Frequency dependence of ionic conductivity of electrolyte solutions

Amalendu Chandra[a]
Department of Chemistry, Indian Institute of Technology, Kanpur, India 208016

Biman Bagchi
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India 560 012
and Department of Chemistry, University of Wisconsin at Madison, Madison, Wisconsin 53706

A theory for the frequency dependence of ionic conductivity of an electrolyte solution is presented. In this theory contributions to the conductivity from both the ion atmosphere relaxation and the electrophoretic effects are included in a self-consistent fashion. Mode coupling theory, combined with time-dependent density functional theory of ion atmosphere fluctuations, leads to expressions for these two contributions at finite frequencies. These expressions need to be solved self-consistently for the frequency dependence of the electrolyte friction and the ion conductivity at varying ion concentrations. In the limit of low concentration, the present theory reduces exactly to the well-known Debye–Falkenhagen (DF) expression of the frequency-dependent electrolyte friction when the non-Markovian effects in the ion atmosphere relaxation are ignored and in addition the ions are considered to be pointlike. The present theory also reproduces the expressions of the frequency-dependent conductivity derived by Chandra, Wei, and Patey when appropriate limiting situations are considered. We have carried out detailed numerical solutions of the self-consistent equations for concentrated solutions of a 1:1 electrolyte by using the expressions of pair correlation functions given by Attard. Numerical results reveal that the frequency dependence of the electrolyte friction at finite concentration can be quite different from that given by the DF expression. With the increase of ion concentration, the dispersion of the friction is found to occur at a higher frequency because of faster relaxation of the ion atmosphere. At low frequency, the real part of the conductivity shows a *small increase* with frequency which can be attributed to the well-known Debye–Falkenhagen effect. At high frequency, the conductivity decreases as expected. The extensions of the present theory to treat frequency-dependent diffusivities of charged colloid suspensions and conductivity of a dilute polyelectrolyte solution are discussed.

I. INTRODUCTION

The dynamics of electrolyte solutions has remained a central area of research in physical chemistry for a long time.[1–6] Despite vigorous activity over many decades, many fundamental problems have remained unsolved which have led to recurrent attempts by theoreticians to address them. The motion of ions in an electrolyte solution is usually described by the specific conductivity (σ) or by the equivalent conductance (Λ) which is the specific conductivity divided by the molar concentration of the salt. The best known expression for the equivalent conductance of an electrolyte solution is the Debye–Huckel–Onsager relation given by[7,8]

$$\Lambda(c) = \Lambda_0 - (A + B\Lambda_0)\sqrt{c}, \qquad (1)$$

where $\Lambda(c)$ is the equivalent conductance of the electrolyte when the molar concentration of the salt is c, Λ_0 is the same at infinite dilution of the electrolyte. A and B are numerical constants which depend on dielectric constant, viscosity, and temperature of the solution and also on charges of the ions.

The problem of ion motion can be naturally divided into several parts. The first is the problem of understanding the limiting ionic conductance Λ_0, which is determined by the statics and dynamics of ion–solvent interactions. Significant progress has been made in recent years in understanding this problem. In particular, it has been pointed out that the ultrafast solvation of ions observed in water and acetonitrile can play an important role in reducing the magnitude of dielectric friction on small rigid ions. This and other aspects have been reviewed recently in Ref. 6. The second important problem is the concentration dependence of the ionic conductance in the limit of small concentration, as embodied in the Debye–Huckel–Onsager square root concentration law given above. Many aspects of this law have been clarified in recent years and studies have been extended to higher concentrations.[9–13] However, a fully molecular theory which is valid at high concentrations, even for the simplest case of strong electrolytes, is yet to be developed. The third important problem is the motion of ions in the presence of an oscillating electric field.[14–20] The last one is the subject of the present article. The above-mentioned list is by no means exhaustive.

