum theories, and the results that were obtained showed better agreement with the experimental variation of Λ_0 with r_{ion} . More recent work by Bagchi and co-workers^{12,13} has generalized this approach to include self motion of the ion as well as the intermolecular orientational correlations of the solvent. Rasaiah, Lynden-Bell, and co-workers^{14,15} carried out computer simulation (MD) studies of alkali ions and halide ions in water. The results they obtained were in good agreement with the experimental results and suggest that the solventberg model of Chen and Adelman is sufficient, although a contribution from dielectric friction cannot be ruled out for smaller ions. More recently, Chandra and co-workers have carried out simulations in which they attempt to find an explanation in terms of changes in hydrogen bonding with variation in the size of the ion.¹⁶

A very similar phenomenon of a size-dependent maximum in particle mobility is found in the diffusion of fluids in zeolites and other porous solids. It occurs when the particle diameter is comparable to that of the void.¹⁷ This unexpected behavior, known as the levitation effect, has two distinct regimes (see Figure 1a). At small guest sizes, the diffusivity $D \propto 1/\sigma_{\text{gg}}^2$. This is termed the linear regime. As the particle diameter approaches that of the void (or neck, the narrowest part of the void in such zeolites in which the void diameter is not uniform throughout), the particle becomes more mobile (the anomalous regime). Finally, the mobility drops rapidly as the particles become too large to traverse the necks. In the anomalous regime (the larger open circle in Figure 1b), the force on a guest atom due to the host atoms from one side of the cage is canceled by the forces that are exerted by the host atoms placed diagonally opposite.¹⁷

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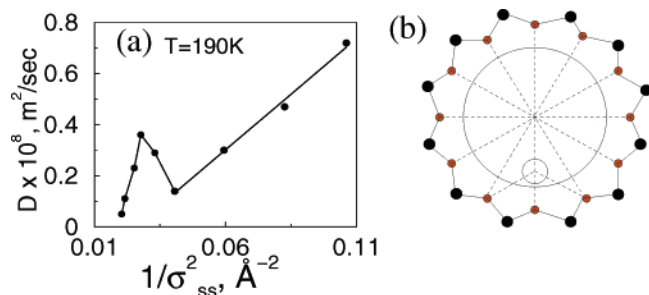


Figure 1. (a) Plot of self diffusivity vs $1/\sigma_{ss}^2$ in NaY. (b) The bottleneck for diffusion is the window in zeolite NaY,¹⁷ shown with Si and O atoms as filled circles. Guest atoms are shown as open circles. For the larger guest with σ_{gg} comparable to that of the 12 ring, there is net cancellation of forces, whereas this does not happen for the smaller guest.

Such a cancellation does not occur in the case of the smaller guest from the LR (smaller open circle, Figure 1b). This levitation effect has been found in all types of porous solids, such as zeolites, aluminophosphates, and so forth, irrespective of the geometrical and topological details as well as the chemical nature of the pore network.¹⁸

The aim of this work is to see how far the ideas of the levitation effect can be extended to the motion of small spheres in liquid water. In earlier work, we have shown that the motion of uncharged solutes diffusing within solvents of larger-sized particles exhibit a diffusive maximum at a particular size.^{28,32} In this paper, we extend the work to the motion of uncharged and charged spheres of varying sizes in liquid water. Spheres of different charges have been investigated, but most of the results presented here pertain to spheres with charges of $\pm 0.3e$. For this choice of charge, two regimes are accessible, namely, a small size regime with diffusion decreasing with size (the linear regime) leading to a diffusion minimum, followed by the anomalous regime in which the diffusion rate increases with ion size to a maximum (the levitation effect), and finally a normal regime in which the diffusion rate decreases with ion size, eventually following Stokes' law.

2. Methods

2.1. Intermolecular Potentials. The SPC/E potential has been used to model water.¹⁹ In this model, the intermolecular interaction between two water molecules is given by

$$\Phi_{ww} = 4\epsilon_{oo}[(\sigma_{oo}/r_{oo})^{12} - (\sigma_{oo}/r_{oo})^6] + \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$

Within this model, the charges are $q_H = +0.4238 = -q_O/2$, $\sigma_{oo} = 3.169 \text{ \AA}$ and $\epsilon_{oo} = 0.6502 \text{ kJ/mol}$.

