Anomalous Ion Diffusion in Dense Dipolar Liquids

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A self-consistent microscopic theory of the mobility of small ions in ultrafast dipolar liquids (like water and acetonitrile) is presented. The theory takes into account the self-motion of the ion and also the bimodal dynamics of the liquid. It is in excellent agreement with the experimental results. In addition, the theory explains the anomalous increase in diffusion for large ions in water for the first time.

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The mobility of small rigid ions in dense dipolar liquids exhibits several anomalous properties that have captured the attention of scientists for a long time [1–4]. Perhaps the most dramatic of these is the total breakdown of the Stokes-Einstein relation for small cations (such as Na^+ and Li^+) [3,4] in highly polar liquids (like water and acetonitrile). Born [2] realized quite early that this breakdown is due to an additional dissipative mechanism that originates from the coupling between the ionic field of the solute and the solvent polarization fluctuations. He coined the term "dielectric friction" to describe this effect. Another anomalous observation is that there is a significant enhancement of the mobility of large ions (such as Rb^+, Cs^+) compared to ions of only slightly smaller size (such as K^+). However, the attempts to describe the dielectric friction, by using the continuum model based calculations [3,4], were unsuccessful as they overestimate the dielectric friction even by more than an order of magnitude. The limitations of a continuum model description can be overcome only by a microscopic formulation of this problem. Such an approach was pioneered by Wolynes and co-workers [1,5]; however, the earlier microscopic theories [5,6] were not successful in explaining the experimental results. Even the computer simulation studies [7] have failed to resolve many of the outstanding issues in this field. It is therefore of great importance to develop a detailed understanding of the mobilities of small ions in dipolar liquids.

What now makes the study of ionic mobility in dipolar liquids an even more interesting problem is the recent discovery that the polarization relaxation in many common dipolar liquids is strongly bimodal [8–11] with an initial *ultrafast Gaussian component* (having a time constant of about 50–100 fs) followed by a slow, exponential-like decay (with a time constant of about 1 ps). The discovery of this bimodal dynamics immediately raises the following question: What can be the role of this ultrafast solvent response in determining the diffusion of ions in these liquids? In particular, one wonders whether the observed anomalous behavior, mentioned above, could be attributed to the bimodal dynamics of the solvent.

In this Letter we present a microscopic calculation of the ionic mobility in the ultrafast dipolar liquids. There are several novel features about this calculation. The effects of bimodal solvent dynamics on ionic mobility have been incorporated for the first time. Second, the effect of the ion's own motion has been included via a self-consistent calculation. Third, the details of ion-solvent static correlations have been taken into account. The results of this calculation are in almost complete agreement with the long known experimental results. We find that both the ultrafast dynamics of the solvent and the self-motion of the solute are critical in determining the mobility of the latter. The present theoretical formulation also provides a physical explanation of this phenomenon.

The microscopic calculation presented here is based on a simple physical picture. Consider a tagged, singly charged ion in a dipolar liquid. For spherical solute ions, the interaction between the ion and the dipolar liquid molecules can be separated into two parts [1–6]. The first part originates from a short-range, spherically symmetric potential that is primarily repulsive. This gives rise to a friction that can be described (with certain limitations) by the Stokes law. We shall refer to this as the bare friction, ζ_0, and this is estimated by using the expression $\zeta_0 = 4\pi\eta r_{\text{ion}}$, where r_{ion} is the radius of the ion and η is zero frequency shear viscosity of the liquid. The second part is due to the long-range ion-dipole interaction and is termed the dielectric friction, ζ_{DF}; this is dominated by the long wavelength solvent polarization fluctuations. Here, it is particularly important to note that these long wavelength polarization fluctuations are the ones primarily responsible [10,11] for the ultrafast Gaussian solvation dynamics observed in experiments. As the size of the ion decreases, ζ_0 decreases, but ζ_{DF} increases rapidly. The diffusion coefficient of the ion is given by $D = k_BT/\zeta$, where $\zeta = \zeta_0 + \zeta_{\text{DF}}$ and k_BT is the Boltzmann constant times the absolute temperature. It is, therefore, the dielectric friction part that is responsible for the observed anomalous ion mobilities in the dipolar solvents.

