

FEATURE ARTICLE

Beyond the Classical Transport Laws of Electrochemistry: New Microscopic Approach to Ionic Conductance and Viscosity

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The concentration dependence of the transport properties (i.e., the conductivity and the viscosity) of an electrolyte solution has been a subject of lively debate for a very long time. The foundation for understanding the transport properties of electrolyte solutions was laid down by Debye, Huckel, Onsager, and Falkenhagen who derived several limiting laws valid at low ion concentration. These classical laws have been rederived several times, although their extension to concentrated solutions has proven to be very difficult. We discuss a new microscopic approach toward understanding the transport laws of electrochemistry. This new approach is based on the general ideas of the mode coupling theory. We show that the mode coupling theory approach is appropriate in the present case because concentration effects arise from collective variables (like charge density and current) which are treated correctly by the mode coupling theory. The new theory can describe the crossover from the low to high concentration seamlessly. Our study yields microscopic expressions of both conductivity and viscosity in terms of static and dynamic structure factors of the charge and number densities of the electrolyte solution. The celebrated expressions of Debye, Huckel, and Onsager for static conductance, of Debye and Falkenhagen for frequency dependent electrolyte friction, and of Falkenhagen for the viscosity follow exactly from the present microscopic theory in the limit of very low ion concentration. Recently derived microscopic expressions of Chandra, Wei, and Patey for the frequency dependent conductivity can also be derived from the present scheme. The present theory is a self-consistent theory. For conductance, the agreement of the present theory with experimental results is satisfactory even up to one molar concentration. For viscosity, the theory seems to give the right trend and suggests directions for further improvement to explain the myriad of unexplained behavior known for a long time.

1. Introduction

The classical transport laws and theories of electrochemistry have been widely applied to understand the effects of ion concentration on the diffusion of ions, ionic conductivity, and the viscosity of electrolytes.^{1–11} The most celebrated among these is the Debye–Huckel–Onsager (DHO) law which predicts a square root concentration dependence of the ion conductance.^{12–13} There are two other laws which are often discussed in the literature. One of these is the Debye–Falkenhagen (DF) theory of the frequency dependence of ionic conductivity.¹⁴ One often refers to Debye–Falkenhagen effect as the anomalous rise of conductivity with frequency at low frequencies which follows from the Debye–Falkenhagen theory. Another well-known theory is the Falkenhagen–Onsager–Fuoss (FOF) theory of the concentration dependence of the excess viscosity of ionic solutions.^{15,16} This theory correctly explains the rise of viscosity with concentration in the limit of *very low* ion concentration.

The classical derivations of these transport laws were highly nontrivial, often involving astute use of electrohydrodynamics and irreversible thermodynamics—the classic 1932 article by Onsager and Fuoss¹⁶ is a case in point. Not only have these

laws been hailed as the intellectual triumphs of the last century, they have also been tremendously successful in explaining concentration dependence of conductance at low ion concentration. However, these laws are certainly not perfect. They are valid only at low ion concentration and are applicable for strongly dissociative salt solutions such as NaCl and KCl in water. Both the successes and the limitations of these classical theories can be traced back to the basic conceptual framework on which they are based. This conceptual framework has two basic ingredients. First, the solvent is treated as a structureless continuum with a given static dielectric constant and viscosity. Second, there exists an ion atmosphere of net opposite charge around each ion due to ion attraction. The radius of this ion atmosphere is the Debye length (λ_D) which has an inverse square root concentration dependence. The validity of the classical laws is crucially dependent on the value of the Debye length. When the Debye length is much larger than the molecular lengths (such as the radius of ions), then the classical description where the solvent is treated as a *dielectric continuum* is valid. The equilibrium theories based on this assumption are often referred to as ion attraction theory or the Debye–Huckel (DH) theory.¹⁷

There have been several attempts to derive and extend the limiting transport laws to higher concentrations from microscopic point of view. Friedman¹⁸ was the *first* to derive the

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limiting law of conductance from the time correlation function formalism at microscopic level. The correlation function approach was also employed by Resibois⁴ to derive the limiting law of conductance. The most notable among the studies at higher concentrations is the work of Friedman and co-workers^{19,20} and of Blum and co-workers.^{21–23} In the former approach, the motion of an ion is described as a Brownian particle in the force-field of other ions of the system. The force-field is described in terms of ionic pair correlation functions. A dynamical theory at Smoluchowski level is used to calculate the transport properties at finite ion concentration. In the approach of Blum and co-workers, one uses the formal expressions of the transport properties derived earlier by Onsager and Fuoss¹⁶ by using the continuity equation approach. These authors provided explicit expressions for the calculation of transport properties as functions of the equilibrium ionic pair correlation functions which are now available from the modern statistical mechanical theory of ionic solutions. Also, the difference between the self-diffusion and the conductivity was explicitly taken into account in the later work by Turq et al.^{22,23} Expressions derived in both the approaches reduce to the DHO law in the limit of low concentration. Also, these theories do considerably better than the original DHO expression at higher concentrations. Much less effort has been devoted to understand the frequency dependence of conductance or the concentration dependence of viscosity.

Computer simulation is a complementary method to study transport phenomena in ionic solutions. Among the simulation techniques, the method of molecular dynamics (MD)²⁴ allows us to study the structural and dynamical properties of both ions and solvent molecules at Born–Oppenheimer level of description. This technique has been used to study self-diffusion and conductivity of simple model solutions such as ions in Stockmayer liquid^{25,26} and also of more realistic solutions such as NaCl, KCl, and ZnBr₂ in water at finite concentrations.^{27–29} However, the implementation of this technique for ionic solutions is computationally very costly because of the multiplicity of components, the long-range nature of ionic interactions, and the very long run that is required to obtain statistically meaningful averages. This is why a great majority of the simulation studies have used techniques of stochastic simulations.²⁴ In these methods, the solution can be treated at the McMillan–Mayer level of description⁹ where solvent particles are not considered explicitly: they are represented by a dielectric continuum and the solute particles interact through solvent averaged potentials. Brownian Dynamics (BD) and Langevin Dynamics (LD) are the two most often used stochastic simulation methods that have been employed to calculate the self-diffusion and conductance of various aqueous ionic solutions.^{30–32} Reasonably good agreement has been found with experimental results for diffusion and conductance. The study of the frequency dependence of conductivity has also been carried out for model ionic solutions.^{25,26,33} These studies also showed the breakdown of Debye–Huckel and Debye–Huckel–Onsager classical laws at finite concentrations. To the best of our knowledge, no simulation study has yet been carried out to calculate the viscosity of ionic solutions.

Certainly one valuable lesson to be learned from the above studies of diffusion and conductance is that the dielectric continuum model itself may be trusted up to concentration as high as 1 M solution; the original DHO law breaks down even at 0.01 M. However, this relative success of the dielectric continuum model may be limited only to the calculation of diffusion and conductance and might not be extendable to other

transport properties, like the viscosity. In addition, there are several aspects of the earlier theoretical approaches which require further improvement. Most importantly, these theories are not self-consistent—a limitation which must be removed before one can treat higher concentrations.

Recently, we have been able to derive all the three above-mentioned classical transport laws using the basic concepts of mode coupling theory and the time dependent density functional theory.^{34–37} The resulting expression for the ionic conductance involves the dynamic structure factors and the current-current correlation functions of the ions. In fact, the ion atmosphere term is shown to correspond to the relaxation of dynamic structure factors of the ions and the electrophoretic term to the time correlation function involving the charge density and the current terms. When microscopic expressions are evaluated, agreement (at least) at par with the earlier theories are found for the electrolyte conductance. This approach also provides microscopic expressions for the frequency dependence of ionic conductivity and for the ionic contribution to the viscosity of an electrolyte solution.

The objective of this Article is to summarize and discuss the mode coupling theory approach to the transport properties of electrolyte solutions. The organization of the rest of the Article is as follows. In the next section, we discuss the elements of the mode coupling theory which shall be used here. Section 3 contains discussion of the zero frequency conductance and derivation of the DHO law. Section 4 contains the discussion of the frequency dependent conductivity and the Debye–Falkenhagen effect. Section 5 summarizes the work on the concentration dependence of viscosity. Numerical results of the electrolyte friction, conductivity and viscosity are discussed in section 6. Section 7 presents a discussion of a full microscopic theory. Section 8 concludes with a discussion of the future problems.

2. Mode Coupling Theory Approach to Electrochemistry

The mode coupling theory (MCT) was originally developed to explain the dramatic decrease in the values of the transport properties near the critical point. More recently, it has been used (with mixed success) to describe the anomalous dynamics in the supercooled liquid near the glass transition.^{38,39} While the basic idea behind the latter development is somewhat different from the former one, the structure of the theory has remained essentially the same. MCT is the natural framework to use for describing the transport phenomena of electrolyte solutions because here one is interested in the effects of collective dynamics such as ion atmosphere relaxation on the single particle properties. For applications to electrolytes, one needs to identify the slow variables which control the dynamics. In an electrolyte solution at not too high concentration, these slow variables are the charge density and the ion current. It is the charge density and the current which give rise to the square root concentration dependence of the conductance and the viscosity through ionic pair correlation functions at low concentration. Actually, the relevant length in the problem is still the Debye length whose inverse goes to zero as the square root of concentration of the ions.

