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ABSTRACT
Over the decades, a great deal of attention has been focused on the solvation and transport properties of small rigid monatomic ions such as Na\(^{+}\), K\(^{+}\), Li\(^{+}\), Cl\(^{-}\), and Br\(^{-}\) due to their importance in physical chemistry. Much less attention has been devoted to polyatomic ions although many polyatomic ions (such as nitrate, acetate, sulfate, and ammonium) are of great importance in biological and chemical processes. While the translational diffusion of smaller rigid ions shows the remarkable nonmonotonic dependence on inverse ion size (known as the “breakdown of Walden product”), the intermediate- to large-sized polyatomic ions (such as nitrate, acetate, and sulfate) exhibit different anomalies pointed out only recently. In this Perspective article, we provide an overview of how rotational diffusion and translational diffusion of these ions themselves are coupled to translational and rotational motions of water molecules. We discuss how diffusion of polyatomic ions is different from that of monatomic ions due to the rotational self-motion of the former that enhances diffusion in specific cases because of symmetry. While a continuum hydrodynamic model fails to describe the motion of polyatomic ions, we discuss how a mode-coupling theory approach can capture many aspects of this coupling between the solute ion and solvent water. We discuss how ionic mobility in water and other dipolar solvents are intimately connected to the dipolar solvation dynamics, in particular to its ultrafast component. We point out how the usual thinking on the relation between the diffusion and entropy needs to be modified in the case of ion diffusion.

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I. INTRODUCTION

The aim of this article is to provide an up-to-date view of the past and present developments in the important area of ion motion in liquid water. Because of the vast nature of the problem, we have limited our perspective to the ions in the liquid water only although many other solvents and binary mixtures demand attention. But it is beyond the scope of our article. There have been an innumerable number of studies on the dynamics of water molecules both in the bulk state and in the presence of solutes and surfaces of various kinds. More recently, the study of jump orientational motion of water molecules and the effect of the solute on this jump motion has drawn intense interest. However, much less attention has been focused on the role of these water dynamics on the motion of solute molecules. This is indeed surprising because one would imagine that the latter is the main point of studying the former. This issue is particularly relevant to small- to intermediate-sized atomic and molecular ions that couple strongly to the surrounding water molecules.

In the case of ions, much attention has remained focused on rigid monatomic ions, such as Li\(^{+}\), Na\(^{+}\), and K\(^{+}\), and other rigid alkali cations and also, to a lesser extent, on halide anions. Much less work has been carried on polyatomic ions. This lacuna is indeed surprising because polyatomic ions are of great importance in chemistry, biology, and also in industry. For example, sulfate ion is quite common as metal sulfates, also as sulfuric acid (H\(_2\)SO\(_4\)). The latter is used in almost every industry such as batteries, paint, fertilizer, ore processing, steel production, and water treatment. KNO\(_3\) and Na\(_2\)SO\(_4\) are used as electrolytes in salt bridges, fertilizers, rocket propellants, and even as detergent. Acetate ion serves as a common buffer. The list is endless.

Having said the above, let us also point out that an understanding of motion of ions in water has remained largely incomplete because, in analytical study, the long-range nature of ion-dipole and ion-ion interaction poses serious problems and this makes a detailed first principle study nearly impossible. For example, an ion-solvent pair correlation function involves both distance and orientation and a reliable expression for the same, even for a spherical ion in a water system, has not been made available. This considerably slowed down the progress of the study of the diffusion and conductivity of an ionic system. There is also the issue of reliable intermolecular potential between the ion and water. Therefore, a considerable amount of work has been directed to develop continuum models based on electrohydrodynamic equations. This approach completely
bypasses the need of intermolecular potential parameters. However, these attempts are not quantitatively successful, as will be described briefly later.

Therefore, the development of a proper perspective of ion motion in water can be developed mainly with the help of computer simulation studies of these complex systems. Almost simultaneously, a mode coupling theory (MCT) approach has been developed recently to study ions’ motion. These two together allowed the development of this modern perspective of the ions’ motion in water.

The primary quantity in theoretical and experimental investigation is the diffusion coefficient or the ionic mobility. The universality of diffusion phenomena is primarily due to the conservation of mass. Compared to the time scale of molecular processes such as momentum relaxation, diffusion is a slow process. When Fick’s law of diffusion is combined with the continuity theorem (which is a statement of the conservation of mass), we obtain the diffusion equation

$$\frac{\partial \rho(x, t)}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2},$$

(1)

Here, \(\rho(x, t)\) is the position \((x)\) and time \((t)\) dependent density, and \(D\) is the self-diffusion coefficient of the species being studied.

Equation (1) provides perhaps the best-known definition of the diffusion constant but gives no information about its microscopic origin or how to calculate it from theoretical models. In the early twentieth century, Einstein embarked on an analysis on the origin of the incessant motion of pollens suspended on the surface of water and it was observed by the botanist Robert Brown using an optical microscope. Einstein introduced several groundbreaking definitions and derived all important relations. First, the diffusion coefficient was defined as

$$D = \lim_{t \to \infty} \frac{\langle (r(t) - r(0))^2 \rangle}{6t},$$

(2)

where \(r(t)\) and \(r(0)\) are the positions of the diffusing particle at time \(t\) and at \(t = 0\), respectively. Equation (2) is for a three-dimensional system, and the limiting step signifies that the mean square displacement of the particle grows linearly with time in the long time limit.

Equation (2) is known as Einstein’s relation, and it opens the door for further microscopic understanding of the self-diffusion coefficient. For example, it could be easily shown that Eq. (2) is equivalent to the following expression for the self-diffusion coefficient:

$$D = \frac{1}{3} \int_0^\infty dt C_{\psi}(t),$$

(3)

where \(C_{\psi}(t) = \langle \psi(0) \psi(t) \rangle\) is the velocity-velocity time correlation function (TCF). Einstein did not derive Eq. (3) but had something equally important. By using the Langevin equation, he derived the following well-known expression between the diffusion and friction \(\zeta\) (this is also known as Einstein relation):

$$D = \frac{k_B T}{\zeta},$$

(4)

where \(k_B T\) is the Boltzmann constant times absolute temperature \(T\). Although based on the phenomenological Langevin equation, Eq. (4) is exact and can be used as a definition of friction.

Interestingly, it relates a single particle property \((D)\) to a mechanical quantity \((\text{friction})\) that is tied to a collective property \((\text{viscosity})\). In reality, however, from its original appearance, this relation has been used to obtain the diffusion coefficient which is partly because of the availability of the hydrodynamic expression of friction that was used by Einstein himself to obtain the diffusion coefficient. A substantial amount of work of time-dependent statistical mechanics is devoted to the calculation of friction on a tagged solute particle, be it a sphere or a molecule of an arbitrary shape.

The relation between the diffusion and friction is the subject of the present Perspective, with due emphasis on moving ions and dipoles in dipolar solvents, specifically liquid water.

As already mentioned, Einstein’s relation between the diffusion and friction is exact but often difficult to use because no easy access to the friction coefficient is available. As mentioned above, Einstein himself used the hydrodynamic relation with a stick hydrodynamic condition for friction on a sphere of radius \(r\) to obtain the values of the self-diffusing coefficient

$$\zeta = 6\pi \eta r.$$

(5)

In Eq. (5), \(\eta\) is the viscosity of the solvent. Equation (5) is well-known in hydrodynamics as a Stokes equation for friction on a sphere. When this equation is combined with Eq. (4), we get \(D = \frac{k_B T}{6\pi \eta r}\), a relation known as the Stokes-Einstein relation.

Our reason for reviewing the above basic relations is to point out that our understanding of diffusion depends crucially on our ability to describe friction. The Stokes hydrodynamic relation between the friction and viscosity was derived under the assumption that sphere is much larger in size than that of the solvent molecules so that we can describe the solvent as a viscous continuum. The Stokes calculation was based on the solution of the Navier-Stokes equation to obtain the flow field of the solvent far away from the solute and the distortion in the flow field near the solute surface. Such a description naturally ignores all the details of the molecularity of solute-solvent interactions and the distortion of the microscopic structure of the solvent around the solute. We shall discuss examples where the simple hydrodynamic description breaks down completely due to the molecular interaction effects.

Although we based the above discussion with an emphasis on diffusion, the friction on a solute itself is an important quantity and finds use in many theoretical descriptions. A notable application is the Kramers expression of the rate of a barrier crossing event in a bistable potential. Kramers expression is given by

$$k^K = \frac{\omega_b}{2\pi} \left[ \frac{\zeta^2}{2} + \omega_b^2 \right]^{-1/2} \exp(-E_{\text{act}}/k_B T).$$

(6)

In Eq. (6), \(\omega_b\) is the harmonic frequency that describes the potential energy minimum of the reactant well, \(\omega_b\) is the frequency that describes the curvature at the barrier top, and \(E_{\text{act}}\) is the activation energy of the reaction. These three parameters describe the reaction potential energy surface. The rate of the reaction is partly determined by the friction \(\zeta\) on the reactive motion. If the motion of an ion is involved, then the friction becomes a dielectric friction that we discuss here.

Equation (6) and its generalization provided by Grote and Hynes are routinely used in the theoretical study of a large
number of chemical reactions, ranging from isomerization dynamics to electron transfer reactions to surface hopping problems. Thus, the friction on a moving ion is an important quantity in its own right.

However, a theoretical evaluation of friction on a solute immersed in a liquid is a formidable task. The friction depends critically on the type of motion involved. For example, friction on rotational motion could be completely different from that on a translational motion. For the case of ions, the picture is even more complicated, particularly for ions in liquid water. This is due to a multitude of factors. First and foremost, the interaction between the charge of the ion and the dipole moment of water is long ranged and anisotropic, and the ion size is often not much bigger than that of the water molecule. Thus, the Stokesian hydrodynamics cannot provide a valid description. Second, both the rotational and the translation motion of water molecules become coupled to the motion of the ions. Therefore, one needs to carefully consider the orientational relaxation of the water molecules as they couple to the ion’s motion in water.

For monatomic ions, there now exists microscopic theoretical description of ion motion in water, which, although not perfect, is sufficiently reliable. In this case, the complexity due to the rotational degrees of freedom of the ion is absent. So, a quantitative description of the ion-dipole correlation is tractable, as we will detail below.

Even for diatomic ions, a reliable quantitative description of the translational and rotational diffusion of ions does not exist. The situation is even more complicated for polyatomic ions. The origin of the complexity and the consequent difficulties are many-fold. First, the friction on a polyatomic ion depends not only on the translational and rotational modes of water molecules but also on the ion’s own rotational and translational modes. Due to the prevalence of the jump motions of water molecules in the liquid state, the motions of polyatomic ions are intricately and intimately connected to these motions.