The motion of ions in the presence of a time-dependent electric field is traditionally described by the frequency-dependent specific conductivity $\sigma(\omega)$ where ω is the oscillation frequency of the external field. The frequency-

[a]Electronic mail: amalen@iitk.ac.in

dependent conductivity is intimately related to the frequency-dependent electrolyte friction. One of the earliest studies of the frequency-dependent electrolyte friction and conductivity was that of Debye and Falkenhagen (DF).[14] These authors considered the dynamic effect of the relaxation of ion atmosphere on the motion of an ion. 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 presence of an oscillating field, the central ion oscillates and the ion atmosphere gets less time to relax and remains less asymmetric. As a result, the effects of the asymmetry of the ion atmosphere is reduced causing a reduction of the electrolyte friction and an *enhancement of the conductivity* at low frequency. 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 friction.[14]

$$\zeta_{DF}(\omega) = \zeta_{DF}(0) \frac{1+\sqrt{q}}{1+[q(1-i\omega\tau_{atm})]^{1/2}}, \qquad (2)$$

where $\zeta_{DF}(0)$ 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

$$\tau_{atm} = \frac{1}{(D_1+D_2)q\kappa_D^2}. \qquad (3)$$

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

$$\kappa_D^2 = \frac{4\pi}{\epsilon k_B T} \sum_{\alpha=1}^{2} \rho_\alpha q_\alpha^2, \qquad (4)$$

where ϵ is the static dielectric constant of the medium, q_α and ρ_α are, respectively, the charge of an ion and bulk number density of species α, k_B is Boltzmann constant, and T is the absolute temperature. The DF theory is valid at very low concentrations. For a typical 0.001 M solution of a 1:1 salt, $\tau_{atm} \sim 10^{-7}$ s and, therefore, the dispersion of the DF friction for such a solution is predicted to occur in the megahertz or below gigahertz 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 gigahertz. 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. Thus one immediate effect of the frequency dependence is the inapplicability of any form like Debye–Huckel–Onsager limiting law.

Recently Chandra, Wei, and Patey (CWP)[19] have addressed the problem of frequency dependence of ionic conductivity. These authors 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 two closed-form expressions of the frequency-dependent conductivity (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 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 form[19]

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^{2} \frac{\rho_\alpha q_\alpha^2 D_\alpha}{1-i\omega D_\alpha m_\alpha/k_B T}, \qquad (5)$$

where m_α is the mass of an ion of species α. Model II of CWP is based on a different expression of the frequency-dependent diffusion coefficient 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 by[19]

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^{2} \rho_\alpha q_\alpha^2 \left[\frac{D_\alpha \Omega_\alpha^2 - i\omega k_B T/m_\alpha}{\Omega_\alpha^2 - \omega^2 - i\omega D_\alpha \Omega_\alpha^2 m_\alpha/k_B T} \right], \qquad (6)$$

where Ω_α is the Einstein frequency of an ion of species α. We note that Ω_α^2 is proportional to the mean square force acting on an ion. The results of CWP were compared with those of molecular dynamics simulations. Their theory is capable of predicting the Debye–Falkenhagen effect at low frequency and was found to provide a reasonable description of the ionic motion at high frequency when there were no ion pairs and tightly bound solvation shells in the solution.[19] However, for many complex systems, the theory of CWP was found to be inadequate which, in part, can be attributed to the absence of full self-consistent calculation of the frequency-dependent electrolyte friction in this theory. It is clear that further work is needed to fully understand the ionic conductivity at finite frequency.

More recently we have developed a self-consistent theory of the zero-frequency conductivity which describes the ionic flow when a static field is applied.[12,13] The theory is based on a combination of the mode coupling theory and the time-dependent density functional approach and included both ion atmosphere relaxation and electrophoretic effects. The theory correctly goes over to the well-known Debye–Huckel–Onsager (DHO) law[7,8] in the limit of very low ion concentration. In addition, it remains valid in the much higher concentration regime where the DHO limiting law fails completely. In the present paper, we extend the above-mentioned theory to investigate electrolyte friction and conductivity at finite frequencies.