The pair potential between water (w) and ion or solute (s) has the form

$$\Phi_{sw} = 4\epsilon_{so}[(\sigma_{so}/r_{so})^{12} - (\sigma_{so}/r_{so})^6] + \sum_{j \neq w} \frac{q_s q_j}{r_{ij}}$$

where subscripts s and i refer to the ion and j to either H or O site on water. The short-range interaction of the ion with water is limited to the oxygen: ϵ_{so} has been taken as 1.5648 kJ/mol in all of the calculations, whereas σ_{so} has been varied from 0.9 to 3.5 \AA . q is the charge and ϵ and σ refer to the Lennard-Jones parameters. The DLPOLY package²⁰ was used in these calculations. Calculations were carried out for $q_i = \pm 0.3|e|$. We have also carried out simulations with higher and lower charges than

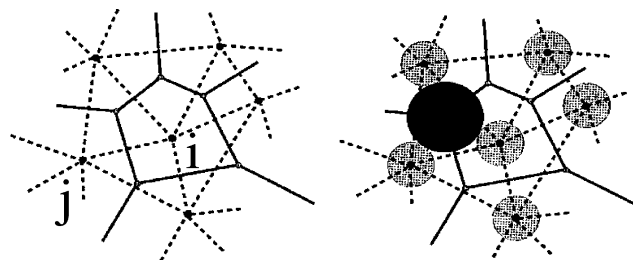


Figure 2. Two-dimensional illustration of the Voronoi–Delaunay dual construction. The central atom (i) is surrounded by atoms (j). (Reprinted with permission from ref 21, Copyright 1997, American Physical Society.)

$0.3|e|$ for which the results are presented here. The results are qualitatively unchanged for these charges.

The ion–ion interactions were accounted for again in terms of the simple (6–12) Lennard-Jones term and the Coulomb term. The short-range interactions are $\sigma_{ss} = 1.5 \text{ \AA}$ and $\epsilon_{ss} = 0.2608 \text{ kJ/mol}$. The value of σ_{ss} was taken to be 1.5 \AA even though σ_{so} was varied over a range.

2.2. Computational Details. Calculations have been carried out in the microcanonical ensemble. The details of the calculation for the model ion are given here. The integration time step is 0.4 fs . The simulation cell has an edge length of 26.0 \AA . A cut off radius of 13.0 \AA was employed. Each simulation consists of 466 water molecules and 64 ions. Of the 64 ions, 32 are positively charged, and the remaining 32 are negatively charged. Thus, the system as a whole is neutral. The charge on the ion was $\pm 0.3e$. Note that the concentration of the ions is not too low but corresponds to a reasonably high molarity. The mass of the uncharged and charged sphere was 18 amu . Calculations have been carried out at 300 K . Properties were calculated from configurations stored at an interval of 30 fs during 400 ps after equilibration has been performed over 150 ps . Velocities are scaled during equilibration to obtain the desired temperature.

To characterize the structure of the “pore space” or “void space” in the water medium, we use the Voronoi construction, which has been employed in similar studies of liquids.²¹ This provides valuable insights into the distribution of voids within water. In any specified configuration of equi-sized particles, the Voronoi polyhedron of a given particle (i) is the set (sub volume) of all points that are closer to i than to any other particle. The vertexes and edges of the Voronoi polyhedra are, by construction, equally far from the closest surrounding particles. A convenient description of the empty or void space can be given in terms of the network formed by the edges of the Voronoi polyhedra. One can visualize the void space as made of “pores”, each of a radius given by the distance of a Voronoi vertex to the surrounding particles minus the particle radius, connected by “channels” or necks of a 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. This has been obtained by assuming water is a sphere with a diameter equal to the LJ parameter, σ_{oo} . This is an approximation that does not affect the results of the MD because the void distribution is used just to obtain an estimate of the size of the guest ion to be introduced. Diffusants of a given radius can find an interconnected path between the voids if the intervening neck sizes are larger than the diffusant radius. However, the motion of water molecules ensures that the void network is restructured dynamically. Thus, even an ion for which there is no interconnected void path at a given time step manages

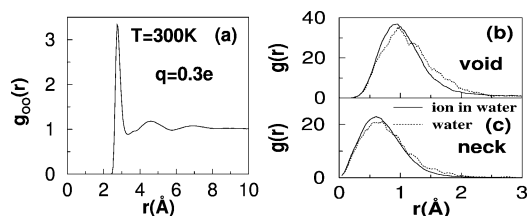


Figure 3. (a) Water–water (OO) radial distribution function for water containing ions of size $\sigma_{SO} = 1.5$ Å. (b) Void size and (c) neck size distribution for pure water and a water solution containing ions of size $\sigma_{SO} = 1.5$ Å. The temperature is 300 K.