Most of the microscopic approaches to friction actually start with Eqs. (3) and (4). For the time being, we shall pursue a simple approach which is based on the Langevin equation for velocity \( \dot{\mathbf{v}} \)

\[
m\frac{d\mathbf{v}}{dt} = -\zeta \mathbf{v}(t) + \mathbf{R}(t),
\]

(7)

where \( m \) is the mass of the solute particle and \( \mathbf{R}(t) \) is the random force. The important aspect of Eq. (7) is that the friction and the random force are related to each other by the fluctuation-dissipation theorem

\[
\langle \mathbf{R}(0) \cdot \mathbf{R}(t) \rangle = 2d\zeta \delta(t),
\]

(8)

where \( d \) is the dimensionality of the system. Since \( \delta(t) \) is an even function of time, one can write down the following simple expression for the friction on the solute particle that experiences the random force

\[
\zeta = \frac{1}{3} \int_0^\infty dt (\mathbf{R}(0) \cdot \mathbf{R}(t)).
\]

(9)

Equation (9) plays an important role although an analytical expression for the random force is not easy to derive or obtain. Zwanzig’s projection operator technique provides an exact procedure to obtain this force, but implementation of the procedure requires approximations. It was only in the 1980s that progress was made in theoretical developments in the form of mode coupling theory that allowed meaningful use of Eq. (9) for dense liquids. Even then, the progress of this theory has remained limited to liquids where molecules interact with radial potential because a wavenumber-based description is rapidly convergent. Difficulty remains for liquids interacting with orientation dependent potential (anisotropic interaction) which unfortunately is the case for most liquids.

The dynamics of electrolyte solutions has remained an area of great research interest for a long time. While the objective of this Perspective article is to understand the translation diffusion of ions—both rigid monatomic ions such as Na\(^+\) and K\(^+\) and polyatomic ones such as nitrate (NO\(_3^-\)), acetate (CH\(_3\)COO\(^-\)), and sulfate (SO\(_4^{2-}\)) ions—this translational diffusion is intimately connected not only with the rotational dynamics of water but also with the ion’s self-rotational motion. Therefore, in the case of polyatomic ions, rotational diffusion of the ions is also of interest.

Figure 1 provides a flowchart showing the course of our discussion. At first, we present an overview of translational friction which is related to both monatomic and polyatomic ions. Then, for diatomic and polyatomic ions we discuss rotational friction. For both cases, we start with continuum model approaches and then discuss microscopic mode-coupling theory and simulation results. Unlike hydrodynamics, mode-coupling theory involves both single particle dynamics and collective dynamics. We connect these theoretical approaches using real-system simulation results, such as the effect of ion dynamics on water dynamics.

II. SIZE DEPENDENCE OF DIFFUSION OF MONATOMIC AND POLYATOMIC IONS: ANOMALIES AND DIFFERENCES

Experimental measurements of the mobility of monatomic alkali cations exhibit a spectacular breakdown of the Stokes-Einstein’s hydrodynamic relation. This has been extensively discussed, and several different explanations have been put forward.
The breakdown, popularly known as the “breakdown of Walden’s product” (which is the product of the limiting ionic conductivity, $\lambda_0$, and solvent viscosity $\eta_0$), is also evident from the plot of diffusivities of alkali cations in water [Fig. 2(a)]. Monatomic halide ions also show a similar trend.11,12 This nonmonotonic dependence of conductivity on inverse ion radius has been attributed to dielectric friction which is the extra friction (in addition to the Stokes friction due to viscosity) because of the interaction of the ion’s charge with the solvent dipoles.

For polyatomic ions, the situation is strikingly different, with several different anomalies. Figure 2(b) shows the experimental diffusivity of some monovalent polyatomic ions of similar sizes. It is evident that the diffusivity of polyatomic ions belongs to two different classes. Nitrate (NO$_3^-$), nitrite (NO$_2^-$), chloride (ClO$_3^-$), perchlorate (ClO$_4^-$), etc., belong to the class with considerably higher (75%-100%) diffusivity than the other class of ions consisting of iodate (IO$_3^-$), bicarbonate (HCO$_3^-$), acetate (CH$_3$COO$^-$), etc. These ions have similar ionic radius. So according to the Stokes-Einstein relation, they are supposed to exhibit similar diffusivity [Stokes-Einstein predicted diffusivity values are shown by black dashed line in Fig. 2(b)].

While Fig. 2(a) has drawn interest for almost a century, the second anomaly [Fig. 2(b)] has been pointed out only recently.13 Figure 2(b) reveals a completely new ingredient in the motion of polyatomic ions that is not present in rigid spherical monatomic ions, not usually discussed and that is a major subject of interest in the present Perspective.

### III. CONTINUUM MODEL THEORIES OF FRICTION AND DIFFUSION

The sharp fall in the limiting ionic conductivity (which is the same as the self-diffusion of the ion) for the smaller-sized monatomic ions, depicted in Fig. 2(a), was attributed earlier to the formation of a “solvent-berg” around the ion.4,15 Subsequent computer simulations and theoretical studies have mostly nullified the picture although a remnant of a structured layer holds true for the lithium ion. However, the water molecules in the first layer of these ions retain significant mobility, may be reduced, especially for Li$^+$, from the bulk value. The commonly accepted picture now invokes the presence of an additional friction due to ion-water interactions, and the total friction is written as

$$\zeta = \zeta_{SE} + \zeta_{DF}, \quad (10)$$

where $\zeta_{SE}$ and $\zeta_{DF}$ are the Stokes friction due to the viscosity of the medium and the dielectric friction due to ion-dipole interactions, respectively. Equation (10) has been widely used although such a clear separation between the Stokes friction and dielectric friction has been a subject question.6,8,16,17

The first attempts to explain the size nonmonotonicity and the observed anomalously low limiting ionic conductivity of small rigid cations such as Li$^+$ and Na$^+$ and anions such as F$^-$ employed the continuum model approach. Boyd18,19 and Zwanzig20 both independently solved electrohydrodynamic equations and obtained expression for the additional friction due to the interaction of the electric field of the ion with the time dependent polarization field of the dipolar liquid. The latter was assumed to be given by a single dielectric relaxation with the time constant given by the Debye relaxation time, $\tau_D$, 18–21

$$\zeta_{DF} = \frac{2}{3} \left( \frac{q^2}{R_{ion}^2} \right) \left[ 1 - \frac{\varepsilon_0}{\varepsilon_{\infty}} \frac{\tau_D}{\tau_0} \right], \quad (11)$$

where $R_{ion}$ and $q$ are the solute radius and the charge in the solute, respectively, and $\varepsilon_0$ and $\varepsilon_{\infty}$ are the dielectric constant at the low-frequency (that is, static) and that at the high-frequency (that is, optical) limits, respectively. $\tau_D$ is the dipole relaxation time.

Later Zwanzig revised the calculation of dielectric friction by taking into account both electrostatics and hydrodynamics and obtained the following expressions for $\zeta_{DF}$ for slip and stick boundary conditions:21

$$\zeta_{DF}^{\text{(stick)}} = \frac{2}{3} \left( \frac{q^2}{R_{ion}^2} \right) \left[ \frac{\varepsilon_0 - \varepsilon_{\infty}}{\varepsilon_0 (2\varepsilon_0 + 1)} \right] \tau_D,$$

$$\zeta_{DF}^{\text{(slip)}} = \frac{4}{3} \left( \frac{\varepsilon_0 - \varepsilon_{\infty}}{\varepsilon_0 (2\varepsilon_0 + 1)} \right) \tau_D. \quad (12)$$

It was argued that the friction coefficient for the slip boundary condition is larger than that for the stick because the former allows a greater relative motion of the ion and the surrounding fluid. The faster motion of the ion allows less polarization relaxation of the solvent, hence the larger drag or dielectric friction.

These simple expressions need no adjustable parameter. The notable feature is the dependence on $q^2/R_{ion}^2$. Thus, the theory predicts that the friction increases with charge, for slow solvent polarization relaxation, and decreases with size. The friction is also predicted to decrease with an increase in the static dielectric constant.
because the field of the ion gets screened better. However, both these expressions overestimate the dielectric friction for small ions and fail to account for the size dependence across the cation series. It especially breaks down for the smaller cations.5,12

A more sophisticated expression for the dielectric friction was derived by Hubbard and Onsager,25 which, in the language of Wolynes, is “the ultimate achievement in a purely continuum theory of ionic mobility.”6 The Hubbard-Onsager (H-O) expression is given by

\[ \zeta_{DF}(\text{stick}) = \left( \frac{17}{280} \right) \frac{\tau B q^2}{R_{\text{ion}}} \frac{e_0 - e_{\infty}}{e_0^2}, \]

\[ \zeta_{DF}(\text{slip}) = \left( \frac{1}{15} \right) \frac{\tau B q^2}{R_{\text{ion}}} \frac{e_0 - e_{\infty}}{e_0^2}, \]

(13)

Note the similar dependence on the main factors. Unfortunately, the H-O expression also fails to account for the size dependence. It underestimates the dielectric friction at intermediate to small sizes. Later, the continuum model theory of dielectric friction was further revised and extended by Hubbard and Kayser22,23 and Felderhof.25

The reason for the failure of the continuum model theories is many-fold: (i) neglect of the molecularity of charge-solvent interactions and thereby underestimation of solute-solvent and solvent-solvent correlations and (ii) inadequate description of solvent dynamics.26 We would like to point out that these theories were developed two to three decades before the discovery of ultrafast solvation dynamics in water, acetonitrile, and methanol.

IV. MICROSCOPIC THEORIES FOR MONATOMIC IONS

The first molecular approach was attempted by Colonomos and Wolynes who used the Kirkwood expression in terms of the force-force time correlation function to obtain the dielectric friction.27 The force that goes into the Kirkwood expression was obtained by using a time dependent density functional theory. We shall refrain from discussing this theory in detail because our aim is to discuss the more involved mode coupling theory approach below. The main merit of the Colonomos-Wolynes molecular approach was the inclusion of the role of translational modes of the solvent in reducing the dielectric friction.

According to Kirkwood’s formula, the total dielectric friction on an ion is given by the force-force time correlation function,28,29

\[ \zeta_{DF} = \frac{1}{3k_B T} \int_0^\infty \! \! dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle, \]

(14)

where \( \mathbf{F}(t) \) is the total force on the ion due to polar interactions at time \( t \), \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. If we decompose the total force on the ion into a short range repulsive part (hard: H) and a long range attractive part (soft: S), the total force-force autocorrelation function and thus the total friction can be written as a sum of four terms as suggested by Allnatt and Rice28

\[ \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = \left\{ F^H(0) \cdot F^H(t) \right\} + \left\{ F^H(0) \cdot F^S(t) \right\} + \left\{ F^S(0) \cdot F^H(t) \right\} + \left\{ F^S(0) \cdot F^S(t) \right\}, \]

\[ \zeta = \zeta_{HH} + \zeta_{HS} + \zeta_{SH} + \zeta_{SS}. \]

(15)

Wolynes in his attempt to formulate a microscopic theory of dielectric friction identified the term \( \zeta_{HH} \) as the Stokes friction and \( \zeta_{SS} \) as the dielectric friction and neglected the other two terms.22 Later by theoretical approach and by computer simulations,5,16,17,31–34 several studies confirmed that the cross terms cannot be fully neglected.