At low concentration, ionic conductance is essentially driven by the self-diffusion of the ions. The latter is a single particle property in the sense that this property can be measured by following the motion of a single tagged ion. However, this single particle motion is intimately connected to the collective, many-body dynamics of the surrounding liquid and this coupling between the collective and the single particle motion makes the

calculation of self-diffusion coefficient of a tagged solute an extremely difficult problem.⁴⁰ One traditional approach has been to relate the friction on the ion to the viscosity of the medium, combined with the use of the exact Einstein relation between diffusion and friction.³⁸ The radius of the ion has often been used as a fit parameter. Although this method had some numerical success, the use of hydrodynamics for small particles has been shown to be seriously flawed on fundamental ground.⁴¹

The mode coupling theory provides a systematic way to treat this coupling between the single particle and the collective dynamics. There are several different approaches to this theory and all of them lead essentially to the same equations. The main idea is to express the friction on the tagged molecule (here ion) in terms of the relevant time correlation functions. For example, diffusion of a molecule should be coupled to density fluctuations which are responsible for relaxation of the surrounding cage and also to the current modes which contribute to the random motion of the molecule via the natural currents present in the liquid. Under some general approximations, the diffusion of a tagged molecule can be written as $D = D_{\text{mic}} + D_{\text{hyd}}$ ⁴² where D_{mic} denotes the microscopic contribution to diffusion which consists of a bare term and the collective density term and D_{hyd} is the hydrodynamic part which contains the contribution from the current modes.

The mode coupling theory has been constructed here considering only the collective ionic modes as the slow variables. This approach is valid at low ion concentration where the solvent modes relax much faster than the ionic modes. An extension of this approach has been discussed in section 7.

The hall mark of any mode coupling theory is a self-consistent calculation of the transport properties and the time correlation functions. For example, the contribution of the density term to diffusion itself depends on the self-diffusion coefficient. One eventually has a “mode coupling necklace” where all the terms are connected to each other, often by nonlinear equations. These equations are to be solved self-consistently. In the present work, MCT will be used to calculate the frequency dependent ionic friction and the self-diffusion coefficients. From the self-diffusion coefficients, we will calculate the conductance and the frequency dependent conductivity. As we will see in section 5, MCT also provides an expression for the ionic contribution to the viscosity in terms of the static and dynamic charge density structure factors of the solution.

3. The Total Electrolyte Friction and Limiting Ionic Conductance

In the limit of very low but finite ion concentration, the conductance is described by the well-known Debye–Hückel–Onsager limiting law^{12,13}

$$\Lambda_{\alpha}(c_{\alpha}) = \Lambda_{\alpha}^0 - [A + B\Lambda_{\alpha}^0]\sqrt{c_{\alpha}} \quad (1)$$

where Λ_{α} is the conductance of the ionic species α at concentration c_{α} and Λ_{α}^0 is the conductance at infinite dilution which is obtained by extrapolating the concentration to zero. A and B are the two constants which are determined by the properties of the ions and the medium.

In this section, we will calculate the conductance from a microscopic calculation of the electrolyte friction. We start with the following generalized Langevin equation for time evolution of the velocity of a single tagged ion of charge q_s ³⁸

$$\frac{\partial}{\partial t}v_s(t) = -\int_0^{\infty} dt'\zeta_s(t-t')v_s(t') + f_s(t) \quad (2)$$

where $\zeta_s(t)$ is the total friction acting on the single tagged ion and $f_s(t)$ is the so-called random force. The Laplace transform of $\zeta_s(t)$ is $\zeta_s(\omega)$ where $-i\omega$ is the Laplace frequency variable and i is the imaginary number. The frequency dependent self-diffusion coefficient $D_s(\omega)$ is related to the friction $\zeta_s(\omega)$ by the following generalized Nernst–Einstein relation

$$D_s(\omega) = \frac{k_B T}{m(-i\omega + \zeta_s(\omega))} \quad (3)$$

where k_B is Boltzmann constant, T is the temperature, and m is the mass of the tagged ion. As discussed in the last section, the total friction on the tagged ion can be decomposed into two parts: A microscopic relaxation term $\zeta_{s,\text{mic}}(\omega)$ and a hydrodynamic term $\zeta_{s,\text{hyd}}(\omega)$. The inverses of these two quantities add to give the inverse of the total ionic friction. The microscopic friction is most easily analyzed by using the Kirkwood’s formula for friction which expresses it in terms of an integration over the force–force time correlation function.⁴³ Since the time dependent force on the tagged ion has contributions from solvent density and polarization fluctuations^{44–46} and also from ion atmosphere fluctuations, one can decompose the total microscopic friction into a solvent contribution $\zeta_{s,\text{mic}}(c=0)$ which is assumed to be a constant independent of ion concentration and a *concentration dependent ion contribution* $\delta\zeta_{s,\text{mic}}(\omega)$ which originates from interaction with the ion atmosphere fluctuations. Here we calculate the ion contribution to the microscopic friction. Thus, the solvent contribution is not calculated microscopically, it determines the ion diffusion at infinite dilution whose value is assumed to be known from experiments.

The hydrodynamic contribution originates from the coupling of the ion velocity to the relevant current modes of the solution. Mode coupling theory directly provides an expression of the contribution of the currents of the system to the diffusion coefficient, that is, to the inverse friction.^{38,47–48} Since the current modes of the solution consists of both the solvent and ion currents, both contribute to the inverse of the friction. The hydrodynamic contribution to the total friction can, therefore, be expressed as^{34,35} $\zeta_{s,\text{hyd}}(z)^{-1} = \zeta_{s,\text{hyd}}(c=0)^{-1} + \delta\zeta_{s,\text{hyd}}(z)^{-1}$ where $\zeta_{s,\text{hyd}}(c=0)$ is the usual viscous friction which now also includes the additional dielectric friction contribution due to the polarization current.^{49,50} $\delta\zeta_{s,\text{hyd}}(\omega)$ represents the electrolyte friction on the tagged ion due to coupling with the ion atmosphere current. The latter is commonly known as the electrophoretic effect. As before, the solvent contribution is not calculated in the present work. It constitutes part of the ion diffusion at infinite dilution which is assumed to be known from experiments. The ion contribution to the hydrodynamic part or the electrophoretic effect is calculated here microscopically by using the mode coupling theory.

3.1. The Calculation of the Ion Atmosphere Contribution to the Microscopic Friction: The Asymmetric Effect

The ion atmosphere contribution to the microscopic electrolyte friction can be calculated from the correlation of the force exerted by the fluctuating ion atmosphere on the tagged ion by using the Kirkwood’s formula.⁴³ In time domain, the microscopic electrolyte friction can be expressed as

$$\delta\zeta_{s,\text{mic}}(t) = \frac{1}{3k_B TV} \int d\mathbf{r} \langle \mathbf{F}_s(\mathbf{r},t) \cdot \mathbf{F}_s(\mathbf{r},0) \rangle \quad (4)$$

where $\mathbf{F}_s(\mathbf{r},t)$ is the force exerted on the tagged ion due to its interaction with all other ions in the solution and V is the volume of the system. An expression for $\mathbf{F}(\mathbf{r},t)$ can be obtained from

density functional theory and it is given by^{34,35}

$$\mathbf{F}(\mathbf{r}, t) = k_B T n_s(\mathbf{r}, t) \nabla \sum_{\alpha} \int d\mathbf{r}' c_{s\alpha}(\mathbf{r}, \mathbf{r}') \delta \rho_{\alpha}(\mathbf{r}', t) \quad (5)$$

where $n_s(\mathbf{r}, t)$ represents the position (\mathbf{r}) and time (t) dependent density distribution of the tagged ion and $\delta \rho_{\alpha}(\mathbf{r}, t)$ is the collective density fluctuation which is equal to $\rho_{\alpha}(\mathbf{r}, t) - \rho_{\alpha}$, where ρ_{α} is the average number density of ionic species α and $c_{s\alpha}(\mathbf{r}, \mathbf{r}')$ is the direct correlation function between species α and the tagged ion. Because of the presence of convolution integral in eq 5 and of isotropy of the system, final expressions are much simpler in the Fourier space. The final expression for the microscopic electrolyte friction has the following simple expression^{34,35}

$$\delta \zeta_{s, \text{mic}}(t) = \frac{k_B T}{3(2\pi)^3} \sum_{\alpha, \beta} \int d\mathbf{k} k^2 c_{s\alpha}(k) \sqrt{\rho_{\alpha} \rho_{\beta}} G_{\alpha\beta}(k, t) c_{s\beta}(k) F_s(k, t) \quad (6)$$

where the wavevector \mathbf{k} is the Fourier variable conjugate to \mathbf{r} and $G_{\alpha\beta}(k, t)$ is the Fourier transform of the ionic van Hove function between species α and β which is defined as

$$G_{\alpha\beta}(k, t) = (N_{\alpha} N_{\beta})^{-1/2} \langle \rho_{\alpha}(\mathbf{k}, t) \rho_{\beta}(-\mathbf{k}) \rangle \quad (7)$$

where $\langle \dots \rangle$ denotes average over an equilibrium ensemble and $\rho_{\alpha}(\mathbf{k}, t)$ is the Fourier transform of $\rho_{\alpha}(\mathbf{r}, t)$. N_{α} and N_{β} are the number of ions of species α and β in the solution, respectively. Later, we will denote the Fourier-Laplace transform of the van Hove function as $G_{\alpha\beta}(k, \omega)$. $F_s(k, t)$ is the self-dynamic structure factor of the tagged ion. Clearly, the effects of self-motion on the ionic friction is contained in $F_s(k, t)$. Equation 6 is an important result. Note that the same expression can be defined from a more rigorous analysis, as the one given by Sjogren and Sjolander.⁴⁷

A microscopic calculation of the density relaxation term requires tractable expressions of the wavenumber (k) and time (t) (or frequency (ω)) dependent ionic van Hove functions. Such expressions can be obtained from the time dependent density functional theory. In the present work, we ignore the explicit dynamical coupling of ions with the solvent and we include the effects of the solvent in an effective manner. Thus, for the calculation of the ion-ion correlations, it is assumed that the solvent is a dielectric continuum with dielectric constant ϵ and the ions interact with a solvent averaged interaction potential, i.e., with a long-range Coulomb potential scaled by the dielectric constant of the solvent.³⁸ Also, the dynamics of ions is now described by generalized Smoluchowski theory with appropriate solvent averaged mean potential and diffusion coefficients. We note that the assumption of solvent continuum for the calculation of the ion-ion correlations is expected to be valid in the limit of very low ion concentrations. Use of time dependent density functional theory leads to the following generalized Smoluchowski equation for the frequency dependent van Hove function^{35,51}

$$G_{\alpha\beta}(k, \omega) = [-\omega + D_{\alpha}(\omega)k^2]^{-1} S_{\alpha\beta}(k) + \frac{D_{\alpha}(\omega)k^2}{-\omega + D_{\alpha}(\omega)k^2} \sum_{\gamma=1}^2 \sqrt{\rho_{\alpha} \rho_{\gamma}} c_{\alpha\gamma}(k) G_{\gamma\beta}(k, \omega) \quad (8)$$

where the $D_{\alpha}(\omega)$ is the frequency dependent diffusion coefficient of species α and $c_{\alpha\beta}(k)$ is the Fourier transform of the direct

correlation function between species α and β . $S_{\alpha\beta}(k) = G_{\alpha\beta}(k, t = 0)$ where $S_{\alpha\beta}(k)$ is the partial static structure factor between species α and β .