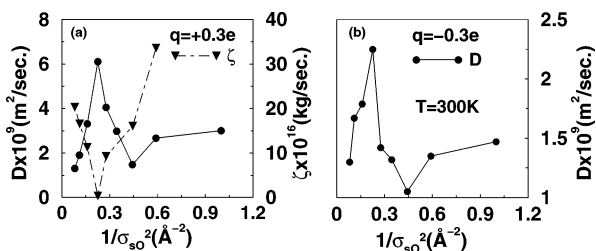


Figure 4. Self diffusivity (D) against $1/\sigma_{SO}^2$ for (a) $q = 0.3e$ and (b) $q = -0.3e$.

to diffuse over a period of time. Voronoi and Delaunay tessellations have been carried out using the algorithm by Tanemura et al.,²² as outlined in Sastry et al.²¹ For each run, the void and neck sizes are calculated for 400 configurations, using the positions of the host particles.

3. Results and Discussion

The host radial distribution function (rdf), $g_{OO}(r)$, has been shown in Figure 3a. The distribution of the void radius (r) for water has been computed from Voronoi analysis and is shown in Figure 3b. Distribution of the neck radius is shown in Figure 3c. Note that the neck radius extends to 2 Å. This and the fact that the void network is dynamically restructuring ensures that even large ions can diffuse. These observations are shown for both pure water and for the solution containing ions. The effect of ions on the water structure can be seen to be small.

The self diffusivities of the ions have been computed from the asymptotic slope of the mean-square displacement. They are plotted in Figure 4a and b against $1/\sigma_{SO}^2$. For sufficiently small values of σ_{SO} , D decreases with an increase in σ_{SO} , as expected on the basis of the kinetic theory. The lowest diffusivity is seen for $\sigma_{SO} = 1.5$ Å. For ions of sizes larger than this size, D begins to increase with size, reaching a maximum for $\sigma_{SO} = 2.1$ Å. Beyond 2.1 Å, D begins to decrease with increase in σ_{SO} . Thus, for larger values of σ_{SO} , a maximum is seen for a particular size of the ion.

The diffusivity of water is 2.6×10^{-9} m²/s as compared to the guest diffusivity of around 6.1×10^{-9} m²/s. The host diffusivity is therefore only about 2.34 times slower than the guest.

In previous studies by Rasaiah, Lynden Bell, and co-workers,¹⁴ the size of the ion was varied along with several other parameters. The results here have been obtained by varying the size of the ion alone. The results suggest that the conductivity maximum has its origin in the size of the ion. If the size of the ion is responsible for the maximum in diffusivity, then such a maximum in diffusivity should also be observed, even for an uncharged solute. We have carried out simulations on uncharged solutes of varying sizes in water. A plot of the self diffusivity (D) against $1/\sigma_{SO}^2$ is shown in Figure 5. The diffusivity maximum exists for the uncharged solute as well.

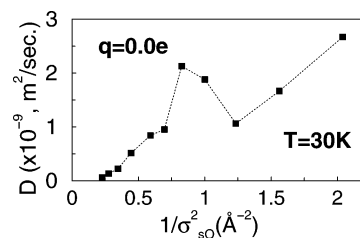


Figure 5. Self diffusivity (D) against $1/\sigma_{SO}^2$ for the uncharged solute. Note the low temperature of 30 K at which these simulations were performed. This corresponds to frozen water. In the absence of the dielectric friction term (which is the case for uncharged solute), the maximum in self diffusivity exists only at rather low temperatures.

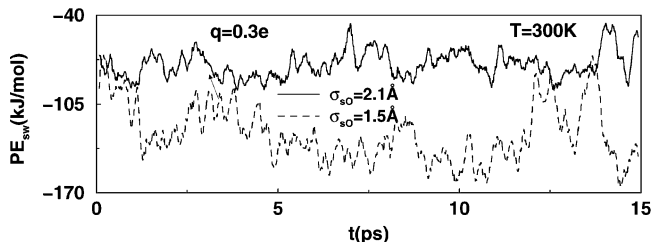


Figure 6. Time variation of the interaction energy between the ion and the water for ions with diameters of 2.1 (maximum mobility) and 1.5 Å (minimum mobility).