In a series of papers, Bagchi et al. reformulated the Kirkwood expression based approach in terms of wavenumber based equations that closely resemble the mode coupling theory approach that was already developed for nonpolar liquids.5,6,35 The difference in the Bagchi approach is that one could develop a consistent theory of dielectric relaxation, solvation dynamics, and dielectric friction. The final expression for the dielectric friction is given by

\[ \zeta_{DF}(z) = \frac{2k_B T \rho_0}{3(2\pi)^2} \int_0^\infty \! \! dt e^{-it} \int_0^\infty \! \! dk k^4 F_{\text{ion}}(k,t) I_{10}(k)^2 F_{\text{solvent}}(k,t). \]

(16)

We shall discuss about this later in detail in Sec. V. Here, \( F_{\text{ion}}(k,t) \) is the self-dynamic structure factor of the ion, \( I_{10}(k) \) is the orientational dynamic structure factor of the dipolar solvent, and \( \zeta_{DF}(z) \) is the ion-dipole direct correlation function.

It is interesting to study a reduction in the microscopic or molecular expressions of the friction to the continuum model prediction. It is always a fruitful exercise because of the valuable insight that such a derivation provides. For example, the reduction in the microscopic expression of the solvation time correlation function to the continuum model prediction and the recovery of the longitudinal time constant are indeed revealing as one finds that while we replace the wavenumber \( k \) dependent relaxation times by the \( k = 0 \) limiting value, the initial solvation energy is obtained by averaging over all the wavenumbers. Similar approximations have to be made in the derivations of the continuum model expression of the rotational dielectric friction36 and the derivation of the expressions of Fatuzzo-Mason-Nee-Zwanig expression of the frequency dependent dielectric function.37,38 We shall discuss the rotational dielectric friction on ions in Sec. VIII.

In the case of limiting ionic conductivity, the situation is a bit more complex. Here we have to consider the contributions of both the density mode and the current mode. Hydrodynamic approaches of Boyd-Zwanig-Hubbard-Onsager included only the contribution of the current mode. By contrast, the molecular approach of Wolynes considered only the density mode. Thus, the contributions considered in the latter study cannot be reduced to that of the former as they are orthogonal contributions. However, numerically the two contributions might approach each other as indeed happens for friction on a tagged spherical solute in a solvent of spherical molecules.39

V. MODE COUPLING THEORY OF ION DIFFUSION: MONATOMIC IONS

The most sophisticated and also the most accurate description of diffusion and transport properties of liquids are provided by the mode coupling theory.40–44 For tagged particle diffusion, one can derive the following simple yet fairly accurate expression for the friction on an uncharged solute

\[ \frac{1}{\zeta} = \frac{1}{\zeta_{\text{ion}}} + \frac{1}{\zeta_{\text{pp}}} + \frac{1}{\zeta_{\text{hyd}}}, \]

(17)
where the terms on the right-hand side (RHS) have the following meanings. $\zeta_{\text{bin}}$ is the friction from the binary (uncorrelated) interaction between the solute and the solvent, $\zeta_{\rho\rho}$ is the correlated many-body interaction which is described by (that is, projected on) the density mode, and $\zeta_{\text{hyd}}$ is the contribution to diffusion due to the hydrodynamic transverse current mode. This expression needs generalization for ions that we shall discuss later. For now, we would just like to point out that the origin of the first two terms on the RHS in Eq. (17) is completely different. The first term comes from binary and correlated collisions which can be described by the density mode, while the second term is due to the transverse current mode, or the flows in the liquid.

We now make an important observation. The electrohydrodynamic approach of Boyd-Fuoss-Zwanzig\textsuperscript{19,20,45} and Hubbard-Onsager\textsuperscript{22} considered only the current mode. It was internally consistent because the Stokes friction is also due to the transverse current mode. The inconsistency arises if we add the friction from the molecular or the structural relaxation term to the current term because for these orthogonal modes, the addition is to be made at the level of diffusion coefficient—not at the level of friction. The two contributions should be considered as two independent contributions to diffusion.

There is, however, an important additional point to be remembered. The numerical estimates of the mode coupling theory calculations of friction on a solute in the solvent of the similar sizes give results that are similar to (but slightly larger than) $4\pi\eta R$—the Stokesian value with the slip boundary condition. This important point is often missed and has been discussed in Refs. 43 and 46.

We now turn to the discussion of ion diffusion and explanation of molecular aspects of the results shown in Figs. 2 and 6(i). There are several new features that enter the discussion here, including a surprising role of the translational diffusion of solvent molecules on the friction of the ion.\textsuperscript{36}

At a molecular level, a small ion facing water molecules experiences multitude of forces. It is easy to see why the point dipole approximation of the continuum models of Boyd-Onsager-Zwanzig could be inadequate because the point dipole fails to produce the orientational structure that forms in the first hydration shell.

Microscopic mode coupling theory (MCT) provides a different approach and a different picture which we discuss below without invoking the complex equations. First, let us differentiate the present approach from that based on hydrodynamic equations. The latter involves assumption of long wavelength and long-time (small wavenumber and small frequency). MCT is a molecular approach that includes spatial and orientational correlations and also dynamics at molecular length scales all the way up to macroscopic distances. Another important positive aspect of MCT is that it includes the local structural changes in the solvent due to the presence of the ions. Self-consistent MCT is a culmination of renormalized kinetic theory of gases\textsuperscript{8} and molecular hydrodynamics\textsuperscript{44} and was formulated in the early 1980s. We have shown a flowchart in Fig. 3 to describe the origin of the concept of MCT. In some respects, the calculation of MCT parallels that of hydrodynamics, except that here the main contributions are made by structural relaxation at microscopic length scales. In extended hydrodynamic theory description, the decay of wavenumber dependent hydrodynamic modes is expressed in terms of frequency and wavenumber dependent transport coefficients. However, this description is valid in intermediate time scales and breaks down in very short and very long time scales. On the other hand, renormalized kinetic theory works well in very short and very long-time responses. These two approaches are combined in mode-coupling theory, and the self-consistency comes into picture through the time correlation function of hydrodynamic modes in terms of transport coefficients (Green-Kubo formulation). The two approaches can be considered to be complimentary in another aspect. From the time of Boltzmann, kinetic theory

![Twin approaches to understand molecular motion](image)

**FIG. 3.** An illustrative (and pedagogical) flowchart showing the origin of mode-coupling theory and the ideas behind it. Note that the two formidable theoretical frameworks are combined to build the mode coupling theory (MCT).
was used to calculate the transport properties, such as viscosity, diffusion, and thermal conductivity. Hydrodynamics, on the other hand, was largely used to obtain the time correlation function, as in Rayleigh-Brillouin spectroscopy. Of course, we do get an expression of friction from hydrodynamics but at the expense of introducing viscosity. Hydrodynamics has no way to provide a value of viscosity.

The basic idea is to describe the static and dynamical influence of the solvent on the tagged solute through the coupling of the slow hydrodynamic modes and their binary product. The end result is always an integration of product of three terms, which are as follows: (i) The time correlation function (TCF) of the solvent mode (such as dynamic structure factor or current correlation functions), \( F_0^\text{solvent}(k, t) \), (ii) a vertex term that accounts for the coupling between the solute and the solvent, \( c_{id}(k) \), and (iii) another time correlation function (TCF) that describes the solute dynamics, \( F_{\text{ion}}(k, t) \). The self-consistency enters, in this case, through the last two terms—the vertex term and the solute dynamic TCF. In this theory, the dielectric friction equation which is solved self-consistently is expressed as given in Eq. (16).

The ion-solvent coupling has a significant solvent orientational component through the coupling of the ion with the dipoles of the solvent. Thus, both the orientational arrangement of the solvent molecules and their orientational relaxation enter into the theoretical description.

We describe the self-consistent MCT calculation through a flow chart given in Fig. 4(a). However, Fig. 4(a) is appropriate for monatomic (spherical) ions. The situation is more complex for polyatomic ions which shall be described later. Mode-coupling theory results are shown to agree well with the experimental result for monatomic ions in methanol [Fig. 4(b)].

The self-consistency, also called boot-strapping, requires use of the expression for frequency and wavenumber dependent transport property, such as diffusion, friction, or memory-kernel, into the expression of the time correlation function that is used to calculate the transport property. That is, the transport property and the time correlation function are made consistent with each other, as described in Fig. 3 and implemented in Fig. 4.

An important aspect of the self-consistency scheme is that it involves both solute and solvent dynamics. Thus, one can envisage that solvent dynamics also gets modified by the solute’s presence and its motion. This MCT scheme can indeed address this oft-debated issue of the effects of ion on dynamics of surrounding water molecules.

VI. ION SOLVATION DYNAMICS AND IONIC MOBILITY

We now discuss an interesting correlation between the ion solvation dynamics and ionic mobility. In solvation dynamics, we probe the polarization response of the dipolar solvent after an optical excitation of an internal dye molecule.\(^{50,51,49}\) The excitation induces a dipole moment in the dye. The subsequent stabilization of the dye can be measured by the red shift of the fluorescence emitted by the dye. The measured relaxation is quantified in terms of a normalized time correlation function, \( S(t) \), defined by

\[
S(t) = \frac{\langle \nu(t) \rangle - \langle \nu(\infty) \rangle}{\langle \nu(0) \rangle - \langle \nu(\infty) \rangle} = \frac{E(t) - E(\infty)}{E(0) - E(\infty)} = \frac{\Delta E(t)}{\Delta E(0)} \tag{18}
\]

where \( \langle \nu(t) \rangle \) is the average frequency of the fluorescence spectrum of the dye at time \( t \). This is assumed to be equal to the energy of the dye, \( E \). The last term on the right-hand side is just a definition. Recently, in a review article, Hynes summarized these aspects of solvation dynamics as well as molecular motion in water.\(^{52}\)

A deeper insight is obtained when we realize that the solvent memory kernel used in the mode-coupling theory expression of the dielectric friction is the same as the one involved in the solvation dynamics. In the long wavelength limit, the relaxation of longitudinal polarization rate is ultrafast and is largely responsible for sub-100 fs solvation dynamics observed in experiments and simulations on water.

The above observation has a significant role in reducing the dielectric friction on a moving ion. Because of the presence of ultrafast solvation, the magnitude of the friction decreases significantly.

---

**FIG. 4.** (a) For convenience and clarity, a flow chart illustrating the complex self-consistent scheme of mode-coupling theory for the translational dielectric friction of a rigid, monatomic ion in water is provided in this figure. Note that a similar self-consistency is to be applied for the solvent memory function, \( \Sigma_{id}(k, z) \) as well. (b) The values of the Walden product \( \Lambda_{D \varphi}(k) \) of rigid, monatomic positive ions are plotted as a function of the inverse ionic radius \( r_{\text{sol}}^{-1} \) in methanol at 298 K. The solid line represents the predictions of the microscopic mode-coupling theory. The filled circles denote the experimental results. The large-dashed and the short-dashed lines are the representatives of the Hubbard–Onsager and the Zwanzig continuum model based theories, respectively (taken from Ref. 49).
because the initial part of the force-force time correlation function decays at an ultrafast rate in the long wavelength limit which has a significant contribution to the dielectric friction. Theoretical studies in fact show that if we progressively remove the ultrafast components, then the limiting ionic conductivity approaches the prediction of Zwanzig theory.