In this work, we derive self-consistent expressions for the frequency-dependent electrolyte friction and the conductivity which incorporate the details of the static and dynamic ion–ion correlations and also the effects of self-motion of the

ions. Both the ion atmosphere relaxation and the electrophoretic effects are calculated at finite frequency and these contributions are combined to obtain the frequency-dependent friction and the conductivity. Self-consistency is essential in this problem because the dynamics of ion atmosphere relaxation and the electrophoretic friction depend on the mobility of the ions themselves. And the mobility of ions depends on the relaxation of these two effects. The above-mentioned self-consistency also demands an inherently non-Markovian theory for the relaxation of the ion atmosphere. It is shown that the DF expression of the frequency-dependent electrolyte friction can be recovered from the present microscopic theory in the limit of low ion concentration when the finite sizes of the ions are ignored and the collective dynamics of the ion atmosphere is described by diffusional motion. Thus, the validity and the limitations of the DF friction becomes clear from the present microscopic approach. The present theory also reproduces the expressions of the frequency-dependent conductivity derived by Chandra, Wei, and Patey[19] when appropriate limiting situations are considered.

Numerical results show that the frequency dependence of the electrolyte friction at finite concentration can be very different from that given by the DF expression. With increase of ion concentration, the dispersion of the friction is found to occur at a higher frequency because of faster relaxation of the ion atmosphere. Numerical results are also presented for the frequency dependence of the real and imaginary parts of the conductivity. At low frequency, the real part of the conductivity changes rather weakly with frequency. In fact, the real part shows a slight increase at low frequency which can be attributed to the Debye–Falkenhagen effect. 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 presence of a static or low frequency field. The Cole–Cole plots of the conductivity reveal a nearly Debye behavior of the conductivity dispersion for very dilute solutions. As the concentration is increased, the dispersion becomes non-Debye at low frequency due to Debye–Falkenhagen effect.

The organization of the rest of the paper is as follows. In Sec. II, we present the theory and in Sec. III, we discuss the reduction to the Debye–Falkenhagen expression. In Sec. IV, we show how the conductivity expressions of CWP can be recovered from the present theory. We discuss the numerical results in Sec. V. Section VI concludes with a summary and a brief discussion on the extensions of the present theory to treat frequency-dependent diffusivities of charged colloid suspensions and conductivity of a dilute polyelectrolyte solution.

II. THEORETICAL FORMULATION

We consider an electrolyte solution consisting of positive and negative ions immersed in a continuum solvent of dielectric constant ϵ. The ions interact through a spherically symmetric short-range potential and a long-range coulombic interaction potential which is scaled by the value of the dielectric constant. The pair potential of interaction between two ions of charge q_α and q_β is given by

$$u_{\alpha\beta}(r) = u_{\alpha\beta}^{SR}(r) + \frac{q_\alpha q_\beta}{\epsilon r}, \tag{7}$$

where r is the distance between the two ions and $u_{\alpha\beta}^{SR}(r)$ is a spherically symmetric short-range interaction potential. This so-called primitive model is well known in the studies of structure and dynamics of electrolyte solutions.[21] Throughout this paper, we label the positive ions as species 1 and the negative ions as species 2. We denote the position ($\mathbf{r}$) and time (t) dependent number density of species α as $\rho_\alpha(\mathbf{r},t)$ and its Fourier transform $\rho_\alpha(\mathbf{k},t)$ is defined by

$$\rho_\alpha(\mathbf{k},t) = \int_{-\infty}^{\infty} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \rho_\alpha(\mathbf{r},t). \tag{8}$$