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The dielectric friction is determined by the ion-dipole force-force time correlation function via the Kirkwood formula [12]. The force density on the tagged ion is given by [6,13,14]

$$\mathbf{F}(\mathbf{r},t) = k_B T n_{\text{ion}}(\mathbf{r},t)\nabla \times \int d\mathbf{r}'\, d\mathbf{\Omega}'\, c_{\text{id}}(\mathbf{r},\mathbf{r}',\mathbf{\Omega}')\,\delta\rho(\mathbf{r}',\mathbf{\Omega}',t), \quad (1)$$

where $n_{\text{ion}}(\mathbf{r},t)$ is the number density of the tagged ion, $\delta\rho(\mathbf{r},\Omega,t)$ is the fluctuation in the position ($\mathbf{r}$), orientation (Ω), and time (t) dependent number density of the dipolar solvent, and $c_{\text{id}}(\mathbf{r},\mathbf{r}',\Omega)$ is the ion-dipole direct pair correlation function (DCF). ∇ is the spatial gradient operator. Next, the density and the direct correlation function are expanded in the spherical harmonics. We then use the standard Gaussian decoupling approximation to obtain the following microscopic expression for the dielectric friction

$$\zeta_{\text{DF}}(z) = \frac{2k_B T\rho_0}{3(2\pi)^2}\int_0^\infty dt\, e^{-zt} \times \int_0^\infty dk\, k^4 |c_{\text{id}}^{10}(k)|^2 S_{\text{ion}}(k,t)\, S_{\text{solvent}}^{10}(k,t)\,, \quad (2)$$

where $c_{\text{id}}^{10}(k)$ and $S_{\text{solvent}}^{10}(k,t)$ are the longitudinal components (that is, projection along the z axis in the k space) of the ion-dipole DCF and the *orientational* dynamic structure of the pure solvent, respectively. ρ_0 is the average number density of the solvent. $S_{\text{ion}}(k,t)$ denotes the self-dynamic structure factor of the ion.

Equation (2) is a mode-coupling, nonlinear expression that involves $\zeta_{\text{DF}}(z)$ on both sides, and it has to be solved self-consistently. This kind of approach is well known in the existing literature of the mode-coupling theory [13–15]. To obtain ζ_{DF} from Eq. (2), we need to specify both $S_{\text{solvent}}^{10}(k,t)$ and $S_{\text{ion}}(k,t)$. The latter is assumed to be given by

$$S_{\text{ion}}(k,t) = \exp[-D_T^{\text{ion}} k^2 t], \quad (3)$$

where the diffusion coefficient of the ion, D_T^{ion}, itself it determined by the total friction ζ. The orientational dynamic structure factor is given by

$$S_{\text{solvent}}^{10}(k,z) = \frac{S_{\text{solvent}}(k)}{z + \Sigma(k,z)}, \quad (4)$$

where $\Sigma(k,z)$ is the generalized rate of orientational density relaxation of the solvent and can be evaluated using the following expression [10,11]

$$\Sigma(k,z) = \left[1 - \frac{\rho_0}{4\pi}c(110;k)\right] \times \left\{\frac{2k_B T}{I[z + \Gamma_R(k,z)]} + \frac{k^2 k_B T}{m\sigma^2[z + \Gamma_T(k,z)]}\right\}, \quad (5)$$