This interesting result partly explains the overestimate of the dielectric friction by the continuum model expression of Zwanzig. The continuum models include contributions from the long wavelength modes but assume that the relaxation of polarization can be described by invoking the single Debye relaxation time-based approach that gives rise to the longitudinal relaxation time. This approximation vastly understimates the rate of the polarization relaxation. Thus, the friction, which is the time integral over the polarization relaxation time correlation function, is overestimated. The same criticism is valid for the approach of Colonomos and Wolynes. In fact, a lack of knowledge of the ultrafast component (prior to 1991 for acetonitrile and 1994 for water) in the solvation dynamics was found to be ultrafast, with 60%–70% of the energy relaxation completed within 100 fs. We thus encounter a rather strange and unique case where a fast process controls a slow relaxation.

Friction on an ion is given by the integration over the force-force time correlation function. It is expected that the polar component of the force-force time correlation function should also decay on the ultrafast time scale, thus reducing its contribution to the total friction. Numerical calculations verified the above picture.

The relative contributions of the two friction terms are shown in Fig. 6(i). Clearly, the polar contribution increases as the size of the ion decreases, and at the same time, nonpolar contribution decreases.

In Fig. 6(i), the example of Li+ ion presents an interesting case. In the absence of the charge, this small ion is expected to move fast, move in a way different from the prediction of hydrodynamics and decouple from solvent viscosity. In the presence of the charge, it generates a strong electric field that forms a structure akin to the solvent-berg model. MCT captures the ensuing effects through two factors, (i) The solute-solvent structure through spatial and orientational correlation functions and (ii) a self-consistency that takes into account the effects of slowdown of the solute on its own friction.

Figures 5(a)–5(d) depict the probability distribution of the square displacement, ∆r^2, for four ions. It shows that the size dependence indeed has a strong effect; while the distribution of displacement of smaller ions such as Li+ and Na+ behaves similarly, that of the larger ions such as K+ and Rb+ behaves significantly different. Such a sharp difference in the distribution curves is not seen in a model solvent such as Stockmayer liquid (LJ spheres with point dipoles at the center).

VII. NUMERICAL TECHNIQUE TO CALCULATE DIELECTRIC FRICTION

Accurate analytical microscopic calculation of friction on a tagged solute ion is an extremely difficult task. In computer simulations, one can obtain this quantity from the Einstein equation by calculating the diffusion coefficient from the mean square displacement of the solute. However, to compute dielectric friction on an ion, we need to separate it from the total friction. Here, we discuss a simple technique employed to compute dielectric friction on an ion. One carries out two categories of simulations, one with proper charges and force-field for ions and another with everything the same but zero charges. Finally, the dielectric friction is
In Figs. 6(a)–6(f), we illustrate the physical situation for charged and uncharged ions, for two cases, Cs⁺ and Na⁺. One can compute Stokes-Einstein friction, \( \zeta_{SE} \), from the diffusivity of the solutes in the absence of any charges on it, and the dielectric friction can be obtained by subtracting \( \zeta_{SE} \) from the total friction of the ionic species [Eq. (10)].

Figures 6(a) and 6(b) show the hydration shells of the Na⁺ ion and an uncharged Na atom. Note the marked difference between the two. Similarly, Figs. 6(c) and 6(d) correspond to those of cesium (Cs). Here, the difference is large despite the much larger size of cesium. In the absence of charge, the structure of hydration shell is destroyed or minimized for both the ions. The change is more pronounced in the case of sodium due to the charge density of the ion [Figs. 6(e) and 6(f)]. We have plotted the square displacement of single ions of Na⁺ and Cs⁺ from an initial timeframe. Cs⁺ ions show larger translational jump than Na⁺ ions, while the reverse is true for the uncharged case.

The differences in surrounding structural arrangements essentially give rise to changes in the dynamics of the ions. Unfortunately, continuum model based hydrodynamic theories fail to capture these aspects while they are incorporated in a sophisticated microscopic theory such as the mode coupling theory.

As we have described earlier, Stokes friction and dielectric friction on these monatomic ions can be obtained from the diffusivity values of charged ions and uncharged atoms. These friction values of five alkali monatomic cations are plotted in Fig. 6(i). This figure shows that while the Stokes friction increases, as expected, with the increase in the size of the atoms (Li–Cs), the dielectric friction shows a sharp decrease after Na⁺ ions. The two lines cross each other at potassium which is thus predicted to experience similar Stokes and dielectric friction.

An important point to note here is that the structure and dynamics of these salt solutions may depend significantly on the polarizability of water molecules. Berne and co-workers demonstrated that in a simulation with a polarizable model of water, the hydrogen bond relaxation time gets lengthened by a factor of between 50% and 100% and the Gibb’s energy of activation for breaking hydrogen bond increases by \( \sim 0.2 \) Kcal/mol.\(^{56,57}\) They also showed that the solvation of a chloride ion in a water cluster changes its nature. In a nonpolarizable model, interior solvation of Cl⁻ is preferred, while in a polarizable model, the ion is solvated near the surface of the cluster. In a recent article, Nguyen et al. showed that a nonpolarizable model cannot reproduce the trend of the diffusion constant of water with the increase in the salt concentration as obtained from experiments.\(^{58}\) The effect of polarizability and/or charge transfer needs to be included in the simulation model to obtain a good agreement with experiment.

**VIII. MOTION OF DIATOMIC IONS**

Diatomic ions with a linear geometry, such as CN⁻ and CO, exhibit markedly different rotational and translational dynamics from the rigid monatomic ions. These ions all have one characteristic that is the hallmark of polyatomic ions: the presence of distributed charges across heteroatoms, which makes their coupling with water molecules strong and complex. Also, unlike monatomic ions, diatomic ions can rotate in response to a fluctuation in the force acting on its atoms. Therefore, the total friction acting on a

\[
\zeta_{DF} = \zeta_{Charged\_ion} - \zeta_{Uncharged\_molecule} = k_B T \left( \frac{1}{D_{Charged\_ion}} - \frac{1}{D_{Uncharged\_molecule}} \right). \tag{19}
\]
polyatomic ion derives its contributions from translational motion, from rotational motion, and also from the coupling of translation-rotational motion. One often discusses the presence of such coupling in terms of a friction tensor where the off-diagonal terms describe translation-rotation coupling as described in the following equation:

\[
\zeta = \begin{bmatrix} \zeta_T & \zeta_{TR} \\ \zeta_{RT} & \zeta_R \end{bmatrix}.
\]

We have already discussed translational friction \( \zeta_T \) in the context of monatomic ions. Now we turn to a discussion of rotational friction. A myriad of theoretical models for rotational friction exist in the literature. This start with the simplest hydrodynamic model of Debye-Stokes-Einstein (DSE) for a sphere

\[
\zeta_R \approx \zeta_{DSE} = 8\pi \eta R^3,
\]

where \( R \) is the ionic radius and \( \eta \) is the viscosity of the bulk solvent. However, similar to the Stokes-Einstein model for translational friction, here also the molecularity of the solute and solvent is neglected.

We briefly discuss here the existing theoretical approaches to obtain the frictional drag on rotational motion (shown in Fig. 7); a more detailed discussion can be found elsewhere.61 In one of the most important work in this specific area, Hu and Zwanzig presented a calculation of the frictional drag on rotating nonpolar ellipsoids (prolates and oblates) by hydrodynamic calculation.62 This was an important contribution because a rotating sphere experiences no frictional resistance under the slip boundary condition, while the stick boundary condition gives too high friction. Thus, the work of Hu and Zwanzig removed an important lacuna. For the rotational dielectric friction, pioneering contributions came from Fatuzzo and Mason63 and Nee and Zwanzig.64,65 Similar to work of Zwanzig on translational friction, as discussed earlier, here also they started with decomposition of the total rotational friction in terms of a hydrodynamic term due to viscosity and a term due to polarization fluctuations

\[
\zeta_{\text{Rot}} = \zeta_{\text{DSE}} + \zeta_{\text{R,DF}},
\]

where \( \zeta_{\text{DSE}} \) is the hydrodynamic contribution to rotational friction obtained from the Debye-Stokes-Einstein (DSE) relation [Eq. (21)] and \( \zeta_{\text{R,DF}} \) is the rotational dielectric friction. This is in fact closely connected to the solvation dynamics of the polar medium.66-68 A continuum model based expression of frequency dependent friction on a point dipole in the center of a spherical cavity was obtained by Nee-Zwanzig in the following form:

\[
\zeta_{\text{DF}}(\omega) = \frac{2k_B T}{\pi \nu} \left( \frac{eS - e_\infty}{eS} \right) \left( \frac{e(\omega) - eS}{2e(\omega) + e_\infty} \right).
\]

Hubbard and Wolynes significantly extended this theory and suggested an interesting inverse dependence of dielectric friction on the rank, \( l \), of the spherical harmonic.69 Later, Ravichandran and Bagchi presented a detailed analysis on the rank-dependence of orientational correlation function.

In a work relevant to the present Perspective, Alavi-Waldecker generalized the theory of Nee-Zwanzig to obtain dielectric friction for an arbitrary charge distribution.70 They derived the following formable expression:

\[
\zeta_{\text{R,DF}} = \left( \frac{8}{R^2} \right) \left( \frac{eS - 1}{2(eS + 1)} \right)^2
\]

\[
\times \sum_{l=0}^{N} \sum_{m=-l}^{l} \sum_{j=1}^{N} \sum_{j=1}^{l} \frac{2l+1}{2l+1} \left( 1 - m^2 S_l \right) \left( 1 + m^2 S_l \right) P_l^m(\cos \theta_j) P_l^m(\cos \theta_j) \cos \theta_j, \tag{24}
\]

where \( P_l^m(x) \) are the Legendre polynomials describing the orientation of the charge at distance \( r_i \) in the space fixed frame. \( R_i \) is the cavity radius, \( (r_i, \theta_i, \phi_i) \) are the polar coordinates of the charges, \( q_i \) is the partial charge of i-th atom, \( eS \) is the static dielectric constant of the solvent, and \( T_D \) is the Debye relaxation time.

An extended molecular theory of orientational relaxation including solvation dynamics was developed by Bagchi et al.73,74 The theory was based on the nonlinear Smoluchowski equation for rotational and translational diffusion where the effective force was obtained from time dependent density functional theory. For a molecular species, a similar theory was developed using the reference interaction site model (RISM).

Rotational dielectric friction, \( \zeta_{\text{R,DF}} \), is related to the torque-torque time correlation function (TTTCF). For a linear molecule or a dipole, it is defined as

\[
\zeta_{\text{R,DF}} = \frac{1}{2k_B T} \int_0^\infty dt \langle N(0) - N(t) \rangle. \tag{25}
\]

As noted earlier in the context of translational friction, \( \zeta_{\text{R,DF}} \) also is not directly accessible from simulation using Eq. (25). Here, \( N(t) \) is the random torque acting on the solute at time \( t \). Here, the effect of solute’s self-motion on the torque it experiences needs to be projected out. Zhou et al. investigated rotational friction by computer simulation by choosing an immobile solute.75 Later, Maroncelli and co-workers pointed out that the treatment suffered from an internal inconsistency.76

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**FIG. 7.** For convenience, we present a chart of the different theoretical formulations developed for the rotational friction over the years. The list is not exhaustive but attempts to capture some of the essential developments.
Another way to obtain $\zeta_{R,DF}$ from simulation is through the angular velocity autocorrelation function and the torque-angular velocity correlation function

$$C_{\omega\omega}(t) = \langle \omega(0) \cdot \omega(t) \rangle,$$

(26)

where $\omega(t)$ is the angular velocity vector at time $t$. Then, the friction coefficient is obtained using Einstein’s relation again.\(^\text{73–75}\)

Due to the distributed charges of diatomic ions, the molecules of liquid water may need to undergo significant structural arrangement to obtain the stable structure, and there could be frustration in water structure.