We may note some important differences in the two cases. In the case of the uncharged solute, the maximum in diffusivity is just twice the value of the diffusivity at the minimum that occurs at the interface between the linear and anomalous regimes. For the case of the ion, the diffusivity at the maximum is three times the value at the minimum. Furthermore, for an uncharged solute, the diffusivity maximum is seen at 30 K, and the maximum disappears at higher temperatures. Previous studies in zeolite confirm that with an increase in temperature the maximum in diffusivity decreases, eventually vanishing at a sufficiently high temperature.²³ For the ion, such a maximum exists even at 300 K, suggesting a more pronounced maximum at lower temperatures.²³ These results suggest that dielectric friction has an important role in the size-dependent maximum of self diffusivity or conductivity. This is consistent with the results of the continuum theories, which predict the existence of a size-dependent maximum based on polarization interactions.^{7–10,24} Finally, the size σ_{SO} at which the maximum is seen is different for a charged and uncharged solute. This is due to the presence of strong electrostatic interactions in the former.

An important aspect of the levitation effect is the rather flat potential energy landscape explored by a particle near the mobility maximum. In contrast, large fluctuations in the potential energy are found for a particle in the linear regime. In Figure 6, we show the time-dependent potential energy, which is the interaction energy of an ion with the water molecules. This is defined as

$$U_{sw} = \sum_w^{N_w} \Phi_{sw} \quad (1)$$

The variation of U_{sw} is shown over a few picoseconds for ion size with maximum and minimum self diffusivities. The minimum occurs at $\sigma_{SO} = 1.5$ Å, and the maximum occurs at $\sigma_{SO} = 2.1$ Å for $q = +0.3|e|$. These results confirm that the energy fluctuations are much smaller for the particle near the diffusivity maximum. This provides further support that the

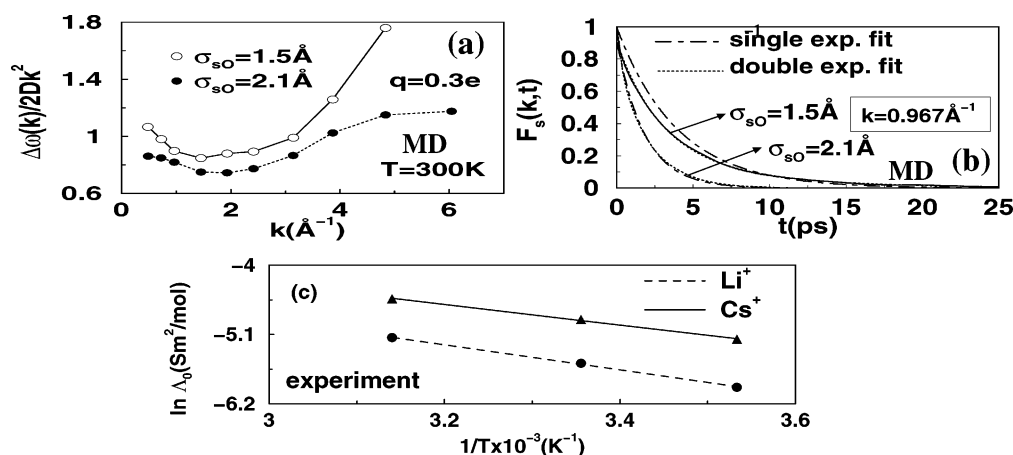


Figure 7. (a) Intermediate scattering function, $F_s(k, t)$, for an ion from LR ($\sigma_{s0} = 1.5$ Å) and AR ($\sigma_{s0} = 2.1$ Å) are shown along with single (e^{-t/τ_1}) and biexponential ($e^{-t/\tau_1} + e^{-t/\tau_2}$) fit. (b) $\Delta\omega(k)/2Dk^2$ as a function of k . (c) Arrhenius plot of Λ_0 (experimental data has been taken from ref 31).

present maximum in self diffusivity can be attributed to the levitation effect.