The coupled equations as given by eq 8 for the van Hove functions can be solved to obtain the following explicit result for the time dependence of the ionic van Hove functions^{35,51}

$$\sum_{\alpha\beta} \sqrt{\rho_{\alpha} \rho_{\beta}} q_{\alpha} q_{\beta} G_{\alpha\beta}(k, \omega) = \frac{1}{Z(k, \omega)} [-i\omega \sum_{\alpha\beta} \sqrt{\rho_{\alpha} \rho_{\beta}} q_{\alpha} q_{\beta} S_{\alpha\beta}(k) + D_2(\omega)k^2 \Delta(k) \{ \sqrt{\rho_1 q_1} S_{11}(k) + \sqrt{\rho_2 q_2} S_{12}(k) \}^2 + D_1(\omega)k^2 \Delta(k) \{ \sqrt{\rho_2 q_2} S_{22}(k) + \sqrt{\rho_1 q_1} S_{21}(k) \}^2] \quad (9)$$

where

$$Z(k, \omega) = -\omega^2 - i\omega \Delta(k) [D_1(\omega)k^2 S_{22}(k) + D_2(\omega)k^2 S_{11}(k)] + D_1(\omega)D_2(\omega)k^4 \Delta(k) \quad (10)$$

and $\Delta(k) = [S_{11}(k)S_{22}(k) - S_{12}(k)^2]^{-1}$. The Laplace transform of the self-dynamic structure factor of the tagged ion can be described by the following equation

$$F_s(k, \omega) = \frac{1}{-i\omega + D_s(\omega)k^2} \quad (11)$$

The analytical solutions of the ionic structure factors and the direct correlation functions are known in the literature. Thus, eqs 6–10, together with the hydrodynamic term discussed later, form a set of self-consistent equations which can be solved to obtain the microscopic electrolyte friction.

3.2. Calculation of the Ion Atmosphere Contribution to the Hydrodynamic Friction: The Electrophoretic Effect. The ion atmosphere contribution to the hydrodynamic friction originates from the coupling of the velocity of the tagged ion with the current mode of the ions. A formal expression of this friction can be derived from mode coupling theory by using $\rho^c(k)\mathbf{j}(-k)$ as the relevant binary product where $\rho^c(k)$ and $\mathbf{j}(k)$ are the charge density and total ion current of the solution, respectively. The hydrodynamic friction is then given by

$$\frac{k_B T}{\delta \zeta_{s, \text{hyd}}(t)} = \sum_k \sum_{k'} \langle u_{0x}, \rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k}) \rangle \langle \rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k}), \rho^c(\mathbf{k}') \times \mathbf{j}(-\mathbf{k}') \rangle^{-1} \times \langle \rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k}), e^{iLt} \rho^c(\mathbf{k}')\mathbf{j}(-\mathbf{k}') \rangle \langle \rho^c(\mathbf{k}')\mathbf{j}(-\mathbf{k}'), \rho^c(\mathbf{k}')\mathbf{j}(-\mathbf{k}') \rangle^{-1} \times \langle \rho^c(\mathbf{k}')\mathbf{j}(-\mathbf{k}'), u_{0x} \rangle \quad (12)$$

where u_{0x} is the velocity of the tagged ion along a particular direction (say, x) and L is the Liouville operator. The vertexes and the time correlation function in the above expression can be evaluated by using the following decomposition of the charge density and the ion current $\rho^c(k) = \rho_0^c(k) + \rho_1^c(k) + \rho_2^c(k)$ and $\mathbf{j}(k) = \mathbf{j}_0(k) + \mathbf{j}_1(k) + \mathbf{j}_2(k)$ where $\rho_0^c(k)$ and $\mathbf{j}_0(k)$ are the charge density and current of the tagged ion and $\rho_{\alpha}^c(k)$ and $\mathbf{j}_{\alpha}(k)$ are those of species α surrounding the tagged ion.

After a straightforward analysis, the following expression is obtained for the electrophoretic friction^{34,35}

$$\frac{k_B T}{\delta \zeta_{s, \text{hyd}}} = \frac{1}{3\pi^2 \rho N} \int_0^{\infty} dt \int_0^{\infty} dk k^2 [\rho_1 G_{11}^d(k, t) - \rho_2 G_{12}^d(k, t)] C^T(k, t) \quad (13)$$

where ρ is the total ion density and N is the total number of ions in the solution. $G_{\alpha\beta}^d(k, t)$ is the distinct part of the van Hove function between species α and β and $C^T(k, t)$ is the transverse part of the current correlation function. Note that the relaxation of the transverse velocity correlation function occurs much faster than the distinct van Hove functions and the major contribution to the above integral comes from the short time region where $G_{11}^d(k, t) \approx h_{11}(k)$ and $G_{12}^d(k, t) \approx h_{12}(k)$ where $h_{\alpha\beta}(k)$ is the Fourier transform of the total pair correlation function between species α and β . We also assume an exponential decay of $C^T(k, t)$ of the following form⁴²

$$C^T(k, t) = \frac{Nk_B T}{m} e^{-\eta k^2 t / \rho m} \quad (14)$$

where η is the viscosity of the solution. Equation 14 can be substituted in eq 13 to obtain an expression for the electrophoretic friction in terms of viscosity η and ionic pair correlation functions.

Note that both $F_s(k, t)$ and $G_{\alpha\beta}(k, t)$ depend on the self-diffusion coefficient of the ions. On the other hand, these correlation functions determine the self-diffusion coefficient through eqs 6–11 and 13. Thus, the calculation of D requires a self-consistent solution of these expressions. This is nontrivial. As already mentioned, such self-consistent calculation is the hallmark of any MCT calculation. In fact, strictly speaking, one should include the expression for viscosity (derived in section 5 below) in this self-consistent calculation. We have neglected this complication here because the concentration dependence of viscosity is not significant at low and intermediate concentrations.

3.3. Reduction to Debye–Huckel–Onsager Limiting Law.

It is shown here how the present molecular theory reduces to the well-known DHO law when applied to solutions of very low concentration. For convenience, the expression for the microscopic friction is rewritten in the following form³⁵

$$\delta\zeta_{s,\text{mic}} = \frac{k_B T}{3(2\pi)^3} \int_0^\infty dt \int d\mathbf{k} k^2 [h_s(k)] [S(k)]^{-1} [G(k, t)] [S(k)]^{-1} [h_s(k)]^\dagger F_s(k, t) \quad (15)$$

where $[h_s(k)]$ is the row matrix $[\sqrt{\rho_1} h_{s1}(k) \sqrt{\rho_2} h_{s2}(k)]$, $[h_s(k)]^\dagger$ is the transpose of $[h_s(k)]$. $[S(k)]$ and $[G(k, t)]$ are the 2×2 structure factor and van Hove function matrices of the ions.

3.3.1. Debye–Huckel Expression. We shall first derive the original Debye–Huckel expression¹² for the asymmetric effect. For this case, we ignore the self-motion, i.e., we set $F_s(k, t) = 1$ and we assume that the diffusion coefficients of the positive and negative ions are equal i.e., we assume $D_s = D_1 = D_2$. In this simplified case, the time integral of the van Hove function is given by

$$\int_0^\infty dt [G(k, t)] = \frac{[S(k)]}{k^2 D_s [S(k)]^{-1}} \quad (16)$$

We substitute eq 16 in eq 15 to obtain the following expression for the microscopic friction

$$\delta\zeta_{s,\text{mic}} = \frac{k_B T}{3(2\pi)^3 D_s} \int d\mathbf{k} [h_s(k)] [h_s(k)]^\dagger \quad (17)$$

Since our goal is to derive the DHO law, we assume the ions to be point ions and use the following Debye–Huckel solution¹⁷

for the Fourier transform of the pair correlation function

$$h_{\alpha\beta}(k) = -\frac{4\pi q_\alpha q_\beta}{\epsilon k_B T} \frac{1}{k^2 + \kappa_D^2} \quad (18)$$

in eq 17 and evaluate the integral over the wavevector space to obtain the following expression for $\delta\zeta_{s,\text{mic}}$

$$\delta\zeta_{s,\text{mic}} = \frac{q_s^2 \kappa_D}{6\epsilon D_s} \quad (19)$$

where κ_D is the inverse Debye screening length given by

$$\kappa_D = \left(\frac{4\pi}{\epsilon k_B T} \sum_\alpha \rho_\alpha q_\alpha^2 \right)^{1/2} \quad (20)$$

The above expression is precisely the one originally derived by Debye and Huckel ignoring self-motion of the tagged ion.¹²