This simple point can be understood by comparing the difference in the dynamics of CN\(^-\) and CO molecules in water.\(^\text{76}\) The arrangement of water molecules around the two molecules is observed to be considerably different [Figs. 8(a) and 8(b)]. Carbon monoxide molecules behave like a hydrophobic solute in an aqueous solution.

There are interesting consequences of this difference. Although a CO molecule rotates faster, it is less connected to the water dynamics. The cyanide ion, being better connected due to the presence of the charges, derives benefits from the jump dynamics of water molecules, as manifested in the trajectories of the two species [Figs. 8(c) and 8(d)]. Here, the translational jump motion of the neighboring water molecules is coupled with that of the CN\(^-\) ion and CO molecules. A similar coupling is observed in their rotational jump also.

The uncharged species, CO molecule, exhibits both the translational ($D_{tr,CO} = 2.68 \times 10^{-5}$ cm\(^2\)/S) and rotational dynamics ($\tau_{CO} = 0.16$ ps) faster than the cyanide ion ($D_{tr,CN} = 2.03 \times 10^{-5}$ cm\(^2\)/S and $\tau_{CO} = 0.58$ ps) in water. Furthermore, the translational motion of these diatomic ions/molecules is again coupled to their own rotational motion. The average displacement of these two solutes as a function of their angle of rotational jumps is shown in Fig. 9 (detailed calculation has been discussed in Ref. 13). Here, different data points of a particular species represent different time frames. For similar time gaps, $\tau$, $2\tau$, etc., CO rotates more and in turn, translational displacement of this species is more than that of the cyanide ion.

In these cases of diatomic molecules, analytical treatment of total friction is more complicated than that for the rigid monatomic ions. The treatment becomes further nontrivial for polyatomic ions.

**FIG. 8.** The radial distribution function (RDF), $g(r)$, of water oxygen atoms surrounding the constituent atoms of (a) cyanide (CN\(^-\)) ion and (b) carbon monoxide (CO) molecule. Trajectories demonstrate coupled translation jump of water molecules with (c) cyanide ion and (d) CO molecule.

**FIG. 9.** These graphs show the average displacements of the solutes CO and CN\(^-\) as a function of the average angle of rotation. Each point marked as $\tau$ and $2\tau$ signifies data at different time frames. Note that CO rotates faster and also translates faster than CN\(^-\).
These categories of diatomic species being intermediate between the monatomic and polyatomic ions help to understand the complex dynamics of polyatomic ions, which we shall discuss in Sec. IX. In the case of polyatomic ions, complexity comes from the geometry and the charge distribution of the ionic species.

IX. DYNAMICS OF POLYATOMIC IONS IN WATER

As discussed, the quantification of the total friction on a polyatomic ion is more nontrivial than that for a spherical ion and a diatomic ion. Experimental data of ionic conductivity at infinite dilution (or ionic diffusivity) suggest that polyatomic ions with similar crystallographic radius but different geometries and charge distributions exhibit different diffusivities in an aqueous medium [Fig. 2(b)]. As pointed out earlier, the most important features that distinguish polyatomic ions from rigid monatomic ions, and among different polyatomic ions, are the distributed charges and different geometries. Chandra and co-workers investigated structural, dynamic, and spectroscopic behavior of several polyatomic ions employing \textit{ab initio} simulation.\textsuperscript{77–79} In an interesting study, they showed how the structure of iodate ions dictates the nature of solvation and makes the anion behave partly as a cation.

In a series of papers, detailed computational analyses of 0.1M aqueous solution of potassium salt, with three different anions, two of them being monovalent ions, such as nitrate, NO$_3^-$, and acetate, CH$_3$COO$^-$ and also of a bivalent ion, sulfate, SO$_4^{2-}$, were presented recently. Simulation details are given in Ref. 59. It was observed that the rotational motion of nitrate ions was significantly coupled to the orientational jump of neighboring water molecules.\textsuperscript{80} Almost a decade ago, researchers found that the rotational motion of water molecules were not merely diffusive in nature but consisted of large magnitude rotational jumps.\textsuperscript{1,81,82} Now, the orientational motion of a solute, such as a nitrate ion that is hydrogen bonded with water molecules, also exhibits jump rotations. Figures 10(a) and 10(b) show two different trajectories of orientational jump motion of both the water molecules and nitrate ion that were hydrogen bonded initially. When the ion-water hydrogen bond gets broken, both exhibit large amplitude rotational jump motions and the two jump motions are correlated, sometimes occur together and sometimes after a short time lag. This is true for other ions also. Clearly, these correlated jump motions are expected to affect the dynamics of the nitrate ion significantly.

Next, it has been observed that the rotational jump of the nitrate ion is also coupled to its own translational motion.\textsuperscript{7} Figures 10(c) and 10(d) show the time evolution of the square displacement of the ion and quaternions of the same trajectory. At a particular time (~80 ps) when the square displacement exhibits a sharp change, the three quaternions (q$_1$, q$_2$, and q$_3$) also exhibit a sudden change which signifies a rotational jump of the nitrate ion. This translation-rotational coupling contributes significantly to the overall dynamics of the polyatomic ions.

Let us first discuss the coupled rotational jump motion of polyatomic ions. It was recently observed that the nitrate ion with its planar geometry could have two different rotational motions in water with significantly different dynamical features. In mechanism 1, the hydrogen bond switches from one nitrate oxygen atom to water oxygen atom and the ion rotates in an out-of-plane manner. In the second mechanism, the hydrogen bond switches between two nitrate oxygen atoms as it undergoes in-plane rotational motion.\textsuperscript{80} In both the mechanisms, during the hydrogen bond switching (HBS), the water jump and nitrate jump are coupled. The probability of the water jump during the nitrate jump with or without a time lag is shown in Figs. 11(a) and 11(b) by P($\phi_{jump}$). Note that the magnitude of the jump angle for both the nitrate ion ($\theta$) and water ($\phi$) is different.

The rotational motions of nitrate and acetate ions have been analyzed in detail.\textsuperscript{13} It turns out that the symmetric nitrate ion rotates much faster ($\tau_2 = 2.35$ ps) than the acetate ion, which, with
its asymmetric charge distribution among the constituent atoms \( (\tau_2 = 6.5 \text{ ps}) \), exhibits hindered rotational motion. On the other hand, the sulfate ion, with higher partial charges on the constituent atoms, exhibits a very slow rotational relaxation \( (\tau_2 = 11.66 \text{ ps}) \) despite being symmetric in nature.\

Interestingly, the solvation shell structures around the nitrate ion and the acetate ion are found to be significantly different (Fig. 12). In the acetate ion, the magnitude of the partial charge of the C2 atom [shown in Fig. 12(e)] is considerably smaller than the other two peripheral oxygen atoms. This causes the water density

![FIG. 11. This figure depicts the variation of \( R_{\text{NO}_a^*} \) (the distance between nitrate nitrogen and water oxygen undergoing H-bond switching), \( \theta \) (angle of nitrate jump) during H-bond switching as well as the probability distribution of water jump \( [P(\phi_{\text{jump}})] \) before and after nitrate jump at time 0 for (a) mechanism 1 and (b) mechanism 2. The results are averaged over all hydrogen bond switching events following mechanism 1 and mechanism 2. (c) Variation of \( \phi \) (angle of water jump) during H-bond switching in mechanism 1 and mechanism 2 (taken from Ref. 80).](image)

![FIG. 12. (a) Computed radial distribution function (RDF) of water oxygen atoms \( (O_w) \) around the constituent atoms of the nitrate ion, (b) showing the nitrate ion with its partial charges on the constituent atoms. (c) The probability distribution function of water molecules around the nitrate ion. [(d)–(f)] correspond to acetate ion (taken from Ref. 13).](image)
to be shifted to two oxygen atoms in the first solvation shell. As a result, the rotational motion of the acetate ion is largely hindered for the asymmetric potential energy surface for rotation which in turn reduces its translational diffusion compared to the nitrate ion in water [shown in Fig. 2(b)].

Similar to diatomic molecules, the study of the average displacement vs the angle of rotation for these two ions provides interesting insights (Fig. 13). Even for a shorter time interval of 2 ps, the behavior of nitrate and acetate ions is seen to be quite different. Figures 13(a), 13(d), and 13(g) correspond to the nitrate ion at different time intervals, Figs. 13(b), 13(e), and 13(h) correspond to the acetate ion, and Figs. 13(c), 13(f), and 13(i) present the difference between the contours of nitrate and acetate ions at different time intervals.

To further analyze the effect of charge distribution symmetry on the dynamics of polyatomic ions, a series of ions were modeled with a similar geometry as the nitrate ion but different charges on the peripheral oxygen atoms of the ion [Fig. 14(a)]. It was observed by molecular dynamics (MD) simulations that rotational motion of the nitrate ion with its full charge distribution symmetry was the fastest and as asymmetry was introduced in the model ions, the rotational motion of the asymmetric ions became slower [Fig. 14(b)]. Similarly, Fig. 14(c) shows that the diffusivity decreases with increasing asymmetry of model ions. These results clearly prove that for asymmetric ions, reduced rotational motion couples to their translational motion and reduces the diffusivity of the ions. Dynamics of polyatomic ions have been studied both theoretically and computationally in a series of work.

All the ions we have discussed till now are monovalent and with a planar geometry. Now, there is a different class of molecules with fully symmetric charge distribution but in a tetrahedral geometry, such as sulfate (SO$_4^{2-}$) and ammonium (NH$_4^+$). Earlier studies suggested that positive and negative ions behave quite differently. Molecular dynamics simulations of sulfate and ammonium were used to perform a comparative study with the dynamics of the methane molecule which has the same geometry but with no charge. All simulations were done with a very low concentration of solute (0.1M). As observed in the diatomic uncharged molecule, CO

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**FIG. 13**. Demonstration of the translation-rotation coupling in nitrate and acetate ions. Here, [(a)–(c)] are the contour plots of the translation-rotation joint probability distribution of the nitrate ion ($P_{	ext{nitrate}}(dr, \theta, \phi)$) and acetate ion ($P_{	ext{acetate}}(dr, \theta, \phi)$), both in water, and the difference in the probability distribution of the acetate ion from that of the nitrate ion, respectively, at a time interval ($\tau$) of 2 ps. [(d)–(f)] correspond to the same quantities at a time interval of 5 ps, and [(g)–(i)] are at 10 ps (taken from Ref. 13).
The solvation shell structure of sulfate ions is fully symmetric. This has an interesting consequence. While orientational caging by hydrogen bonds makes rotation by Brownian diffusion slow, rotational jump motions are partly facilitated because successful jump rotation from one energy minimum to another is possible for the symmetric nature [Fig. 15(a)]. The torques on sulfate ions and nitrate ions in water are found to have the distributions shown in Fig. 15(b). It is evident from this figure that the rotational jump motion of sulfate ions is feasible, even though it is rare, in comparison with the singly charged nitrate ions, due to the high partial charges of constituent atoms of the sulfate ion. The latter causes the formation of a strong hydrogen bond with the surrounding water molecules. Therefore, rotational jump motions are less frequent compared to nitrate ions. This in turn increases the orientational decay time constant of sulfate ions, as illustrated in Fig. 15(c).