where m, σ, and I characterize the mass, the diameter, and the average moment of inertia of each solvent molecule, respectively. $c(110;k)$ is the (110) component of the two particle direct correlation function of the solvent in the wave-vector ($\mathbf{k}$) space. $\Gamma_R(k,z)$ and $\Gamma_T(k,z)$ are the rotational and the translational dissipative kernels, respectively, of the solvent. $\Gamma_R(k,z)$ can be obtained directly from experiments such as dielectric relaxation, far-infrared (FIR) line shape, and Kerr relaxation measurement of the neat solvent by approximating $\Gamma_R(k,z)$ by its $k = 0$ limiting value. For example, $\Gamma_R(k,z)$ may be related to frequency dependent dielectric function, $\epsilon(z)$, as follows [10]:

$$\frac{2k_B T}{I[z + \Gamma_R(k=0,z)]} = \frac{(\epsilon_0 - 1)}{3Yn^2}\,\frac{z[\epsilon(z) - n^2]}{\epsilon_0 - (z)}, \quad (6)$$

where $3Y$ is the polarity parameter of the solvent with dipole moment μ and is given as $3Y = (4\pi/3)\beta\mu^2\rho_0$. $\beta = (k_B T)^{-1}$. ϵ_0 and n^2 are static and optical dielectric constants of the solvent, respectively. In the present calculations, $\Gamma_R(k,z)$ for water has been obtained using the above relation in the following way. The frequency dependent dielectric function $\epsilon(z)$ in the low frequency regime is described by a Debye relaxation with a time constant τ_D equal to 9.3 ps, while at high frequency, $\epsilon(z)$ derives major contributions from the librational and intermolecular vibrational motions of the hydrogen bonded network. These high frequency motions appear as three peaks around 700, 200, and 50 cm^{-1} as found in FIR line-shape studies. Similarly, $\Gamma_R(k,z)$ in acetonitrile was obtained from the known experimental results of the Kerr relaxation of this liquid [11]. $\Gamma_T(k,z)$ in each case has been obtained using the known value of the respective translational diffusion coefficient, D_T. For water, additional contributions from the intermolecular vibrations have also been taken into account [10].

The static ion-dipole direct correlation function $c_{\text{id}}^{10}(k)$ is obtained using the mean spherical approximation (MSA) given by Chan, Mitchel, and Ninham [16] in the limit of zero ionic concentration. The other important input is $c(110;k)$, which has again been obtained from MSA corrected for both the limits of $k \to 0$ and $k \to \infty$ by using the XRISM results of Rainari, Resat, and Friedman [17]. The details are available elsewhere [10,11]. *It should be emphasized that the above procedure gives nearly perfect agreement between theory and experiment for solvation dynamics in water and acetonitrile* [10,11]. We have used $T = 298$ K in all the calculations.

In Fig. 1, the generalized rate of solvent polarization relaxation, $\Sigma(k,t)$, is plotted as a function of time for two different wave vectors to show the bimodal response of the liquid. It is clear that the relaxation of the macroscopic (that is, $k \simeq 0$) polarization modes occurs on a time scale much shorter than that of the microscopic (that is, $k\sigma \simeq 2\pi$) polarization modes.

The experimental results on ionic mobilities are most conveniently represented by plotting the inverse of an "apparent" Stokes radius r_{Stokes} against the inverse of the crystallographic radius, r_{ion}. The Stokes radius is