3.3.2. Onsager's Correction: DHO Expression. Next, we derive Onsager's correction¹³ by including the self-motion but still assume that the diffusion coefficients are equal. The microscopic friction can now be written as

$$\delta\zeta_{s,\text{mic}} = \frac{k_B T}{3(2\pi)^3} \int_0^\infty dt \int d\mathbf{k} k^2 [h_s(k)] [S(k)]^{-1} [G'(k, t)] \times [S(k)]^{-1} [h_s(k)]^\dagger F_s(k, t) \quad (21)$$

where $[G'(k, t)]$ is the modified van Hove function matrix given by $[G'(k, t)] = e^{-D_s k^2 t} [G(k, t)]$. The time integral of the modified van Hove matrix can be derived from the molecular hydrodynamic equations described earlier and is given by

$$\int_0^\infty dt [G'(k, t)] = \frac{[S(k)]}{D_s k^2 + D_s k^2 [S(k)]^{-1}} \quad (22)$$

We substitute eq 22 in eq 21 and use the relation between the structure factor and the pair correlation function matrices to obtain

$$\delta\zeta_{s,\text{mic}} = \frac{k_B T}{6D_s(2\pi)^3} \int d\mathbf{k} [h_s(k)] \times \left\{ 1 - \frac{1}{2}[h(k)] + \frac{1}{4}[h(k)]^2 \dots \right\} [h_s(k)]^\dagger \quad (23)$$

where $[h(k)]$ is the 2×2 matrix of ion–ion pair correlation functions. The various terms in the right-hand side of the above equation can be evaluated analytically by using Debye–Huckel solution for the ionic pair correlation functions, and the final result is³⁵

$$\delta\zeta_{s,\text{mic}} = \frac{q_s^2 \kappa_D}{6\epsilon D_s} (2 - \sqrt{2}) \quad (24)$$

The above expression is identical with the one derived by Onsager¹³ for a binary electrolyte by including the self-Brownian motion of the tagged ion. We note that the quantity $(2 - \sqrt{2})$ is denoted as the w factor in DHO law for a binary electrolyte.

3.3.3. The Generalized DHO Expression. Now we consider the more general case where self-motion is included and the diffusion coefficients of the positive and negative ions are taken to be unequal, i.e., $D_1 \neq D_2$. In this case, the time integral of

the modified van Hove function matrix is given by

$$\int_0^\infty dt[G'(k,t)] = \frac{[S(k)]}{k^2[D_s] + k^2[D][S(k)]^{-1}} \quad (25)$$

where

$$[D_s] = \begin{bmatrix} D_s & 0 \\ 0 & D_s \end{bmatrix}$$

and

$$[D] = \begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix}$$

Again, we substitute eq 25 in eq 21, use the relation between the structure factor and the pair correlation function and evaluate the integral over wavevector space to obtain the following final expression for the microscopic friction

$$\delta\xi_{s,\text{mic}} = \frac{q_s^2 \kappa_D}{6\epsilon D_s} 2 \left[1 - \left(1 - \frac{\sum_\alpha \rho_\alpha q_\alpha^2 D_s / (D_s + D_\alpha)^{1/2}}{\sum_\alpha \rho_\alpha q_\alpha^2} \right)^2 \right] \quad (26)$$

The above expression reduces to the DHO expression for electrolyte friction when D_s is taken to be equal to D_1 and D_2 . Also, the above expression becomes identical with the one of Onsager (derived in 1945)⁵² and of Friedman and co-workers¹⁹ when D_s and D_α ($\alpha = 1, 2$) terms in the right-hand side of the above equation are replaced D_s^0 and D_α^0 which are the values of the ion diffusion coefficients in the limit of infinite dilution.

Now we discuss the calculation of the hydrodynamic term in the limit of zero ion size and very low concentration. In this limiting situation, the Debye–Huckel solution of the ionic pair correlation functions can be used. We also set $\sigma = 0$ in eq 13 and we evaluate the integral over the wavevector space to obtain

$$\frac{1}{\xi_{s,\text{hyd}}} = \frac{1}{\xi_{s,\text{hyd}}(c=0)} - \frac{\kappa_D}{6\pi\eta} \quad (27)$$

where the second term represents the electrophoretic contribution to the total diffusion. We note that the above expression for the electrophoretic contribution is a general result which does not depend on any hydrodynamic boundary condition. This is exactly what was pointed out by Onsager.¹³

Equations 26–27, together with the relation between the diffusion coefficient and the conductance⁵³ and between c_α (the concentration of α th species in moles per liter) and ρ_α provide the following general equation for the conductance at very low concentration

$$\Lambda_\alpha(c_\alpha) = \Lambda_\alpha^0 - \left[\frac{\sqrt{2\pi N_0 q_\alpha^2 F}}{3\pi\eta(1000\epsilon k_B T)^{1/2}} + \frac{\sqrt{2\pi N_0 q_\alpha^2 |q_\alpha| w_\alpha} \Lambda_\alpha^0}{3\sqrt{1000(\epsilon k_B T)^{3/2}} \Lambda_\alpha^0} \right] \sqrt{c_\alpha} \quad (28)$$

where

$$w_\alpha = 2 \left[1 - \left(\frac{1}{2} \sum_\beta \frac{\Lambda_\alpha}{\Lambda_\alpha + \Lambda_\beta} \right)^2 \right] \quad (29)$$

where N_0 is Avogadro number and F is Faraday. The above equations are to be solved self-consistently, in general, to obtain

the numerical values of the conductances of positive and negative ions. Note that the factor w_α goes over exactly to the DHO value $(2 - \sqrt{2})$ for a binary electrolyte when one assumes $\Lambda_1 = \Lambda_2$. More importantly, in the same limit eq 28 becomes identical with the DHO limiting law. Furthermore, the above equation reduces to the expression of Friedman and co-workers¹⁹ when one replaces Λ_α terms in the right-hand side of the equation by Λ_α^0 . This is exact to the order $\sqrt{c_\alpha}$. Equation 29 predicts different values of w_α for positive and negative ions when their mobilities are different. The original DHO law does not reflect this asymmetry although it was later noticed by Onsager.⁵²

4. Frequency Dependent Ionic Conductivity: Debye–Falkenhagen Effect

The frequency dependent specific conductivity $\sigma(\omega)$ describes the motion of ions in the presence of a time dependent external field, where ω is the oscillation frequency of the field. When an ion moves in electrolyte solution, the atmosphere cannot immediately follow the motion of the central ion and becomes asymmetric causing a retarding effect on the motion of the ion. At zero frequency, this relaxation effect leads to the $B\Lambda_0\sqrt{c}$ term in eq 1. In the presence of an oscillating field, the central ion oscillates and the ion atmosphere gets less time to relax and cannot follow the oscillations of the ion. The average effect is that the ion atmosphere remains more symmetric (or less asymmetric) compared to that for a moving ion in a static field. As a result, the effects of the asymmetry of the ion atmosphere is reduced causing a net *reduction* of the electrolyte friction and an *enhancement of the conductivity* at low frequency. This “anomalous” increase of conductivity at low frequency is known as the Debye–Falkenhagen effect.¹⁴ At high frequency, the conductivity decreases because the ions oscillate so fast that the net ionic motion along a particular direction is smaller than that in the presence of a static or low-frequency field. By using a diffusion equation approach for the time dependence of ion atmosphere, Debye–Falkenhagen derived the following rather unusual looking expression for the frequency dependent electrolyte friction¹⁴

$$\xi_{\text{DF}}(\omega) = \xi_{\text{DF}}(0) \frac{1 + \sqrt{q}}{1 + [q(1 - i\omega\tau_{\text{atm}})]^{1/2}} \quad (30)$$

where $\xi_{\text{DF}}(0)$ is the zero-frequency friction, $q = 1/2$ for a symmetric binary electrolyte and τ_{atm} is the relaxation time of the ion atmosphere given by

$$\tau_{\text{atm}} = \frac{1}{(D_1 + D_2)q\kappa_D^2} \quad (31)$$

Here, D_1 and D_2 are the self-diffusion coefficients of the positive and negative ions, respectively, and κ_D is the inverse Debye screening length defined by eq 20.

As the DF expression is based on Debye–Huckel theory, it is valid only at very low ion concentrations. For a typical 0.001 M solution of a 1:1 salt, $\tau_{\text{atm}} \sim 10^{-7}$ s, and therefore, the dispersion of the DF friction for such a solution is predicted to occur in the MHz region. The electrophoretic force, on the other hand, responds at rates comparable to that of molecular velocity correlations. The velocity correlation times in solutions are of the order of 0.1 ps, and thus, the dispersion of the electrophoretic contribution occurs at a frequency much higher than GHz. In DF theory, the frequency dependence of the electrophoretic

effect is not considered. Thus, the well-known *Debye–Falkenhagen effect* of increasing conductivity with frequency arises solely from the decrease of the friction from the ion atmosphere.

Actually, the Debye–Falkenhagen effect seems to have never been confirmed satisfactorily. In a new twist to this old problem, Anderson, in a paper entitled “The Debye–Falkenhagen Effect: Experimental Fact or Fiction?”,⁵⁴ has recently questioned the original analysis of Falkenhagen. The difficulty of observing this effect is that the effect is predicted at very small concentration and also the magnitude of the effect is rather small.