The ultraslow dynamics of sulfate ions in water with its higher charge affects the dynamics of the entire system significantly (we shall discuss about this in Sec. XIII).

A mode-coupling theory (MCT) formalism has recently been developed and employed to describe the rotational coupled translational motion of polyatomic molecules. In Figs. 16(a) and 16(b), schematic pictures of the difference between the orientational relaxation of solvent molecules with the solute motion in monatomic and polyatomic solutes are shown. Unlike for monatomic solutes as described earlier [by Eq. (16)], it is now required to include the orientation Ω of solutes in a force-force time correlation function. The resulting expressions are complex, with Eq. (16) being the first term of a series of terms that originate from spherical expansion of two densities and the direct correlation function and integration over all the variables.

This effect can be incorporated, albeit approximately, by a modified self-dynamic structure factor of the ion

$$F_{\text{ion}}(k, z) = \frac{1}{z + D_{\text{ion}}k^2 + \tau_{\text{ion}}^{-1}}.$$  

Therefore, Eq. (16) needs to be modified for the friction on a polyatomic solute to

$$\zeta_{\text{ion}}(z) = \frac{2\kappa_0 T_0}{3(2\pi)^2} \int_0^\infty dt e^{-\frac{z}{2t}} \int_0^\infty dk k^4 e^{-D_{\text{ion}}k^2 t} \left[ \frac{1}{z + D_{\text{ion}}k^2 + \tau_{\text{ion}}^{-1}} \right] |\tilde{u}_D^2(k)|^2 \times F_{\text{solvent}}^{10}(k, t) + \kappa_0 T_0 \int_0^\infty dt e^{-\frac{z}{2t}} \int_0^\infty dk k^4 e^{-D_{\text{ion}}k^2 t} |\tilde{u}_D^2(k)|^2 \times F_{\text{solvent}}^{10}(k, t).$$  

Here, methane also behaved like a hydrophobic molecule in terms of both structural and dynamical features with considerably faster translational and rotational dynamics.

Sulfate ions due to high partial charges exhibit an ultraslow rotational and translational dynamics (Table I). Ammonium ions on the other hand are considerably faster. However, although their translational diffusivity is comparable with nitrate ions (with single negative charge), the rotational dynamics of ammonium ions is much slower than that of the nitrate ions.

In summary, a number of factors play important roles in deciding both structural and dynamical features of these polyatomic ionic solutes: the overall charge, then the individual partial charges of constituent atoms, symmetry of the molecule, its geometry, etc. These complex factors make the determination of friction on these solutes prohibitively hard, both analytically and computationally.

**Table I. Comparison of diffusivity and orientational relaxation time of sulfate, ammonium, and methane.**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D_{\text{Exp.}}$ ($\times 10^{-5} \text{ cm}^2/\text{S}$)</th>
<th>$D_{\text{Simu}}$ ($\times 10^{-5} \text{ cm}^2/\text{S}$)</th>
<th>$\tau_{\text{2}}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>1.065</td>
<td>0.95</td>
<td>11.66</td>
</tr>
<tr>
<td>Ammonium</td>
<td>1.957</td>
<td>2.15</td>
<td>8.39</td>
</tr>
<tr>
<td>Methane</td>
<td>\ldots</td>
<td>3.1619</td>
<td>0.071</td>
</tr>
</tbody>
</table>

**FIG. 14.** A hypothetical calculation to demonstrate the role of symmetry in the charge distribution on the orientational relaxation of a polyatomic ion. (a) Model ion with the same geometry as that of the nitrate ion, but the charges on peripheral atoms are different ($q_a = q_b$), (b) orientational correlation function, $C_2(t)$, of the nitrate ion ($q_a/q_b = 1$) and the model ions ($q_a/q_b = 1$) in water, and (c) diffusivity of the nitrate ion and the same model ions in water. Note that both the diffusion and the rotational relaxation are the fastest for the symmetric ion (taken from Ref. 13).
In order to comprehend the role of rotational motion on the dynamics of a polyatomic ion better, let us compare the limiting case of a rotationally frozen (RF) ion ($\tau_R = \infty$) with one that is rotationally mobile (RM) and hence can couple to the dynamics of the hydrogen bonding network structure of water. The diffusivity of rotationally mobile ions is given by the zero frequency friction $\zeta_{RM \text{ion}}(z = 0)$ which is lower than $\zeta_{RF \text{ion}}(z = 0)$ due to the shift in the frequency caused by the self-rotation [Fig. 16(c)]

$$\zeta_{RF \text{ion}}(z = 0) = \frac{2k_B T \rho_0}{3(2\pi)^2} \int_0^{\infty} dk k^4 F_{\text{ion}}(k, t) e^{-D_{\text{ion}}k^2t/\tau_{\text{solvent}}(k, t)} ,$$

$$\zeta_{RF \text{ion}}(z = 0) = \frac{\zeta_{\text{ion}}(z = 1/\tau_R)}{\tau_{\text{RM \text{ion}}}(z = 0)} .$$

(29)
Now, a simple (albeit a bit crude) approximation [Eq. (30)] allows one to obtain a semiquantitative result of diffusivity given by Eq. (31)

$$
C^{\text{DF}}(z = 0) = C \int_0^\infty dt e^{-\frac{t}{\tau}} = C^* TR,
$$

$$
C = \frac{2k_B T \rho_0}{3(2\pi)^{3/2}} \int_0^\infty dk k^4 e^{-1} \int_{\mathbf{R},q} C_{q,0}^2 \left( z = 0 \right) = \frac{C_{q,0}^2}{\rho_0} \tau_{R,q} \left( z = 0 \right) = \frac{C_{q,0}^2}{\rho_0} \tau_{R,q} \left( z = 0 \right). \quad (30)
$$

As shown in Fig. 14(b), by gradual introduction of asymmetry into the model ions, the diffusivity gradually decreases. If one now uses the rotational decay constants of those model ions and assumes that the constant $C$ for all the model ions is the same, one obtains the ratio $C_{q,0}^2/\rho_0$ given in Table II: This MCT formalism is found to agree fairly well with simulation results except for $q_{0s}/q_{0b} = 0.125$ which is due to the approximation $C_{q,0}^2/\rho_0 = 0.125$ as the constant $C$ involves the direct correlation function between the solute and solvent which is significantly different for these two model ions.

<table>
<thead>
<tr>
<th>$q_{0s}/q_{0b}$</th>
<th>$C_{q,0}^{\text{MCT}}$</th>
<th>$D_{q,0}^{\text{MCT}}/D_{q,0}^{\text{id}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>0.32</td>
<td>0.65</td>
</tr>
<tr>
<td>0.5</td>
<td>0.57</td>
<td>0.74</td>
</tr>
<tr>
<td>1.5</td>
<td>0.85</td>
<td>0.86</td>
</tr>
<tr>
<td>2.0</td>
<td>0.67</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table II. Comparison of the simulation results with that obtained from semiquantitative mode-coupling theory.

Now, for a liquid such as water, orientational ordering plays an important role in determining the total entropy of the system because here an equilibrium thermodynamic property is said to determine a transport property. The Adam-Gibbs relation was initially proposed for viscosity.

In a recent perspective article, Dyre had discussed excess entropy scaling in detail. Chakravarty showed earlier that excess entropy scaling was not obeyed for tetrahedral systems such as water and silica at moderate pressure and dense liquid state points. While most of the discussions focus on the variation of diffusion when entropy changes with temperature or pressure and the solute-solvent system is left unchanged, here we have an interesting situation where diffusion changes substantially, while the temperature and pressure remain unchanged, but the solute-solvent system is changed.

The question that arises now is can any of the above two relatively successfully expressions describe the variation of diffusion and entropy as size of the solute varies? This is certainly a crucial question.

For polyatomic molecules, the entropy of the solute must contain the rotational entropy. For a liquid with polyatomic molecules such as water, if we neglect the vibrational contribution, the total entropy can be decomposed as

$$
S = S_{tr} + S_{id} + S_{ex}(\{\rho(r,\Omega)\}, T). \quad (35)
$$

$S_{ex}$ is the excess entropy that arises from the correlation of liquid molecules which again derives its contribution from both translational and rotational motions. The translational entropy of an ideal gas system, $S_{id}$, is given by the well-known Sackur-Tetrode equation

$$
S_{id}^{\text{ST}} = \frac{5}{2} R + R \ln \left[ \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]. \quad (36)
$$

And the rotational entropy of ideal gas of polyatomic molecules can be written as

$$
S_{id}^{\text{ROT}} = \frac{3}{2} R + R \ln \left( \frac{8\pi^3}{\rho_0} \left( I_A I_B I_C \right)^{1/2} \frac{k_B T}{h^2} \right)^{3/2}. \quad (37)
$$

Here $I_A$, $I_B$, and $I_C$ are the components of moments of inertia along three principle axes. For a symmetric molecule with a given total moment of inertia, the rotational entropy is highest as $I_A = I_B = I_C$. Here, $\rho_0$ is the symmetric factor; for an asymmetric molecule, it is 1, for $H_2O$, it is 2, etc. In the entropic unit (eu) at 1 atm pressure and 298 K temperature, the ideal translational entropy of water ($S_{id}^{\text{ST}}$) is 17.41 eu and the ideal rotational entropy, $S_{id}^{\text{ROT}}$, is 5.45 eu, which is about 30% of the translational contribution.

In the usual applications of the diffusion-entropy relations, the entropy is assumed to be given by the solvent, and the role of solute seems to have been neglected. However, the excess entropy is due to correlations and it changes depending on the nature of solutes in an aqueous solution. For an atomic system, the translational part of the excess entropy can be approximated by a two-body excess entropy, $S_2 (S_{id}^{\text{mol}} = S_2)$, that is measured by the two body pair correlation function or radial distribution function (RDF), $g(r)$. The well-known relation between the entropy and RDF is given by

$$
S_2 = N k_B \int_0^\infty \left\{ g(r) \ln[g(r)] - [g(r) - 1] \right\} r^2 dr. \quad (38)
$$

Now, for a liquid such as water, orientational ordering plays an important role in determining the total entropy of the system.
because depending on the nature of the solute, structural ordering of water changes significantly. In water, orientational correlations imposed by hydrogen bonding give rise to spatial ordering. The orientational tetrahedral order parameter, $q_{\text{tet}}$, can capture the change in the local tetrahedral network of water molecule in the presence of solutes and is defined as

$$q_{\text{tet}} = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left( \cos \psi_{jk} + \frac{1}{3} \right),$$

(39)

where $\psi_{jk}$ is the angle between the bond vectors $r_{ij}$ and $r_{ik}$, where $j$ and $k$ label four nearest neighbor oxygen atoms of $i$-th oxygen atoms of water. For an ideal tetrahedral structure, this order parameter becomes 1, and for ideal gas, it is zero.