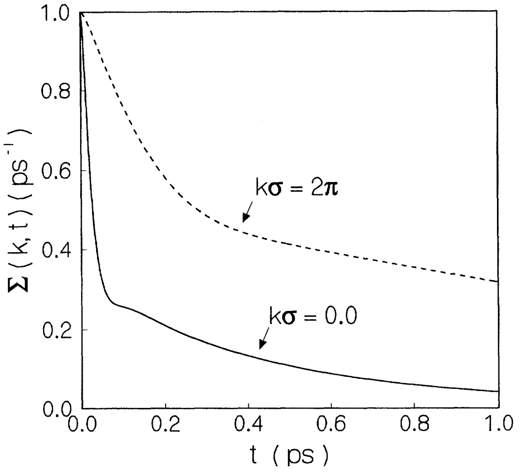

FIG. 1. The generalized rate of solvent polarization relaxation $\Sigma(k,t)$ in water is plotted as a function of time in ps for two different values of the wave vector k. $\Sigma(k,t)$ has been evaluated using Eq. (5). The solid and dashed lines represent the macroscopic ($k\sigma = 0$) and the microscopic ($k\sigma = 2\pi$) polarization relaxation of the solvent, respectively. The parameters used to characterize the solvent are as follows: $\epsilon_0 = 78$, $n^2 = 1.77$, $\mu = 1.87$ D, $\rho_0 = 0.033\,35$ Å^{-3}, $\sigma = 2.8$ Å, $\eta = 0.89$ cP, and $D_T = 2.5 \times 10^{-5}$ cm^2 s^{-1}. For details of the full frequency dependence of $\epsilon(z)$, see Ref. [10].

evaluated using the relation, $r_{\text{Stokes}} = r_{\text{ion}} + (\zeta_{\text{DF}}/4\pi\eta)$, where $\zeta_{\text{DF}} = \zeta_{\text{DF}}(z = 0)$ is obtained by solving Eq. (2) self-consistently. The results of our calculation for water and acetonitrile are shown in Figs. 2 and 3, respectively, and compared with those available from experiments. The agreement is clearly excellent. The mobilities of ions calculated from the Stokes law, the continuum theory of Zwanzig, and the overdamped, Markovian theory of Colonomos-Wolynes (CW) are also shown in both figures. For smaller ions such as Li$^+$, the dielectric friction becomes 5 to 6 times larger than the bare friction itself, thereby invalidating the Stokes law. Consequently, the mobilities of the smaller ions become much less than the values calculated from Stokes law and exhibit a pronounced diffusion anomaly. The present calculations reveal that the ultrafast Gaussian part of the bimodal solvent response plays an important role in determining the mobilities of the ions. In fact, if this Gaussian component is neglected, then the ion experiences a much larger friction and the calculated mobility becomes comparable to that predicted by Zwanzig. This component was also neglected by CW in their calculation of friction in water, and thus the mobilities were underestimated. However, the reason for the overestimation of the same by CW in acetonitrile is not precisely known and remains a puzzle to us.

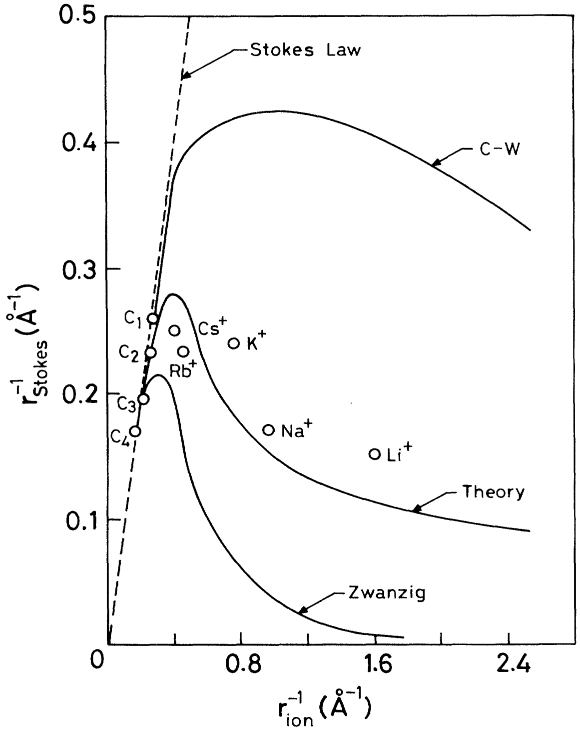

FIG. 2. The inverse of the calculated Stokes radius (r_{Stokes}) is plotted against the inverse of the crystallographic radius (r_{ion}) in acetonitrile. The solid line denotes the results of the present theory, which are compared with the Stokes law (dashed line) and the known experimental results (open circles). The predictions of the theories of Zwanzig and Colonomos-Wolynes (CW) are also shown. Stokes law is found to be valid for large tetra-alkyl ammonium ions C_1–C_4, where $C_n = (\text{CH}_3)_n\text{N}^+$. The following parameters are used for acetonitrile: $\mu = 3.97$ D, $\rho_0 = 0.0114$ Å^{-3}, $\sigma = 4.48$ Å, $\eta = 0.34$ cP, $D_T = 4.3 \times 10^{-5}$ cm^2 s^{-1}, and $\tau_D = 3.21$ ps. For further details, see the text.