In the following we discuss the recent mode coupling theory analysis of this problem. We calculate the frequency dependent electrolyte friction and the ionic diffusion coefficients by using the same theory discussed in the last section. It is assumed that the frequency dependent conductivity $\sigma(\omega)$ is related to the frequency dependent ionic diffusion coefficients $D_\alpha(\omega)$ by the following generalized Nernst–Einstein relation³⁶

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^2 \rho_\alpha q_\alpha^2 D_\alpha(\omega) \quad (32)$$

We note, however, that the frequency dependent ionic conductivity can, in general, be related to the Fourier transform of the ionic current-current time correlation function.³⁸ Since the electric current is a collective dynamical quantity, its time correlation function comprises of a self-part that corresponds to a summation over the velocity autocorrelation functions of the ions and a cross part involving the sum of the correlation functions of the velocities of distinct ions. The generalized Nernst–Einstein relation (eq 32) includes only the self-part and the cross part is ignored. Although the importance of the cross part is smaller than the self-part, it may not be negligible at high ion concentrations. However, at low and moderate ion concentrations, the contribution of the cross part is expected to be much smaller than that of the self-part. For example, at 0.5 M concentration of aqueous NaCl solution, an analysis of the simulation data of self-diffusion coefficients and conductivity reveals that the cross term reduces the static conductivity by less than 5%.²⁷ We also note that in the calculation of the static and dynamic ionic structure factors which appear in the final expressions of the friction and the conductivity, the solvent is treated as a dielectric continuum. At high concentrations, the molecular details of the ion–solvent and solvent–solvent correlations may become important. Because of these approximations, the present theory is limited to solutions of not too high concentration (less than 1 M solution). However, the theory has been found to give reliable results for the static conductance of strong electrolytes even up to 2 M concentration.^{34,35}

As explained in the last section, the total friction acting on the tagged ion is decomposed into two parts. The first part is due to the microscopic interaction of the tagged ion with the surrounding ions and the second part originates from the hydrodynamic coupling of the velocity of the tagged ion with the current modes of the surrounding particles. The time dependent microscopic electrolyte friction, $\delta\zeta_{s,\text{mic}}(t)$ is given by eq 6 of section 3. The frequency dependence of the hydrodynamic (or the electrophoretic part) is obtained by a generalization eq 13 to frequency domain. After the frequency dependence of the microscopic and hydrodynamic frictions are obtained, we calculate the frequency dependent diffusion coefficients of the ions by using the Generalized Einstein relation (eq 3) and then we obtain the frequency dependent conductivity from the generalized Nernst–Einstein relation (eq 32).

4.1. Derivation of Debye–Falkenhagen Form of Frequency Dependent Friction. Here we identify the limiting conditions under which the present theory reduces to the well-known Debye–Falkenhagen expression (eq 30) of the frequency dependent electrolyte friction. We note that in Debye–Falkenhagen theory, the frequency dependence of only the ion atmosphere relaxation contribution is considered and that of the electrophoretic term is ignored. Accordingly, we consider only the microscopic electrolyte friction as given by eq 6.

The ions are assumed to be point ions as in the Debye–Huckel theory. The use of the DH solutions of the direct correlation function and the diffusive limit of ionic van Hove functions leads to the following expression of the time dependent friction

$$\zeta_{s,\text{mic}}(t) = \frac{q_s^2 \kappa_D^2}{3\epsilon} \left[\frac{e^{-D\kappa_D^2 t}}{\sqrt{2\pi Dt}} + \kappa_D e^{D\kappa_D^2 t} \{ \Phi(\sqrt{2\kappa_D^2 Dt}) - 1 \} \right] \quad (33)$$

where $\Phi(x)$ is the error function and it is assumed that all ions have the same diffusion coefficient D . We note that the above expression of time dependent electrolyte friction becomes identical with the one derived by de Leon et al.⁵⁵ when the diffusion coefficient D in the right-hand side of eq 33 is replaced by D^0 , which is the value of the ion diffusion coefficient in the limit of infinite dilution.

The Fourier–Laplace transform of eq 33 can be carried out analytically to obtain the following expression of the frequency dependent friction

$$\zeta_{s,\text{mic}}(\omega) = \frac{q_s^2 \kappa_D}{6\epsilon D} \frac{1}{1 + \frac{1}{\sqrt{2}} [1 - i\omega/D\kappa_D^2]^{1/2}} \quad (34)$$

The expression of the frequency dependent friction as given by eq 34 can be rewritten in the following form

$$\zeta_{s,\text{mic}}(\omega) = \zeta_{s,\text{mic}}(0) \frac{1 + \sqrt{q}}{1 + \sqrt{q} [1 - i\omega\tau_{\text{atm}}]^{1/2}} \quad (35)$$

where τ_{atm} is defined in eq 31. Equation 35 is identical with the DF expression (eq 30). Thus, it is clear from the above analysis that the present microscopic theory reduces to the DF theory in the limit of low ion concentration when finite sizes of the ions are ignored, electrophoretic effects are not included, and the collective dynamics of the ion atmosphere relaxation is described by diffusive motion.

We note that the DF theory incorporates the cross dynamical coupling of ions at the level of ion atmosphere relaxation (or the ionic van Hove functions) but not at the level of ionic velocity or current relaxation. Thus, like the present theory, the DF expression also does not include the effects of the so-called current cross terms. The contribution of such cross correlations is expected to be vanishingly small in the limit of low ion concentration, and therefore, the DF expression is regarded as the correct limiting expression of the frequency dependent ion atmosphere friction in an electrolyte solution.

4.2. Derivation of the Conductivity Expressions of Chandra, Wei, and Patey. Chandra, Wei and Patey (CWP)²⁶ have recently derived analytical expressions of $\sigma(\omega)$ by employing a non-Markovian equation of motion of the self-van Hove function of a tagged ion. By employing exactly known short and long time constraints upon the ionic self-van Hove function, these authors derived closed-form expressions of the frequency dependent conductivity for two models, referred to as models I

and II. Model I depends on an expression of the frequency dependent diffusion coefficient which ensures that the short time dynamics up to the second frequency moment and also the long time dynamics of the self-van Hove function are described correctly. The final expression of the conductivity is described by a multiple Debye form²⁶

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^2 \frac{\rho_{\alpha} q_{\alpha}^2 D_{\alpha}}{1 - i\omega D_{\alpha} m_{\alpha} / k_B T} \quad (36)$$

where m_{α} is the mass of an ion of species α . The model II of CWP is a generalized version which correctly describes the short time dynamics up to the fourth frequency moment and also the long time dynamics of the ionic self-van Hove functions. In this model, $\sigma(\omega)$ is given by²⁶

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^2 \rho_{\alpha} q_{\alpha}^2 \left[\frac{D_{\alpha} \Omega_{\alpha}^2 - i\omega k_B T / m_{\alpha}}{\Omega_{\alpha}^2 - \omega^2 - i\omega D_{\alpha} \Omega_{\alpha}^2 m_{\alpha} / k_B T} \right] \quad (37)$$

where Ω_{α} is the Einstein frequency of an ion of species α , so Ω_{α}^2 is proportional to the mean square force acting on an ion. The CWP theory is capable of predicting the increase of conductivity at low frequency. However, no attempt was made by CWP to derive the DF expression.

It is discussed here that the main expressions of CWP can be obtained from the present formalism. To recover the expression of Model I (eq 36), we ignore the frequency dependence of $\zeta_s(\omega)$ in the Einstein relation and replace it by the zero-frequency value ζ_s so that

$$\begin{aligned} D_s(\omega) &= \frac{k_B T}{m_s} \frac{1}{-i\omega + \zeta_s} \\ &= \frac{D_s}{1 - i\omega D_s m_s / k_B T} \end{aligned} \quad (38)$$

where, in deriving the second equality, we have used the Einstein relation $\zeta_s = k_B T / D_s m_s$. On combining eq 38 with the Nernst–Einstein relation (eq 32), one obtains eq 36, which is the CWP model I expression of the frequency dependent conductivity. Thus, in this limiting case, the frequency dependence of the conductivity originates entirely from the inertial effects.

Also, when $D_1 = D_2$ and $m_1 = m_2$, the frequency dependence of the conductivity is described by a simple Debye form

$$\sigma(\omega) = \frac{\sigma}{1 - i\omega D m / k_B T} \quad (39)$$

where σ is the conductivity at zero frequency. We note that the simple Debye form has been used in the literature as an empirical expression for $\sigma(\omega)$.²⁵

To derive the expression of model II (eq 37), we approximate the time dependence of the total friction as friction as

$$\zeta_s(t) = \zeta_s(t=0) e^{-t/\tau_s} \quad (40)$$

where $\zeta_s(t=0)$ is described by the spatial integral of the zero-time force-force correlation which is equal to the square of the Einstein frequency Ω_s of the tagged ion. The relaxation time τ_s can be eliminated in favor of the diffusion coefficient D_s by using the Einstein relation described above, and the resultant

expression after Laplace transformation gives

$$\zeta_s(\omega) = \frac{\Omega_s^2}{-i\omega + D_s m_s \Omega_s^2 / k_B T} \quad (41)$$

Equation 41, on combining with the generalized Einstein relation and eq 32, gives eq 37, which is the model II expression for $\sigma(\omega)$. Thus, in this model, the frequency dependence of conductivity originates from both the inertial and the non-Markovian effects.

5. Concentration Dependence of the Viscosity: Falkenhagen Expression

Viscosity of an electrolyte solution is long known to show anomalous dependence on ion concentration.^{7,56,57} For some ions (like LiCl, NaCl, and BaCl₂ in water), the viscosity increases monotonically with concentration, while for some others (like KCl, KBr, or KI), the viscosity increases slightly at very low concentration, then it decreases as the ion concentration is increased and finally it increases again at higher concentration.^{7,58} This anomalous concentration dependence of viscosity clearly has a complex origin which, to the best of our knowledge, has not even been addressed to from a microscopic theory.