We now investigate the wavenumber, k , and the dependence of the diffusion properties 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 self part of the dynamic structure factor, $S(k, \omega)$, $S_s(k, \omega)$, is proportional to $2Dk^2$. At large k values, $\Delta\omega(k)$ varies as $1/k$. The motion in the intermediate range of k values is strongly influenced by the intermolecular potential. It is therefore interesting to see the behavior of $\Delta\omega(k)$ in the intermediate k region for the linear and anomalous regimes. Furthermore, previous work has shown that for systems interacting with a purely repulsive term (with no attractive dispersion term), there is no levitation effect, and diffusivity maximum is not seen.¹⁷ Note that the full width at half-maximum of the self part of $S(k, \omega)$ provides an estimate of the magnitude of the self diffusivity, $\Delta\omega(k) \propto D(k)$, where $D(k)$ is wavevector-dependent self diffusivity. The dynamic structure factor, $S_s(k, \omega)$ was obtained from the Fourier transform of the intermediate scattering function $F_s(k, t)$ for several sizes of the guest. $F_s(k, t)$ was computed by taking a powder average²⁵ to enable a direct comparison with the experiment.

Figure 7a shows the dependence of the ratio of the full width at half-maximum, $\Delta\omega(k)$, to $2Dk^2$ on wavenumber k , for $\sigma_{s0} = 1.5$ Å and $\sigma_{s0} = 2.1$ Å. To understand the behavior of $\Delta\omega(k)/2Dk^2$, it is instructive to study the pioneering work of Nijboer and Rahman.²⁶ They have calculated $\Delta\omega(k)/2Dk^2$ for liquid argon at $\rho^* = 0.8442$ and $T^* = 0.722$. The fluid is at relatively high density and low temperature, where an argon atom is likely to diffuse only slowly. They found that $\Delta\omega(k)/2Dk^2$ exhibits a pronounced minimum and maximum. The minimum in $\Delta\omega(k)/2Dk^2$ was seen at a value of k at which the structure factor $S(k)$ showed maximum correlations. Levesque and Verlet²⁷ have reported $\Delta\omega(k)/2Dk^2$ for a argon liquid at low density and high temperature ($\rho^* = 0.65$ and $T^* = 1.872$) and found that $\Delta\omega(k)/2Dk^2$ decreased monotonically with an increase in k . From Figure 7a, we see that the minimum for a smaller-sized ion ($\sigma_{s0} = 1.5$ Å) is pronounced, suggesting a noticeable decrease in self diffusivity at intermediate k . This implies that the ion slows down perceptibly at intermediate k . The larger-sized guest ($\sigma_{s0} = 2.1$ Å) shows only a shallow minimum in $\Delta\omega(k)/2Dk^2$ as a function of k . This indicates that despite its larger size it does not slow significantly at intermediate k . Recent work²⁸ on the diffusion of guest molecules of varying sizes in zeolites suggests that this slow down may be due to an energetic barrier encountered by the guest at the region where there is narrowing

of the void dimension, commonly referred to as the neck. Thus, the larger-sized guest may be encountering a lower barrier than the smaller-sized guest. This is in excellent agreement with the previous results on the diffusion of guests of varying sizes in zeolites.^{17,29} This is also consistent with the potential energy landscape seen in Figure 6, which shows smaller fluctuations for the larger-sized guest.

The negative part of the velocity correlation functions is due to the cage effect, showing that the charged (as well as the uncharged) particles encounter a barrier in getting past the shell of the water molecules surrounding it. Previous studies on zeolites as well as dense fluids^{17,30} have shown that a particle from the linear regime encounters a free energy barrier at the bottleneck, whereas in the anomalous regime, either such a barrier is absent or the barrier height is lower. This interpretation appears to hold well even for an ion in water.

The pronounced minimum and maximum in $\Delta\omega(k)/2Dk^2$ (see Figure 7a) at intermediate k for the particle in the linear regime is likely to lead two well-separated time scales for motion. This corresponds to fast decay associated with motion within the "cage" and slow decay for motion past the cage. The intermediate scattering function, $F_s(k, t)$ for $\sigma_{s0} = 1.5$ and 2.1 Å particles are shown in Figure 7b along with a fit to a single ($e^{-t/\tau}$) and double exponential decay for $k = 0.57$ Å⁻¹. A single exponential decay provides a good fit to the $F_s(k, t)$ for the 2.1 Å particle but not to 1.5 Å, which is consistent with the behavior of $\Delta\omega(k)/2Dk^2$.