In this paper, we are interested in calculating the frequency-dependent friction on a moving ion and the frequency-dependent conductivity of the solution. For this purpose, we consider a single tagged ion of charge q_s. The velocity of the tagged ion is $v_s(t)$ at time t. Its time evolution can be described by the following generalized Langevin equation:[21]

$$\frac{\partial}{\partial t} v_s(t) = -\int_0^\infty dt\, \zeta_s(t-t')\, v_s(t') + f_s(t), \tag{9}$$

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 frequency-dependent friction $\zeta_s(\omega)$ is defined as the Laplace transform of $\zeta_s(t)$,

$$\zeta_s(\omega) = \int_0^\infty dt\, e^{i\omega t} \zeta_s(t). \tag{10}$$

The self-diffusion coefficient $D_s(\omega)$ is related to the friction $\zeta_s(\omega)$ by the following generalized Einstein relation:[21]

$$D_s(\omega) = \frac{k_B T}{m} [-i\omega + \zeta_s(\omega)]^{-1}, \tag{11}$$

where m_s is the mass of the tagged ion. In the present work, our focus will be on the calculation of the frequency-dependent friction $\zeta_s(\omega)$ and the frequency-dependent self-diffusion coefficient $D_s(\omega)$. Once the frequency-dependent self-diffusion coefficient $D_s(\omega)$ is known, the frequency-dependent conductivity $\sigma(\omega)$ can be calculated by using the following generalized Nernst-Einstein relation;[19,21]

$$\sigma(\omega) = \frac{1}{k_B T} \sum_{\alpha=1}^{2} \rho_\alpha q_\alpha^2 D_\alpha(\omega), \tag{12}$$

where ρ_α and q_α are defined in Sec. I. We note in this context that the frequency-dependent electric conductivity can, in general, be related to the Fourier transform of the electric current–current time correlation function.[21] Since the electric current is a collective dynamical quantity, its time correlation function comprises 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. (12)] includes only the self part and thus the cross part is ignored in the present work.

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 concentrations, the contribution of the cross part is expected to be rather small. 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%.[11] We also note that the solvent is considered to be a dielectric continuum in the present theory. 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.

The total friction acting on the tagged ion can be decomposed into two parts. The first part is due to the microscopic interaction of the tagged ion with the surrounding solvent molecules and 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. Thus, the total friction on the tagged ion can be written as[22]

$$\frac{1}{\zeta_s(\omega)} = \frac{1}{\zeta_{s;\text{mic}}(\omega)} + \frac{1}{\zeta_{s;\text{hyd}}(\omega)}. \tag{13}$$

As discussed in Ref. 22, Eq. (13) has a simple physical interpretation. A tagged ion diffuses by two mechanisms. The first one is by the random walk caused by its interactions with the surrounding solvent and ion molecules. The second is the random walk caused by the natural currents or flows present in the liquid. These two contributions to diffusions are additive, as they originate from two different types of motions. However, the mechanisms are coupled at a dynamic level which, in this theory, enters nicely through self-consistency mentioned earlier.

The microscopic friction is most easily analyzed by using the Kirkwood's formula[23] for friction which expresses it in terms of an integration over the force–force time correlation function. Since the time-dependent force on the tagged ion has contributions from solvent density and polarization fluctuations and also from ion atmosphere fluctuations, one can decompose the total microscopic friction into a solvent contribution $\zeta_{s;\text{mic}}(c=0)$[24,25] which is assumed to be a constant independent of ion concentration and a concentration-dependent ion contribution $\delta\zeta_{s;\text{mic}}(\omega)$. In the present work, we calculate the frequency dependence of the ion contribution to the microscopic friction. Thus, the solvent contribution is not calculated in the present work. 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, inverse of friction.[26–28] Since the current modes of the solution consists of both the solvent and ion currents, the hydrodynamic contribution to the total friction can be expressed as[12,13]

$$\frac{1}{\zeta_{s;\text{hyd}}(\omega)} = \frac{1}{\zeta_{s;\text{hyd}}(c=0)} + \frac{1}{\delta\zeta_{s;\text{hyd}}(\omega)}, \tag{14}$$