At very low concentration, the increase in viscosity with ion concentration can be well described by the well-known expression derived by Falkenhagen many decades ago. The expression of Falkenhagen is valid for symmetrical electrolytes and is given by^{5,6,15}

$$\eta(c) = \eta_0 + \frac{\kappa_D \zeta_0}{480\pi} \quad (42)$$

where $\eta(c)$ is the viscosity of the electrolyte solution when the molar concentration of the salt is c , η_0 is the same of the pure solvent, ζ_0 is the friction on an ion in the solution at infinite dilution, and κ_D is the inverse Debye screening length. The Falkenhagen expression was later extended to asymmetrical electrolytes by Onsager and Fuoss.¹⁶ Note, however, that at the heart of the derivation of Falkenhagen and also of Onsager and Fuoss is the Debye–Huckel theory of ion atmosphere. Since the Debye–Huckel theory is valid at very low concentrations, so is the Falkenhagen–Onsager–Fuoss expression. In fact, the validity of Falkenhagen expression seems to be limited to *even lower* concentrations than that of the DHO law of conductance for reasons we discuss below.

5.1. Mode Coupling Theory Formulation for Viscosity. Our starting point for the calculation of viscosity of the solution is the following Green–Kubo formula³⁹

$$\eta = \lim_{k \rightarrow 0} \frac{1}{k_B T V} \int_0^{\infty} dt \langle \sigma^{zx}(k,0) \sigma^{zx}(k,t) \rangle \quad (43)$$

where $\sigma^{zx}(k,t)$ is the transverse (or off-diagonal) component of the wavevector (\mathbf{k}) and time dependent stress tensor. Clearly, $\sigma^{zx}(k,t) = \sigma^{xz}(k,t)$. Moreover, because of the inherent isotropy of the solution, the time correlation function $\langle \sigma^{zx}(k,0) \sigma^{zx}(k,t) \rangle$ is independent of the particular combination (zx) of the Cartesian indices, it can equivalently be replaced by (xy) and (yz) components. The total transverse stress tensor of an ionic solution contains contributions from both solvent and ions and it can be written as

$$\sigma^{zx}(k,t) = \sigma_{\text{sol}}^{zx}(k,t) + \sigma_{\text{ion}}^{zx}(k,t) \quad (44)$$

where $\sigma_{\text{sol}}^{\text{zx}}$ and $\sigma_{\text{ion}}^{\text{zx}}$ denote, respectively, the solvent and ion contributions to the transverse stress. Accordingly, the viscosity can be written as

$$\eta = \eta_{\text{sol}} + \eta_{\text{ion-sol}} + \eta_{\text{ion}} \quad (45)$$

where the terms in the right-hand side of the above equation represent, respectively, the solvent, ion–solvent, and ion contributions to the viscosity. At low concentration, the solvent contribution η_{sol} is expected to be very close to the to the viscosity of the pure solvent η_0 . Since we are interested in dilute solutions in the present study, we assume that η_{sol} is equal to η_0 . The ion–solvent contribution involves dynamical cross correlation between the transverse ion stress and the transverse solvent stress. The magnitude of such dynamical cross correlation is expected to be small for dilute solutions. Thus, the major ion dependent contribution comes from η_{ion} . In the present work, we calculate this ionic contribution, i.e., the one arising from ion–ion transverse stress correlation

$$\begin{aligned} \eta_{\text{ion}} &= \lim_{k \rightarrow 0} \frac{1}{k_{\text{B}}TV} \int_0^{\infty} dt \langle \sigma_{\text{ion}}^{\text{zx}}(k,0) \sigma_{\text{ion}}^{\text{zx}}(k,t) \rangle \\ &= \lim_{k \rightarrow 0} \frac{m^2}{k_{\text{B}}TVk^2} \int_0^{\infty} dt \langle \dot{J}_x(k,0) \dot{J}_x(k,t) \rangle \end{aligned} \quad (46)$$

where $\dot{J}_x(k,t)$ is the time derivative of the transverse ion current. It is assumed that the wavevector \mathbf{k} is along the z -axis and that all ions of the solution have the same mass m . We note that the ionic contribution to the viscosity was identified as the excess viscosity in earlier studies^{15,16} although, strictly speaking, it becomes the excess viscosity only in the limit of very low ion concentration where solvent–ion cross dynamical stress correlation becomes vanishingly small. In the following, we employ the mode coupling treatment of Geszti⁵⁹ to derive a simplified microscopic expression of this ionic contribution η_{ion} .

Since we assume that the ionic contribution to viscosity arises only from the interaction between the ions and that the solvent modes relax much faster than the ionic modes in dilute solutions (as discussed before), one can use the collective ionic variables to describe the dynamics of the correlation functions of eq 46. We treat the mode–mode coupling among four variables of ionic current density $j_{\alpha}(\mathbf{k})$ ($\alpha = 1, 2, 3$) and the charge density $\rho_c(\mathbf{k})$. Clearly, $\rho_c(\mathbf{k}) = q_1\rho_1(\mathbf{k}) + q_2\rho_2(\mathbf{k})$. The Green–Kubo formula of eq 46 can now be rewritten as

$$\eta_{\text{ion}} = \lim_{\epsilon \rightarrow 0} \lim_{k \rightarrow 0} \frac{m^2}{k^2V} \int_0^{\infty} dt \langle QLj_1(\mathbf{k}) | \exp(iQLQt - \epsilon t) | QLj_1(\mathbf{k}) \rangle \quad (47)$$

where L is the same Liouville operator which appeared in eq 12 and Q is the projector onto the manifold of dynamical variables orthogonal to ionic current density and the charge density. The time evolution operator $\exp[iQLQt - \epsilon t]$ acts on the space of dynamical variables. The standard approximation in the mode–mode coupling expansion is to consider the subspace of various binary products of the basic variables. Among such binary products, the odd ones with respect to time inversion do not contribute to the viscosity; thus only the even combinations need be retained. Of these, the most important contribution comes from the charge density combination $\rho_c\rho_c$ because this term decays slowly, particularly at low concentration when the Debye length (λ_{D}) is large (because the ion atmosphere relaxation time is given by $\lambda_{\text{D}}^2/D_{\text{ion}}$). The contribution of the current combination jj is expected to be small because

the current correlation function decays much faster (its relaxation time being determined by m/ζ). The jj term is, therefore, neglected in this work and we consider the contribution from the $\rho_c\rho_c$ term.

The final expression of the excess viscosity is given by³⁷

$$\eta_{\text{ex}} = \frac{k_{\text{B}}T}{60\pi^2} \int_0^{\infty} dk \int_0^{\infty} dt k^4 S'_c(k)^2 F_c(k,t)^2 / S_c(k)^4 \quad (48)$$

where $S_c(k)$ and $F_c(k,t)$ are, respectively, the static and dynamic charge density structure factors of the ions in the solution. $S'_c(k)$ represents the derivative of $S_c(k)$ with respect to the wavevector k . Note that this expression has the same form as the one derived by Geszti,⁵⁹ except that the structure factor here refers to that of charge density—not atomic and molecular density. $F_c(k,t)$ thus describes the relaxation of ion atmosphere at all length scales.

If one includes the current–current contribution to the viscosity, an additional term enters in eq 48. The expression is similar, except $F_c(k,t)$ gets replaced by the current–current correlation function, with a few additional changes. As already discussed, the contribution of this term to viscosity is small and is usually neglected. It should be pointed out here that an expression like eq 48 has been used to address the observed anomalous rise of viscosity of polyelectrolyte solutions at very low polyelectrolyte concentrations.^{60,61} In this case, one needs to consider both the mass and charge density of the polyelectrolytes as the slow variables.

5.2. Reduction to the Falkenhagen Expression. In this section we show that the present theory of the ionic viscosity nicely reduces to the Falkenhagen expression^{5,6,15} for a binary symmetric electrolyte in the limit of very low ion concentration. At low concentration, we use the Debye–Huckel expressions of the ionic pair correlation (which is an exponentially decaying function of the distance) and the direct correlation functions. The dynamic charge structure factor $F_c(k,t)$ is determined in the following way. We assume that the dynamics of ion atmosphere relaxation occurs by diffusive motion; thus, we ignore the frequency dependence of $D(\omega)$ in eq 8. The inverse Laplace transformation of eq 8 then gives the following dynamical equation for $F_c(k,t)$ ³⁷

$$\frac{\partial F_c(k,t)}{\partial t} = -Dk^2[1 - 2\rho_1c_{11}(k)]F_c(k,t) \quad (49)$$

so that

$$\int_0^{\infty} [F_c(k,t)/S_c(k)]^2 dt = \frac{1}{2D(k^2 + \kappa_{\text{D}}^2)} \quad (50)$$

where, in deriving the above equation, we have used the Debye–Huckel expression of the direct correlation function. We now substitute eqs 50 in eq 48 and use the Debye–Huckel solutions of the ionic structure factors to obtain

$$\begin{aligned} \eta_{\text{ex}} &= \frac{k_{\text{B}}T\kappa_{\text{D}}^4}{30\pi^2D} \int_0^{\infty} dk \frac{k^2}{(k^2 + \kappa_{\text{D}}^2)^3} \\ &= \frac{\kappa_{\text{D}}\zeta}{480\pi} \end{aligned} \quad (51)$$

where the Einstein relation between the diffusion coefficient and the friction is used in deriving the second equality. Equation 51 becomes identical to the Falkenhagen expression of excess

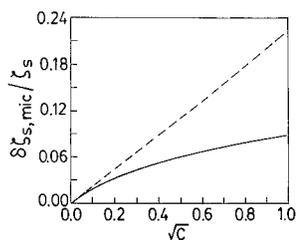


Figure 1. The ion atmosphere contribution to the microscopic friction is plotted against the square root of ion concentration (in molarity) for a 1:1 electrolyte. The values of different parameters describing the solution are described in the text. The details of the calculations are available in ref 35. The solid curve shows the results of the present theory and the dashed curve represents the predictions of DHO theory. (Reprinted with permission from ref 35. Copyright 1999 American Institute of Physics.)

viscosity when the ionic friction is replaced by its value at infinite dilution. The same expression was also derived by Fuoss and Onsager.¹⁶