As shown in Fig. 3, the present theory could quantitatively reproduce the abnormally high diffusion coefficients of the large ions (for example, Cs$^+$ and Rb$^+$) in water. Within the framework of the present theory, this can be explained by examining the explicit form of $c_{\text{id}}^{10}(k)$ given by Chan, Mitchel, and Ninham [16]. When the size of the ion becomes comparable to that of the solvent, the hard-sphere Percus-Yevick part of c_{id} acts against its electrostatic part, and this results in a partial reduction of the orientational order. This enables the ion to move more freely in the solvent. This effect is often termed the microscopic "structure breaking" of the liquid [18]. The enhancement of the ionic mobility due to the self-motion is another interesting observation of this calculation. As expected, this particular feature is most important for the light solute ions like Li$^+$; our microscopic theory gives a value for the mobility of Li$^+$ in water, which is 20% greater than that calculated in the fixed-solute case.

The success of the above calculations motivated us to examine the diffusion coefficient of a charge bubble in water—the bubble is assumed to be of the same size as a water molecule. The only difference is that this bubble does not experience any bare friction. When

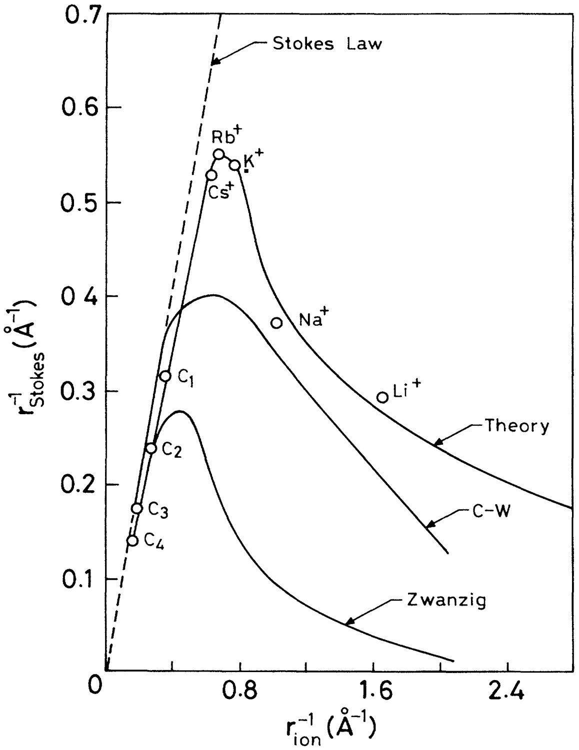

FIG. 3. The inverse of the calculated Stokes radius (r_{Stokes}) is plotted against the respective crystallographic radius (r_{ion}) in water. The representation remains the same as in Fig. 2. The relevant solvent parameters required to estimate r_{Stokes} in water are the same as in Fig. 1.

one assumes that the bubble-dipole direct correlation function is still given by the MSA, then the self-consistent calculation gives a value of 2.2×10^{-4} cm^2 sec^{-1}, which is surprisingly close to the known diffusion coefficient of a solvated electron in water [19]. However, this calculation is only suggestive—because the electron-dipole direct correlation function should be calculated quantum mechanically. We leave this as a future problem.

How a charge moves from place to place is a question that is likely to remain relevant for some time to come—so was the prophecy of Wolynes in his classic review [1] on the ion-solvent dynamics. In this Letter we show that it is possible to take into account many different aspects of ionic mobility from first principles and, at the same time, explain the anomalous diffusion behavior of small ions.

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