where $\zeta_{s;\text{hyd}}(c=0)$ is the viscous friction which also includes the additional dielectric friction contribution due to the polarization current[29,30] and $\delta\zeta_{s;\text{hyd}}(\omega)$ represents the electrolyte friction on the tagged ion due to coupling with the ion atmosphere current, which is commonly known as the electrophoretic effect. In the following, we calculate the frequency dependence of the ion atmosphere contributions $\delta\zeta_{s;\text{mic}}(\omega)$ and $\delta\zeta_{s;\text{hyd}}(\omega)$.

A. Calculation of the time-dependent microscopic friction, $\delta\zeta_{s,\text{mic}}(t)$

The time-dependent microscopic electrolyte friction, $\delta\zeta_{s,\text{mic}}(t)$, is calculated by using the following Kirkwood formula:[23]

$$\delta\zeta_{s,\text{mic}}(t) = \frac{1}{3k_BT} \int d\mathbf{r}\langle F(\mathbf{r},t)F(\mathbf{r},0)\rangle, \tag{15}$$

where $F(\mathbf{r},t)$ is the time-dependent force exerted on the tagged ion due to its interaction with all other ions in the solution. An expression for $F(\mathbf{r},t)$ can be obtained from time-dependent density functional theory and the microscopic friction can be formally expressed as an integral over the wave vector space in the following form:[13,31]

$$\delta\zeta_{s,\text{mic}}(t) = \frac{k_BT}{3(2\pi)^3} \sum_{\alpha,\beta} \int d\mathbf{k}\, k^2 c_{sa}(k)\sqrt{\rho_\alpha\rho_\beta}$$
$$\times G_{\alpha\beta}(k,t)c_{s\beta}(k)F_s(k,t), \tag{16}$$

where $F_s(k,t)$ is the self-dynamic structure factor of the tagged ion. $G_{\alpha\beta}(k,t)$ is the ionic van Hove function defined by

$$G_{\alpha\beta}(k,t) = (N_\alpha N_\beta)^{-1/2}\langle\rho_\alpha(\mathbf{k},t)\rho_\beta(-\mathbf{k},0)\rangle, \tag{17}$$

where $\langle\cdots\rangle$ denotes average over an equilibrium ensemble. N_α and N_β are, respectively, the number of ions of species α and β in the solution. We denote $G_{\alpha\beta}(k,\omega)$ as the frequency-dependent van Hove function obtained by Laplace transformation of $G_{\alpha\beta}(k,t)$. Use of time-dependent density functional theory leads to the following equation for the frequency-dependent van Hove function:[13,32]

$$G_{\alpha\beta}(k,\omega) = [-i\omega + D_\alpha(\omega)k^2]^{-1}S_{\alpha\beta}(k)$$
$$+ \frac{D_\alpha(\omega)k^2}{-i\omega + D_\alpha(\omega)k^2}$$
$$\times \sum_{\gamma=1}^{2}\sqrt{\rho_\alpha\rho_\gamma}c_{\alpha\gamma}(k)G_{\gamma\beta}(k,\omega), \tag{18}$$

where the frequency-dependent diffusion coefficient $D_\alpha(\omega)$ is related to friction by Eq. (11). $S_{\alpha\beta}(k) = G_{\alpha\beta}(k,t=0)$ where $S_{\alpha\beta}(k)$ is the partial static structure factor between species α and β. $S_{\alpha\beta}(k)$ is related to the Fourier transform of the pair correlation function $h_{\alpha\beta}(k)$ by the following relation:

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}\,h_{\alpha\beta}(k). \tag{19}$$