We have computed the activation energy (E_a) for charged particles with minimum (1.5 Å) and maximum (2.1 Å) diffusivity from Arrhenius plots. The values of E_a for 1.5 - and 2.1 -Å sizes for positively charged ions are 5.32 and 3.17 kJ/mol, respectively, and for the negatively charged ion, the E_a values are 5.53 and 3.57 kJ/mol. We have plotted the logarithm of Λ_0 of Li^+ and Cs^+ against the reciprocal temperature (Figure 7c). The data are of Kay and Evans³¹ and pertain to aqueous solution. The activation energies (E_a) of Li^+ and Cs^+ are 16.61 and 13.56 kJ/mol, respectively, suggesting a considerably lower activation energy near the conductivity maximum. This agreement of the experimental activation energy supports the interpretation that the diffusivity or conductivity maximum is due to the levitation effect.

4. Conclusions

In this paper, we have drawn analogies between the diffusion of charged particles in water and the diffusion of guest species in porous solids such as zeolites. In both cases, there is a

maximum diffusion rate as a function of size. We suggest that the levitation effect, which has been studied previously only in porous solids, also appears to play an important role in the diffusion of charged (and uncharged) species in water. The results of uncharged solutes also exhibit a similar maximum. This supports the view that the maximum in conductivity of an ion of a particular size might have its origin in the levitation effect. Recently, we have shown that a maximum in the diffusion coefficient is seen even in a simple Lennard-Jones liquid as well.^{28,32}

Previous work has shown that height of the maximum in self diffusivity is dependent on the strength of the interaction between the diffusant and the surrounding medium (e.g., zeolites). In fact, in the absence of the dispersion interaction, the maximum vanishes¹⁷ completely. The Lennard-Jones interaction potential between the ion and water that we have chosen in this study is significantly higher than that for real ions such as bromide or fluoride ions. We did this deliberately to obtain a reasonable maximum for the uncharged case. The maximum in the diffusivity of uncharged atoms exists only at low temperatures, and this is because the interactions of such an uncharged solute with the solvent are relatively weak. For the case of the ion with a charge of $0.3e$, the additional electrostatic interactions increase the relative interaction of the ion with the water, leading to existence of a maximum in self diffusivity that is pronounced and that persists up to room temperature and beyond. However, the relatively large ϵ , the Lennard-Jones interaction parameter between the ion and the water, make the molecular dynamics integration unstable if we place larger charges on the ion. This is the reason that we do not use higher charges in this work. However, larger charges can be chosen for the ion if the magnitude of the ϵ is reduced. Realistic models¹⁴ for ions such as Na^+ , K^+ , Cl^- , and Br^- do indeed have smaller values of ϵ .

The analogies between the diffusion of guests in zeolites and the charges in solution as also uncharged solute in solvent are several. We find the existence of both a minimum and a maximum diffusivity of charged spheres as a function of size; the decrease in oscillations in both the velocity and force autocorrelation functions near the diffusion maximum. Different dependencies of the width of the self part of the dynamic structure factor on k and the single and biexponential decay of the self part of the intermediate structure factor are seen again for guest diffusion in zeolites as well as in ions in water. The decrease in the activation energy for the diffusion of a particle corresponding to the diffusion maximum are seen again both in porous and dense media.

We also carried out simulations with ions of differing charges ($q_s = \pm 0.1$ and $\pm 0.5|e|$). These results are the same (qualitatively) as those presented here. The presence of the ions does affect the void distribution in the solvent to a certain extent. Figure 3b shows that in the solutions studied in this work the changes are small. However, we found that the void distribution in the vicinity of the ion is different from those found elsewhere. It is also likely that the ions preferentially occupy voids of certain sizes.

However, there are some differences that are noteworthy. In the case of porous solids, the limited flexibility of the solid lattice, such as zeolite, leads to a sharp decrease in self diffusivity with an increase in size beyond the diffusion

maximum. In contrast, in water the decrease in self diffusivity is gradual for two reasons. First, a liquid provides a medium that is relatively more flexible than that provided by a solid, enabling even larger ions to diffuse through. Second, the rate at which liquid restructures in time allows a solute to diffuse even if the voids in the liquid are smaller than the solute radius. In fact, under this condition in which the solute radius is larger than the void radius, Stokes' law is valid.

This picture differs from the standard pictures of the solventberg model and the dielectric friction model. In fact, all three models have a role to play under different conditions. Ions such as Li^+ and Ca^{2+} with high surface charge densities probably carry a shell of solvation water with them as they move. But these are special cases. Our calculations with different charges on the ion suggest that dielectric friction plays an important role. But we consider that the levitation effect, experienced by diffusing ions that are of similar sizes to the voids in water, is the principal explanation of the diffusion maximum as a function of size.

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