6. Numerical Results at Finite Concentration: Departure from Classical Laws

The numerical results of the electrolyte friction, conductivity and the viscosity are discussed for symmetric binary salt solutions at varying concentrations. All ions of the solutions are assumed to be charged hard spheres of equal diameter σ for simplicity. The solutions are completely specified by specifying the reduced charge $q_1^* = \sqrt{q_1^2/k_B T \sigma}$, the reduced ion density $\rho_1^* = \rho_1 \sigma^3$ and the dielectric constant ϵ . The pair correlation functions for the evaluation of the quantities $S_{\alpha\beta}(k)$ and $c_{s\alpha}(k)$ are obtained from the solutions of Attard.⁶² In this scheme, the functional forms of the ionic pair correlation functions are the same as given by Debye–Huckel theory. However, the screening parameter which enters into the mathematical expressions is *not* the one of Debye–Huckel theory but a renormalized one. In real space, the expression of the pair correlation function $h_{\alpha\beta}(r)$ is given by

$$h_{\alpha\beta}(r) = -\frac{q_\alpha q_\beta}{\epsilon k_B T (1 + \kappa \sigma)} \frac{\kappa^2}{\kappa_D^2} \frac{e^{-\kappa(r-\sigma)}}{r} \quad (52)$$

where the screening parameter κ is related to the Debye screening parameter κ_D by the following relation

$$\kappa = \frac{\kappa_D}{[1 - (\kappa_D \sigma)^2/2 + (\kappa_D \sigma)^3/6]^{1/2}} \quad (53)$$

The above solution of the ionic pair correlation function with the renormalized screening length has been found to be accurate up to 1 M concentration for monovalent electrolytes and it considerably extends the range of validity of the classical Debye–Huckel theory. The Fourier transform of the pair correlation function can be obtained readily from eq 52.³⁵

6.1. Static Electrolyte Friction and Conductance. The numerical results of the electrolyte friction and conductance as predicted by the present microscopic theory are described in Figures 1–4.⁶³ The results of the ion atmosphere contribution to the electrolyte friction of a tagged ion, $\delta\zeta_{s,mic}$, are shown in Figure 1. In these calculations (and also the ones of Figures 2–3 and 5–8), the value of the reduced charge q^* is 14.1, which corresponds to the charge of a univalent ion of diameter 2.82 Å at $T = 298$ K. The reduced ion density ρ_1^* is varied from 0.0

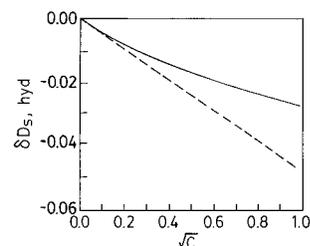


Figure 2. The ion atmosphere contribution to the hydrodynamic part of ion diffusion is plotted against the square root of ion concentration. The different curves are as in Figure 1. (Reprinted with permission from ref 35. Copyright 1999 American Institute of Physics.)

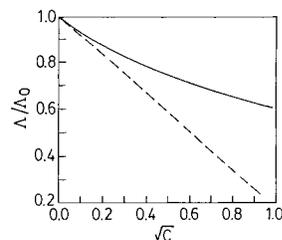


Figure 3. The total conductance is plotted against the square root of ion concentration. Λ_0 represents the conductance at infinite dilution. The different curves are as in Figure 1. (Reprinted with permission from ref 35. Copyright 1999 American Institute of Physics.)

to 0.0135 which corresponds to changing the concentration from 0.0 to 1.0 M where M is the molarity of the solution. The results of DHO law are also included in the figure for comparison. The DHO law predicts a linear increase of $\delta\zeta_{s,mic}$ with the square root of ion concentration whereas the present theory predicts a nonlinear dependence at finite ion concentration. Here by finite ion concentration we mean a concentration regime higher than 0.05 M or so. In the limit of very low ion concentration (<0.05 M), the results of the present theory coincides with those of DHO law, as expected. However, at finite concentration the electrolyte friction is found to be much smaller than the prediction of the DHO law. Also, it changes rather weakly with concentration compared to the prediction of the DHO law. The electrophoretic contribution to the diffusion of the tagged ion is shown in Figure 2. In this figure, $\delta D_{s,hyd}$ is plotted against square root of ion concentration where $\delta D_{s,hyd} = k_B T / \zeta_{s,hyd} - k_B T / \zeta_{s,hyd}^0$. The results of $\delta D_{s,hyd}$ are shown in units of $k_B T / \eta \sigma$. Again, DHO results are shown for comparison. At finite concentration, the predictions of the present theory are seen to be significantly different from those of the DHO law.

In Figure 3, we have shown how the ion conductance changes with square root of ion concentration for the same model solution. The values of the conductance at different concentrations are normalized by its limiting value at zero concentration. The details of the calculations are described in ref 35. Significant departure from DHO linear behavior is observed at finite concentration where a much weaker and nonlinear dependence of the conductance on square root of ion concentration is predicted by the present microscopic theory. The relative contributions of the microscopic relaxation and electrophoretic effects to the conductance have also been computed.³⁵ The two effects have been found to exhibit different concentration dependence at higher ion concentration. Also, the electrophoretic effect has been found to be more important than the microscopic relaxation effect at finite ion concentration. This is in agreement with the findings of Altenberger and Friedman¹⁹ in their Smoluchowski level description of ion conductance. The results shown in Figures 1–3 are obtained by using Attard's solutions⁶² of the ionic pair correlation functions. To verify the accuracy

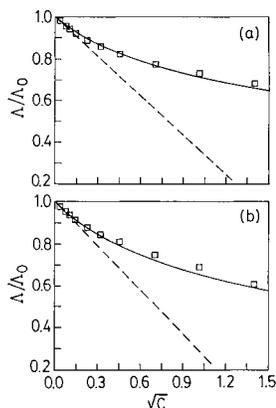


Figure 4. The total conductance of aqueous (a) KCl and (b) NaCl solutions is plotted against the square root of ion concentration. The details of the calculations are available in refs 34 and 35. The solid curve represents the predictions of the present theory and the squares represent the experimental results. (Reprinted with permission from ref 34. Copyright 1999 American Chemical Society.)

of these results, calculations have also been carried out by using hypernetted chain (HNC) approximation of the ionic pair correlations and the results of conductance with HNC solutions have been found to be remarkably close to the ones of Figure 3.³⁵

Finally we compare the predictions of the present theory with experimental results of real ionic solutions. Both KCl and NaCl solutions are chosen as examples. The details of the numerical calculations can be found in refs 34 and 35. The theoretical predictions for these solutions along with experimental results are shown in Figure 4. The experimental results are available in the textbook of Glasstone¹ and also in ref 19. It is clear from this figure that the theoretical predictions are in excellent agreement with the experimental results even at high concentrations. This is quite impressive given that the theory does not involve *any* adjustable parameter.

6.2. Frequency Dependent Electrolyte Friction and Conductivity. The electrolyte friction and the conductivity become complex quantities at finite frequencies. We decompose the frequency dependent microscopic electrolyte friction into its real and imaginary parts as follows

$$\delta\zeta_{s,\text{mic}}(\omega) = \delta\zeta'_{s,\text{mic}}(\omega) + i\delta\zeta''_{s,\text{mic}}(\omega) \quad (54)$$

Similar decomposition is also made for the electrophoretic friction and the conductivity functions for the discussion of numerical results at finite frequencies. The frequency dependence of the real and imaginary parts of the microscopic electrolyte friction have been calculated for 0.01 and 0.1 M solutions of a 1:1 electrolyte at room temperature.³⁶ The results for the 0.1 molar solution are shown in Figure 5. The values of the friction at different frequencies are normalized by its zero-frequency value and the reduced frequency $\omega^* = \omega\sigma^2/D$. At low concentration and at low frequency, the results of the present theory have been found to be quite close to the DF results.³⁶ However, at high concentration, the results of the present theory show significant departure from the DF results, especially at high frequency. Also, with increase of ion concentration, the dispersion of the electrolyte friction is found to occur at a higher frequency because of faster relaxation of the ion atmosphere.³⁶

In Figure 6, we have shown the frequency dependence of the electrophoretic term for the 0.1 M solution. The dispersion of the electrophoretic contribution is seen to occur at a much higher frequency as one would expect. In fact, any noticeable

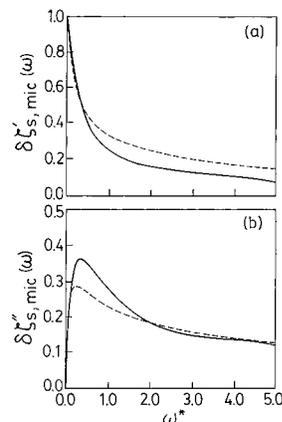


Figure 5. The (a) real and (b) imaginary parts of the frequency dependent microscopic electrolyte friction on an ion are plotted against frequency for a 0.1 M solution of a 1:1 electrolyte. The details of the calculations are available in ref 36. The solid and the dashed curves represent, respectively, the results of the present theory and of Debye-Falkenhagen expression (eq 30). (Reprinted with permission from ref 36. Copyright 2000 American Institute of Physics.)

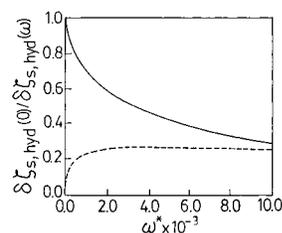


Figure 6. The electrophoretic friction on an ion is plotted against frequency for a 0.1 M solution of a 1:1 electrolyte. The solid and the dashed curves represent, respectively, the real and the imaginary parts. (Reprinted with permission from ref 36. Copyright 2000 American Institute of Physics.)

change in the electrophoretic term is found only above $\omega^* = 10^3$ which corresponds to a frequency well above the GHz region. The dispersion of the solvent contribution to the ionic friction, which is assumed to be a constant in the present calculations, is also expected to occur in this frequency domain. The solvent contribution, being a larger effect, may dominate the dispersion of the total ionic friction at such high frequencies.