The four coupled equations ($\alpha, \beta = 1,2$) as given by Eq. (18) can be solved analytically to obtain the following explicit results for the frequency dependence of the ionic van Hove functions:

$$G_{11}(k,\omega) = \frac{1}{Z(k,\omega)}[\{-i\omega + D_2(\omega)k^2(1-\rho_2 c_{22}(k))\}$$
$$\times S_{11}(k) + D_1(\omega)k^2\sqrt{\rho_1\rho_2}c_{12}(k)S_{21}(k)], \quad (20)$$

$$G_{12}(k,\omega) = \frac{1}{Z(k,\omega)}[\{-i\omega + D_2(\omega)k^2(1-\rho_2 c_{22}(k))\}$$
$$\times S_{12}(k) + D_1(\omega)k^2\sqrt{\rho_1\rho_2}c_{12}(k)S_{22}(k)], \quad (21)$$

$$G_{21}(k,\omega) = \frac{1}{Z(k,\omega)}[\{-i\omega + D_1(\omega)k^2(1-\rho_1 c_{11}(k))\}$$
$$\times S_{21}(k) + D_2(\omega)k^2\sqrt{\rho_1\rho_2}c_{21}(k)S_{11}(k)], \quad (22)$$

$$G_{22}(k,\omega) = \frac{1}{Z(k,\omega)}[\{-i\omega + D_1(\omega)k^2(1-\rho_1 c_{11}(k))\}$$
$$\times S_{22}(k) + D_2(\omega)k^2\sqrt{\rho_1\rho_2}c_{21}(k)S_{12}(k)], \quad (23)$$

where

$$Z(k,\omega) = -\omega^2 - i\omega\Delta(k)[D_1(\omega)k^2 S_{22}(k) + D_2(\omega)k^2 S_{11}(k)]$$
$$+ D_1(\omega)D_2(\omega)k^4\Delta(k), \quad (24)$$

and

$$\Delta(k) = [S_{11}(k)S_{22}(k) - S_{12}(k)^2]^{-1}. \quad (25)$$

In deriving Eqs. (20)–(25) we have also used the following relation between $c_{\alpha\beta}(k)$ and $S_{\alpha\beta}(k)$ for a two-component system:

$$1 - \rho_1 c_{11}(k) = \Delta(k)S_{22}, \quad (26)$$

$$\sqrt{\rho_1\rho_2}c_{12}(k) = \Delta(k)S_{12}(k), \quad (27)$$

and a similar relation between $c_{22}(k)$ and $S_{11}(k)$. These relations can be derived from the Ornstein–Zernike equations relating the direct and the pair correlation functions.[21] We note that the time dependence of the van Hove functions can be obtained through Laplace inverse transformation. The Laplace transform of the self-dynamic structure factor of the tagged ion can be described by

$$F_s(k,\omega) = \frac{1}{-i\omega + D_s(\omega)k^2}, \quad (28)$$

where $D_s(\omega)$ is the frequency-dependent self-diffusion coefficient of the tagged ion. We still require the solutions of the static structure factors and the direct correlation functions for the calculation of the microscopic electrolyte friction. We note that the direct correlation functions are related to the static structure factors by Eqs. (26) and (27) and the static structure factors are related to the pair correlation functions by Eq. (19). Thus, we require the solutions of the pair correlation functions for the calculation of the quantities $S_{\alpha\beta}(k)$ and $c_{s\alpha}(k)$. We need to specify the nature of the short-range interaction between ions for this purpose. We consider the ions to be charged hard spheres with their diameters becom-

ing the parameters of the model solution and we use the solutions of Attard[33] for the ionic pair correlations which are quite accurate even at high concentrations.