For dilute (0.1M) aqueous solutions of the chloride salt of monatomic alkali cations, the calculated two-body excess entropy, $S_{\text{ex}}$, fails to capture the trend in diffusivity of these alkali cations. It has been pointed out recently that the same can be captured nicely if one computes a tetrahedral entropy as discussed below. A distribution of the local tetrahedral order parameter, $q_{\text{tet},i}$, is shown in Fig. 17(b). Although the bulk liquid structure is hardly affected by the presence of the ions in this low concentration of solutes [Fig. 17(a)], the hydrogen-bond network structure of water in the first hydration shell of the ions exhibits a remarkably different nature for these different sized ions. This leads to significant entropy differences in these solutions and different diffusivities of the ions.

Fortunately, the tetrahedral entropy of water may be calculated using the expression derived by Kumar et al.$^{91}$

$$S_{\text{tet}} = S_{0} + \frac{3}{2} k_{B} \int_{q_{\text{tet},\text{min}}}^{q_{\text{tet},\text{max}}} \ln(1 - q_{\text{tet}}) P(q_{\text{tet}}) dq_{\text{tet}},$$

(40)

where $k_{B}$ is the Boltzmann constant and

$$S_{0} = k_{B} \left[ \ln \Omega_{0} + \frac{3}{2} \ln \frac{8}{3} \right].$$

(41)

The values of tetrahedral entropy for different ionic solvation shells are found to exhibit a clear nonmonotonic behavior with ionic size.$^{92}$

In fact, the orientational arrangement and ordering induced on water by ions and ion pairs can lower the “local” entropy significantly. Investigations of the arrangement of water molecules around two similar sized ions have been carried out, with one positively charged ($K^{+}$) and the other negatively charged ($Cl^{-}$). It is observed that the tetrahedral order parameter of water around these similar sized ions is significantly different. The value of tetrahedral entropy ($S_{\text{tet}} - S_{0}/k_{B}$) obtained for the first solvation shell water molecules of $K^{+}$ is $-1.097$, and that of $Cl^{-}$ is $-0.909$. It is to be noted here that this is the value of the excess entropy as the more negative it becomes, the actual entropy is reduced more. These results partly explain the enhanced diffusivity of anions over cations [shown in Fig. 2(a)].

For polyatomic ions, the situation is even more interesting as the solute, also, exhibits rotational jump motion and translation-rotation coupling. As discussed earlier [Eq. (35)], the entropy of the solute increases due to the rotational contribution. The rotational jump motions of the polyatomic solute are a way to explore the rotational conformation, the associated excess entropy. Otherwise, the dynamics would be slower due to the highly correlated and structured solute and solvent system. These interesting and important aspects of ion dynamics demand future work in this direction.

XI. INTERACTION BETWEEN SINGLE PARTICLE AND COLLECTIVE DYNAMICS

The mode coupling theory correctly brings out the collective nature of the single particle dynamics. The self-diffusion coefficient is a single particle property. Thus, the ions execute a complex random walk which is coupled to the rotational and translational motions of water molecules. The trajectory of ions in water reflects the dynamics of surrounding water [Figs. 8(c) and 8(d)]. In fact, the relationship between the diffusion and entropy is a reflection of the coupling between the single particle and collective dynamics.

As depicted in the explanatory MCT flow chart (Fig. 4), the calculation of dielectric friction involves both the self-dynamic structure factor of the ion, $F_{\text{out}}(k, t)$, and the coherent orientational dynamic structure factor of the solvent, $F_{\text{solvent}}^{\text{tot}}(k, t)$. For nonpolar spherical systems, the analogous quantity is $F(k, t)$. $F(k, t = 0) = S(k)$ is the static structure factor that describes pair correlation in an interacting system. A recent theoretical study by Nandi et al. investigated the reduction of the mode coupling theory to a relationship between the diffusion and entropy.$^{93}$

There have been reports of long range orientational ordering of water around a solute which in turn suggests that ions interact at extraordinarily large separations.$^{94}$ At present, this appears to be a controversial issue. While a few experiments seem to suggest the presence of interionic interaction at large separations, simulations...
find no clear evidence of such a presence. Water and other ions effectively screen the interionic interaction.

XII. INTERACTION BETWEEN IONS: MULTIPLE SCATTERING SCENARIO

As mentioned, there is yet no clear consensus about the distance of separation beyond which molecular aspects of ion-water interaction do not affect ion-ion interaction. This is because not only does the long range nature of ion-ion interaction propagate through the intervening water molecules, but also the water molecules undergo orientational and structural change, and the two ions can “feel” each other in a way different from what would be dictum of the continuum model. In the continuum model based theories of Debye-Hückel-Onsager who developed the ion atmosphere theory, or even in the Chandra-Bagchi mode coupling theory that uses an effective continuum model. In all these theories, the effects of the medium on the interaction between the ions, the molecularity of the solvent was neglected. In all these theories, the effects of the medium on the interaction between any two ions is described by using the dielectric constant and the force of interaction between two charges q, and q, decays with separation r which is given by the screened Coulomb’s law (SCL). Although asymptotically the force between any two ions in a dielectric medium must approach SCL, a question has been raised about the minimum separation where SCL could become valid.

Numerical simulations with model potentials show that the effect of one ion on another in water varies considerably from what is predicted by the screened Coulomb’s law (SCL). The water molecules tend to solvate the ions in a specific manner, as demanded by electrostatics, but the ensuing arrangements around two ions can interfere with each other, leading to a pronounced departure from the prediction of the SCL. However, the SCL is restored when the separation is typically larger than 15 Å or so. At short separations, one finds an interesting ordered arrangement of the water molecules around the ions, as shown in Fig. 18. Such interactions affect not only the motion of ions but also those of water molecules in electrolyte solutions at high concentrations.

Clearly, powerful forces are at play at small separations between ions. This raises the possibility that at somewhat higher concentrations, water plays an important role in mediating effective interactions between the ions. The situation becomes more complex when multiple ions interact through water. Thus, water introduces an effective three and four particle interactions envisaged neither in the screened ions interact through water. Thus, water introduces an effective three and four particle interactions envisaged neither in the screened Coulomb’s law nor in analytical theories, such as mode coupling.

XIII. EFFECT OF ION DYNAMICS ON THE SOLVENT DYNAMICS

As discussed earlier, the presence of the ion and its dynamics affect the structure and dynamics of the surrounding water not to a large extent. Hynes and co-workers demonstrated the interesting shift in water reorientational dynamics in different types of hydration shells including anionic, hydrophobic, etc. A simulation study at a small concentration of 0.1M salt solution finds that the dynamics of water changes significantly. In an aqueous nitrate solution, the diffusivity of SPC/E (extended simple point charge model) water is found to have a value of 2.97 × 10⁻⁵ cm²/s, whereas in an aqueous sulfate solution, the diffusivity of water is obtained as 2.21 × 10⁻⁵ cm²/s. The translational dynamics and rotational dynamics of sulfate ions are much slower than those of the nitrate ions. The diffusivities of ions and water in these two systems are given in Table III.

Interestingly, mode-coupling theory can straightforwardly explain this effect of ion dynamics on water dynamics. In Eqs. (16) and (28), we have shown the mode-coupling theory expression for friction on the monatomic and polyatomic ions, respectively. An electrolyte solution, the total friction on a water molecule derives its contributions from ion-water and water-water interactions. Ion-water contributions are shown in Eqs. (16) and (28). Now, for water-water interaction, it again has dependencies on self- and cross-interactions as given below.

\[
\Gamma_{i}^\text{int}(z) = \Gamma_{\text{bare}} + A \int_0^\infty \int_0^\infty dk \, \sum_{l,m} c_{l,m}^2(k) F_{l,m}^{\text{int}}(k,t),
\]

\[
\Gamma_{i}^\text{tot}(z) = \Gamma_{\text{bare}} + A \int_0^\infty \int_0^\infty dk \, \sum_{l,m} F_{l,m}^{\text{tot}}(k,t),
\]

TABLE III. Dynamics of cation, anion, and water in aqueous KNO₃ and aqueous Na₂SO₄.

<table>
<thead>
<tr>
<th></th>
<th>KNO₃ in water</th>
<th>Na₂SO₄ in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation (K⁺) Anion (NO₃⁻)</td>
<td>2.05 ± 0.06</td>
<td>1.67 ± 0.07</td>
</tr>
<tr>
<td>Cation (Na⁺) Anion (SO₄²⁻)</td>
<td>1.56 ± 0.03</td>
<td>0.95 ± 0.08</td>
</tr>
</tbody>
</table>
where the constant $A = \frac{\rho \cdot c_{i,l,m}(k)}{\Omega}$ is the $l_i l_j m$-th coefficient of the direct correlation function between the solute and solvent, and $F_{l,1,m}(k, t)$ and $F_{l,1,m}(k, t)$ are self- and cross-terms of the orientational correlation function, defined as

$$F_{l,1,m}(k, t) = \left\{ e^{i k r_{1}(1) - r_{1}(0)} Y_{lm}(\Omega_{1}(0)) Y_{lm}(\Omega_{1}(t)) \right\}, \quad (43)$$

$$F_{l,1,m}(k, t) = \sum_{k} \left\{ e^{i k r_{1}(1) - r_{1}(0)} Y_{lm}(\Omega_{1}(0)) Y_{lm}(\Omega_{1}(t)) \right\}. \quad (44)$$

Now, ion-water interaction modifies the collective dynamics of solvent which in turn modifies the self-motion of water by Eq. (42). This boot-strapping, which is the hallmark of mode coupling theory, comes here real handy in explaining a rather complex dynamical process. Note that neither a hydrodynamic theory nor a continuum model based description can explain these intricate interdependencies of coupled solute-solvent dynamics. Therefore, MCT provides rich insight into ion-water dynamics and provides a great perspective over the entire dynamical process.

XIV. IONS IN AQUEOUS BINARY MIXTURES

Binary mixtures constitute important class of solvents that exhibit remarkable composition dependence in their physical and chemical properties and potentially can serve as the solvent for electrolyte solutions in practical applications. Although there have been a large number of studies on binary mixtures, relatively few studies have appeared on the conductivities and thermodynamic properties of ions in binary mixture.

Water-ethanol binary mixtures have drawn a great deal of attention recently. Both computer simulation and experimental studies have shown that these mixtures exhibit multiple composition dependent anomalies. There are two broad range of compositions, one between 10% and 20% and another between 30% and 40%. The dependent anomalies. There are two broad range of compositions, studies have shown that these mixtures exhibit multiple composition dependent anomalies. There are two broad range of compositions, one between 10% and 20% and another between 30% and 40%. The composition of anomalous dependence is found to depend on the concentration of number density and current density in the mode coupling theory of transport processes of dense liquids.