The results of the frequency dependence of real and imaginary parts of the ion conductivity are shown in Figure 7 for 0.01 and 0.1 M solutions. The real part shows a slight increase at low frequency and then it decreases at high frequency as one would expect. The initial increase at low frequency can be attributed to the Debye-Falkenhagen effect. It is seen that the primary dispersion of the conductivity occurs at a much higher frequency than that of the microscopic electrolyte friction. The dispersion of the microscopic electrolyte friction is primarily determined by the inverse relaxation time of the ion atmosphere. The frequency dependence of the conductivity, on the otherhand, is determined by the frequency dependent diffusion coefficient $D(\omega)$. The primary dispersion of $D(\omega)$ occurs at a much higher frequency than that of the electrolyte friction because of the presence of $-i\omega$ term in the generalized Einstein relation which connects the diffusion coefficient to the friction at finite frequencies. Sometimes the experimental results of the frequency dependent conductivity are analyzed in terms of the so-called Cole-Cole plots where the imaginary part of the conductivity is plotted against the real part at different frequencies. Such Cole-Cole plots show non-Debye behavior at higher ion concentration.³⁶ This is not unexpected as the Debye form of $\sigma(\omega)$ (eq 39) is valid only in limiting situations as discussed in

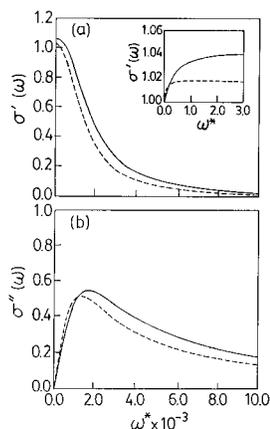


Figure 7. The (a) real and (b) imaginary parts of the frequency dependent conductivity are plotted against frequency for 0.01 M (dashed curves) and 0.1 M solutions (solid curves) of a 1:1 electrolyte. The details of the calculations are available in ref 36. (Reprinted with permission from ref 36. Copyright 2000 American Institute of Physics.)

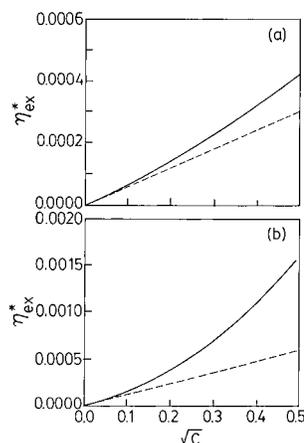


Figure 8. The ionic contribution to the viscosity is plotted against the square root of ion concentration (in molarity) for solutions of (a) 1:1 and (b) 2:2 electrolytes. The details of the calculations are available in ref 37. The reduced viscosity $\eta_{ion}^* = \eta_{ion}/\sigma/\zeta_0$. The solid curves show the results of the present theory and the dashed curves represent the predictions of Falkenhagen expression (eq 42). (Reprinted with permission from ref 36. Copyright 2000 American Institute of Physics.)

section 4 and, in general, the dispersion of the conductivity shows a more complex behavior.

6.3. Ionic Contribution to the Viscosity. The results of the ionic contribution to the viscosity of a 1:1 salt solution at varying concentration are shown in Figure 8a. The values of various parameters are the same as in Figure 1. In this figure, the results of the Falkenhagen expression are also included for comparison. The Falkenhagen expression predicts a linear increase of η_{ion} with square root of ion concentration whereas the present theory predicts a nonlinear dependence at finite ion concentration. In the limit of very low ion concentration (<0.05 M), the results of the present theory coincides with those of Falkenhagen, as expected. However, at finite concentration the excess viscosity is found to be much higher than the prediction of the Falkenhagen expression. In Figure 8b, we present the results for a 2:2 electrolyte. Here $q^* = 28.2$ and the values of other parameters are the same as in the previous figure. A much stronger dependence of the excess viscosity on ion concentration is found compared to the results of 1:1 electrolytes. Also, the deviations from the Falkenhagen limiting behavior are found to be much more in this case which can be attributed to the stronger ion-ion correlations.

The microscopic theory predicts a stronger increase of viscosity with increase of ion concentration, especially for ions of higher valence which is in qualitative agreement with experimental results. At finite concentration, the viscosity increases nonlinearly with square root of concentration³⁷ contrary to the linear increase predicted by the Falkenhagen expression. Although the present theory proves to be an improvement over the Falkenhagen expression, a quantitative comparison of the viscosity data^{7,58} show that for many electrolytes (like NaCl in water), the viscosity is still underestimated by the present theory at higher concentrations. Clearly, much more work is needed to fully understand the concentration dependence of the viscosity. We note that although the static and dynamic ion-ion correlations and the screening effects are included in the present work, the molecular details of the ion-solvent and solvent-solvent correlations are missing. It would be interesting to study how these ion-solvent and solvent-solvent correlations contribute to the excess viscosity of an electrolyte solution. The main approximation in the present formalism seems to be the neglect of the binary terms involving the solvent density in the set of slow variables. In a generalized theory, not only the charge and size of the ions, but the molecular details of solvent could also be important. Second, we may need to include the contributions of charge currents. Although the charge current is not a conserved quantity, its contribution needs to be evaluated. However, it is believed that the binary terms involving the ion-solvent and solvent-solvent correlations hold the key to many of the surprising results of the concentration dependence of viscosity.

7. Toward a Full Microscopic Theory: A Future Problem

There is yet no first principles theory of electrolyte conduction and viscosity which treats the ions and the solvent molecules at the same level. This is what we refer to as a fully microscopic theory. Since the solvent molecules here are dipolar, one needs to include not only the position but also the orientation of these molecules. Not only the solvent-solvent but the ion-dipole interactions are also orientation dependent. This is exactly the difficulty which has limited any progress toward a full theoretical description. Here we describe some of the progress made recently.

In the calculation of the total microscopic friction, we require an expression for the dielectric friction from ion-solvent interaction. This can be derived by using the density functional theory, along with Kirkwood's formula and is given by

$$\delta\zeta_{mic,solv}(t) = \frac{2k_B T}{3(2\pi)^3} \sum_{\alpha=1}^2 \int d\mathbf{k} d\Omega k^2 c_{s\alpha}(k) \times \sqrt{\rho_\alpha \rho_3} G_{\alpha 3}(k, \Omega, t) c_{s3}(k, \Omega) F_s(k, t) + \frac{k_B T \rho_3}{3(2\pi)^3} \int d\mathbf{k} d\Omega d\Omega' k^2 c_{s3}(k, \Omega) G_{33}(k, \Omega, \Omega', t) \times c_{s3}(k, \Omega') F_s(k, t) \quad (55)$$

where ρ_3 is the density of the solvent (species 3), $c_{s3}(k, \Omega)$ is the wavevector and angle (Ω) dependent direct correlation function between the tagged ion and the solvent, and $G_{\alpha 3}(k, \Omega, t)$ and $G_{33}(k, \Omega, \Omega', t)$ are the ion-solvent and solvent-solvent van Hove functions, respectively. This expression is a generalization of the friction for limiting ionic conductivity^{45,46} to finite concentration; the quantities $c_{s3}(k, \Omega)$, $G_{\alpha 3}(k, \Omega, t)$ and G_{33} -

(k, Ω, Ω', t) now depend on ion concentration. One can similarly derive an expression for the dielectric friction from solvent polarization current modes.

The calculation of the ion–solvent and solvent–solvent van Hove functions will require solutions of a coupled hydrodynamic equations of the type discussed by Bagchi and Chandra⁶⁴ for dipolar liquids, but now for a composite system with ions. This leads to a set of coupled equations which can be linearized with respect to density and momentum fluctuations. Recently, Mahajan and Chandra⁶⁵ have solved such linearized hydrodynamic equations to obtain the time dependence of various ion–ion, ion–solvent and solvent–solvent van Hove functions. The implementation of such generalized solutions for the calculation of electrolyte friction is yet to be carried out. The decrement of dielectric constant^{49,66–72} with ion concentration is another issue which is still not fully understood and not explicitly included in the existing theories of electrolyte friction and conductance. This effect will enter naturally once the dynamical coupling with the solvent modes is treated explicitly. The detailed theory will no doubt be quite involved, but will certainly be highly rewarding.

8. Summary and Conclusions

In this article a review is presented mainly of our recent work on the microscopic derivations of the limiting transport laws of electrochemistry and their generalizations to higher concentrations. All the three transport laws have been derived from the mode coupling theory approach. These derivations required identification of the proper dynamical variables and the use of appropriate time correlation functions. Although the derivations are by no means trivial, we believe that they are more transparent and easily understandable than the original derivations. The present analysis also leads to a better understanding of the origin of the often unusual forms of these laws. For example, the derivation of Falkenhagen–Onsager–Fuoss form^{15,16} for viscosity very clearly reveals the origin of the $1/480\pi$ factor in the expression of the excess viscosity.

Numerical calculations of the full expressions show much better agreement with experimental results than the limiting expressions at small but nonnegligible concentrations, like 0.5 M. In fact, the agreement for the static conductance is quite impressive. The study of excess viscosity seems to suggest that direct solvent involvement might be playing a crucial role, even at as low a concentration as 0.1 M.

While we propose the full molecular theory, where the dynamical coupling between the solvent and the ions are treated explicitly in the calculation of the friction and the viscosity, as the most important problem in this area, there are several approximations in the present formulation that require improvement. For example, no account of the collective effects arising from the velocity cross correlations between different ions have been considered. Such a correlation is zero at $t = 0$ and small at small times, but can be significant at intermediate times for higher ion concentrations, like 1 M. However, we feel that the approximation involved in neglecting the explicit ion–solvent coupling at molecular level will play a far bigger role at higher concentrations.

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