B. Calculation of the hydrodynamic friction—The electrophoretic term

The ion atmosphere contribution to the hydrodynamic friction originates from the coupling of the tagged ion velocity with the collective ion current of the system.[12,13] 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, respectively, the charge density and total ion current of the solution. The hydrodynamic friction is then given by

$$\frac{k_BT}{\delta\zeta_{s,\text{hyd}}(\omega)} = \int_0^\infty dt\, e^{i\omega t}\sum_k \sum_{k'} \langle u_{0x}, \rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k})\rangle$$
$$\times \langle\rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k}), \rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k})\rangle^{-1}$$
$$\times \langle\rho^c(\mathbf{k})\mathbf{j}(-\mathbf{k}), e^{i\mathcal{L}t}\rho^c(\mathbf{k'})\mathbf{j}(-\mathbf{k'})\rangle$$
$$\times \langle\rho^c(\mathbf{k'})\mathbf{j}(-\mathbf{k'}), \rho^c(\mathbf{k'})\mathbf{j}(-\mathbf{k'})\rangle^{-1}$$
$$\times \langle\rho^c(\mathbf{k'})\mathbf{j}(-\mathbf{k'}), u_{0x}\rangle, \quad (29)$$

where u_{0x} is the velocity of the tagged ion along a particular direction (say, x) and $e^{i\mathcal{L}t}$ is the time evolution operator. The vertices and the time correlation function in Eq. (29) can be evaluated to obtain the following formal expression for the hydrodynamic friction:

$$\frac{k_BT}{\delta\zeta_{s,\text{hyd}}(\omega)} = \frac{1}{3\pi^2 N}\int_0^\infty dt\, e^{i\omega t}\int dk\, k^2[q_1 + \rho_1 q_1 h_{11}(k)$$
$$+ \rho_2 q_2 h_{12}(k)]^2\sum_{\alpha\beta}\sqrt{\rho_\alpha\rho_\beta}q_\alpha q_\beta$$
$$\times [F_{s\alpha}(k,t)\delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}G_{\alpha\beta}^d(k,t)]$$
$$\times \left[\sum_{\alpha\beta}\sqrt{\rho_\alpha\rho_\beta}q_\alpha q_\beta\{\delta_{\alpha\beta} + \sqrt{\rho_\alpha\rho_\beta}h_{\alpha\beta}(k)\}\right]^{-2}$$
$$\times [C^L(k,t) + 2C^T(k,t)], \quad (30)$$

where N is the total number of ions in the solution. $F_{s\alpha}(k,t)$ is the self van Hove function of an ion of species α, and $G_{\alpha\beta}^d(k,t)$ is the so-called distinct van Hove function between species α and β. $C^L(k,t)$ and $C^T(k,t)$ are, respectively, the longitudinal and the transverse current correlation functions of the ions. The decay of the longitudinal current occurs at a much faster time scale than that of the transverse current.[21] For nonpolar liquids, it is known that the contribution of the longitudinal current to zero and low frequency friction is negligible (less than 5%) compared to the transverse term.[26,27] Therefore, the contribution of the longitudinal current relaxation to the hydrodynamic friction is expected to be important only at very high frequency and we have ignored it in the present calculations. We also note that it is the transverse part which leads to the Stokes–Einstein relation for nonpolar molecules.[27] For electrolytes, the transverse term leads to the electrophoretic term of Debye–Huckel.[13] In the

present work, we also assume a symmetric binary electrolyte with ions of equal size such that $h_{11}(k)=h_{22}(k)$. Equation (30) then simplifies to

$$\frac{k_BT}{\delta\zeta_{s,\text{hyd}}(\omega)} = \frac{2}{3\pi^2\rho N}\int_0^\infty dt\, e^{i\omega t}\int dk\, k^2 F_s(k,t)C^T(k,t)$$

$$+ \frac{2}{3\pi^2\rho N}\int_0^\infty dt\, e^{i\omega t}\int dk\, k^2[\rho_1 G_{11}^d(k,t)$$