In a notable study, Bošković et al. investigated properties of KCl in a water-ethanol binary mixture. They observed a maximum in viscosity at around 20% mole fraction of ethanol. The viscosity maximum was found to be markedly asymmetric. The limiting ionic conductivity, however, showed a monotonic decrease with ethanol composition. The decoupling of limiting ionic conductivity was surprising. This deserves further study.

Another surprising observation was the presence of a maximum in the Walden product of KCl at EtOH composition of 10%. Since the Walden product already absorbs the effects of composition dependence of viscosity, the maximum at 10% is somewhat surprising. This could be attributed to nonhydrodynamic factors, such as preferential solvation.

It has been argued that water-ethanol mixture exhibits large scale fluctuations around 10% of EtOH. This maximum could be connected to such fluctuations which could give rise to enhancement of conductivity. Ions in an aqueous binary mixture could offer a rich field of research.

XV. MACROMOLECULAR POLYATOMIC IONS

It is fitting to discuss here the case of polyatomic macromolecular ions, such as DNA, RNA, and protein. These ions themselves are surrounded by other ions, not just the counterions but also the ions from the buffer. Electrophoresis is widely used to separate these kinds of polyelectrolytes. To investigate a better condition for separation, the dynamics of DNA electrophoresis has been studied extensively. Theoretically, dynamics of DNA or protein is studied using the anisotropic friction model in three-dimensional space by projecting the object along a particular axis. The hydrodynamic Stokes friction is calculated using a sophisticated technique called the triaxial ellipsoid method developed by Harding. DNA shows interesting conformational change events in the polymer solution as it migrates through the medium, and this is coupled to the conformational change in the polymers in the medium by a transient entanglement coupling mechanism.

Dielectric relaxation of an aqueous DNA solution gives highly nonexponential frequency or time dependence as evident from the Cole-Cole plot. This non-Debye behavior has been attributed to counterion fluctuations around DNA. The fluctuations have further been decomposed in terms of correlated motions of positively charged counterions along the negatively charged DNA phosphate backbone.

XVI. CONCENTRATION DEPENDENCE OF IONIC MOBILITY

Diffusion of individual ions gets profoundly influenced by the presence of other ions in the liquid because of the long range interaction. The concentration dependence of ion diffusion has been studied since the pioneering work of Debye, Huckel, and Onsager (DHO). These authors introduced the concepts of ion atmosphere relaxation and electrophoretic effect. The widely known expression of concentration dependence of ionic mobility is given by

$$\Lambda(c) = \Lambda_{0} - (A + Bc_{i}) \sqrt{c}, \quad (45)$$

where $A$ and $B$ are constants that depend on material constants, such as viscosity, dielectric constants, and universal constants such as the Avogadro number.

Despite its elegance and beauty, the Debye-Huckel-Onsager limiting law is valid only at very low concentrations, often less than 0.1M. Turq, Dufreche, and co-workers generalized the DHO law by using a mean spherical approximation approach which is fairly successful in providing a quantitative description until about 1M concentration. Chandra and Bagchi developed a quantitative theory inspired by the mode coupling theory of transport processes of dense liquids. The crucial observation in this theory is that the important slow variables in the dynamics of electrolyte solutions are the charge and the current densities. This logic runs parallel to the use of number density and current density in the mode coupling theory of nonpolar liquids. There are several new inputs in the implementation of the theory. In addition to the self-consistency discussed above, a fairly accurate expression for separation dependence of the ion-pair correlation function, presented by Attard, is used in the numerical work. The required direct correlation function is obtained by using the Ornstein-Zernike relation. The friction was calculated by integrating over the wavenumber space and both charge density contribution, which is the ion atmosphere term in the DHO treatment, and the current density term, which is the electrophoretic term, are treated at equal footing in Fig. 19, a comparison between the experiment, DHO theory, and the MCT prediction is shown.
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PERSPECTIVE

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In the case of electrolyte solution, the mode coupling theory with the additional slow variables is, as expected, a bit more involved. The resulting expressions are complex, but most importantly, they can all be reduced, under appropriate boundary conditions, exactly to the respective continuum model expressions.

A. Debye-Falkenhagen theory of frequency dependent friction

Debye-Falkenhagen (DF) predicted an unusual frequency (or time) dependence of the electrolyte friction which has indeed been observed in experiments.\footnote{115,116} This expression is given by

$$\zeta(\omega) = \frac{1}{1 + \frac{1}{\zeta^2}[1 - i\omega \tau_{atm}]}^{1/2}, \quad (46)$$

where $\tau_{atm}$ is the ion atmosphere relaxation time which is inversely proportional to the ion self-diffusion coefficient. Although the original derivation is not readily available, the mode coupling theory derivation is straightforward. First, one notes that since the electrochromeffect involves current density, the relaxation is fast and is ignored in DF and one considers only the atmosphere relaxation term. Second, the peculiar form of the ion atmosphere relaxation term naturally arises when we use diffusional approximation for the self- and the collective intermediate scattering function, as detailed in Ref. 113. When one includes the electrophoretic term, one finds an initial fast decrease in friction.

Chandra-Wei-Patey pointed out that frequency dependent friction can contain interesting information about an electrolyte solution.\footnote{117} It can capture the coupling between the translational motion of ion and rotational motion of solvent modes which they termed as the "dynamical solvent effect."

B. Onsager-Fuoss expression for concentration dependence of viscosity

Onsager and Fuoss\footnote{118} derived the following elegant expression for the excess viscosity $\eta_{excess}(c)$ due to the presence of the ions:

$$\eta_{excess}(c) = \frac{k_B T}{480\pi} \int_0^\infty dk k^3 F_c(k, t)^2 S_c(k)^4, \quad (48)$$

Although this expression looks simple, its derivation as presented by Onsager and Fuoss is highly nontrivial. On the other hand, MCT provides a simple and elegant derivation of the above expression. In fact, this derivation and its generalization can be truly regarded a significant triumph of the mode coupling theory.

As in dense liquids, the viscosity is determined by the transverse current–current correlation function. In the present case, it is the charge current correlation function. In the long wavelength limit. This procedure also serves to bring out the limitation of the continuum model expression. The full expression provides a stronger dependence of viscosity on concentration as indeed has been observed in experiments.

C. Concentration dependence of ion diffusion: Resolution of an anomaly

Several different experimental techniques have been used to measure the diffusion coefficient of an ion in an electrolyte solution. Two such experiments are NMR and quasi-elastic neutron scattering (QENS). Experiments, however, uncovered an interesting anomaly. When the diffusion coefficient of an ion was measured, it was found that the diffusion coefficient values reported by QENS were about 20% larger than those reported by NMR experiments. The puzzle was solved by using the mode coupling theory which allowed a calculation of the time dependent diffusion

$$D(t) = D_0 - 1.35 \times 10^{-13} c^{1/2} T \left[ 1 - \frac{8 k_B T}{3\zeta^2} \right]^{1/2}, \quad (49)$$

where $D_0$ is the self-diffusion coefficient in the long time from the initial value of $D(t)$.
One needs to observe that QENS is a short time measurement, while NMR is a long time measurement. Thus, diffusion measured by QENS probes friction effectively at short times which in this case is smaller than that measured by NMR. Thus, the difference is essentially a consequence of the time dependent response (or, viscoelasticity) of the electrolyte solution. If we delve a little deeper, it was due to the difference in time scales between the ion atmosphere relaxation and electrophoretic effect.

XVII. CONCLUSION

Although the journey of electrochemistry began as early as in the nineteenth century with Arrhenius, Nernst, Ostwald, and many others and was developed further by Debye, Huckel, Onsager, and others, many aspects of the dynamical features are yet to be unraveled even today. As many electrolytes with complex structures are routinely used in chemical industry, biology, and environmental processes, their structural and dynamical features are crucially important to understand.

In this Perspective article, we have attempted to summarize theoretical and computational advances in our understanding of the motion of ions in water. In the study of ion motion, a central role is played by ion diffusion as the ionic conductivity is closely related to this quantity which is the primary observable in an electrolyte solution. Theoretical study of diffusion proceeds through evaluation of the friction on an ion. The physics and chemistry behind the structural and dynamical features of monatomic ions are fairly well understood and well-studied. The same, however, is not true for diatomic and polyatomic ions where self-rotational jump motions of both the ions play an important role in the course of their overall dynamics. The situation becomes particularly intriguing because water molecules themselves are known to exhibit large amplitude jumps. For molecular ions, the jump motions of the solute and the solvent become coupled to give rise to new features. For example, a recent study by Banerjee et al. demonstrated that the coupled rotational jump of water and polyatomic solutes along with the translational-rotational coupling gives rise to a noticeably faster diffusion of symmetric ions (such as the nitrate ions) than the same for the asymmetric ions.

A valuable insight is obtained by studying the entropy of the ionic solutes. These ions cause an entropic cost to the system due to enhanced orientational ordering that gives rise to a “tetrahedral ordering” of water molecules that cage the ions. The rotational jumps of the symmetric polyatomic ions contribute to the total entropy of the system and increase their translational diffusion; on the other hand, slower rotational jump motion of the asymmetric ions reduces the translational motion of the ion. The jumps help realize the configuration space otherwise not easily attainable by the ions caged by the surrounding water molecules.

In order to develop a deeper, long-term perspective, we have discussed both the continuum model approaches and the microscopic theories, along with experimental and computer simulation results. Because of the long-range nature of ion-dipole and dipole-dipole interactions, a continuum model was initially thought appropriate. The continuum model theories developed by Boyd, Zwanzig, Onsager, and Hubbard provide elegant, nontrivial but closed form expressions that succeed in giving a semiquantitatively accurate description, in the sense that they all capture the nonmonotonic dependence of diffusion on ion size but fails at a quantitative level. We have discussed three essential aspects that get neglected in the continuum model theories but captured in a microscopic theory. First, it ignores the significant contribution of ion-solvent correlations at molecular length scales to the friction. This leads to an underestimation of the dielectric friction. Second, the memory function that is responsible for the ultrafast, sub-100 fs solvation dynamics in water, and also involved here to lower the value of the dielectric friction, is approximated by an overdamped slow diffusive kernel. This approximation leads to an overestimation of the friction. Third, the role of the translational modes of the solvent molecules in hastening the decay of ion-solvent correlations at molecular length scales. These are the same modes that give rise to the breakdown of the Onsager’s “inverse snow-ball picture.”

This leads again to an overestimation of the friction. The sum result is an incomplete description of the ion size dependence of the observed result.

For polyatomic ions with distributed charges, implementation of either the continuum model or the mode coupling theory is nontrivial. However, the area has seen some progress recently. This progress in analytical theoretical approaches has been driven by computer simulation results. We attempted to provide perspective into the rich dynamical features exhibited by these ions during their motion in water. Still, there remain a large number of systems in this classical area that deserve further study. An interesting class of systems that have scanty been explored is the binary mixture where the structure and dynamics of the ion-solvent system remain to be studied. Depending on the interaction between two different components and their coupling to different ions, i.e., monatomic, diatomic, and polyatomic, it is expected to possess a wide range of interesting structural and dynamical properties which are yet to be understood both by experiments and computations. Another area that remains neglected is the time or frequency dependent properties of electrolyte solutions involving polyatomic ions. They can provide valuable insight into the structure and dynamics of this class of systems.

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