$$-\rho_2 G_{12}^d(k,t)]C^T(k,t), \tag{31}$$

where ρ is the total ion density of the solution. We note that the first term on the right-hand side of Eq. (31) gives the ion contribution to the usual Stokes (or viscous) friction and the second term represents the so-called electrophoretic friction. In the following calculations, we will focus on the electrophoretic friction only because it is the most important hydrodynamic contribution to the total ionic friction. We also note that the relaxation of the transverse velocity correlation function occurs much faster than the distinct van Hove functions so that $G_{11}^d(k,t)$ and $G_{12}^d(k,t)$ in Eq. (31) can be approximated by their zero time values $h_{11}(k)$ and $h_{12}(k)$, respectively. Since the transverse current does not couple with density relaxation, its relaxation can be described quite well by an exponential function with a relaxation time inversely proportional to the shear viscosity of the medium as follows:

$$C^T(k,t) = \frac{Nk_BT}{2m}e^{-\eta k^2 t/\rho m}. \tag{32}$$

We note that the decay of the transverse ionic current as given by Eq. (32) is different from that of the pure solvent in the sense that the viscosity which appears in Eq. (32) is concentration dependent. In the numerical calculations, however, the viscosity is taken as an input parameter. We next substitute Eq. (32) in Eq. (31) to obtain the following simple expression for the frequency-dependent electrophoretic friction:

$$\frac{k_BT}{\delta\zeta_{s,\text{hyd}}(\omega)} = \frac{k_BT}{3\pi^2\rho m}\int_0^\infty dt\, e^{i\omega t}\int dk\, k^2[\rho_1 h_{11}(k)$$

$$-\rho_2 h_{12}(k)]e^{-\eta k^2 t/\rho m}. \tag{33}$$

We have solved Eqs. (16) and (33) for the microscopic and the electrophoretic frictions iteratively to obtain the self-consistent results of the frequency-dependent electrolyte friction at varying concentrations. The results of frequency-dependent friction are then used to calculate the frequency-dependent ion diffusion and conductivity by using Eqs. (11) and (12), respectively.

III. DERIVATION OF DEBYE–FALKENHAGEN FORM OF FREQUENCY-DEPENDENT FRICTION

In this section we identify the limiting conditions under which the present theory reduces to the well-known Debye–Falkenhagen expression [Eq. (2)] 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 electro-

phoretic term is ignored. Accordingly, we consider only the microscopic electrolyte friction as given by Eq. (16) and rewrite it in the following form:

$$\delta\zeta_{s,\text{mic}}(t) = \frac{k_BT}{3(2\pi)^3}\int d\mathbf{k}\, k^2[C_s(k)][G(k,t)]$$

$$\times[C_s(k)]^\dagger F_s(k,t), \tag{34}$$

where $[C_s(k)]$ is a row matrix defined by

$$[C_s(k)] = [\sqrt{\rho_1}c_{s1}(k)\ \sqrt{\rho_2}c_{s2}(k)], \tag{35}$$

and $[C_s(k)]^\dagger$ is the transpose of $[C_s(k)]$. $[G(k,t)]$ is the 2×2 van Hove function matrix with elements $G_{\alpha\beta}(k,t)$, $\alpha,\beta=1,2$. Clearly, $[G(k,t)]$ becomes the structure factor matrix $[S(k)]$ at $t=0$. We assume that the ions are point ions and use Debye–Huckel (DH) theory[34] of ion–ion pair correlations. The ion–ion partial structure factor is then given by

$$S_{\alpha\beta}(k) = \delta_{\alpha,\beta} - \frac{4\pi q_\alpha q_\beta\sqrt{\rho_\alpha\rho_\beta}}{\epsilon k_BT}\frac{1}{k^2+\kappa_D^2}, \tag{36}$$

where the inverse Debye screening length κ_D is defined by Eq. (4). The ion–ion direct correlation function for the point ions in DH theory can be obtained by combining Eqs. (26) and (27) and (36) and it is given by

$$c_{\alpha\beta}(k) = -\frac{4\pi q_\alpha q_\beta}{\epsilon k_BT}\frac{1}{k^2}. \tag{37}$$

We next assume that the relaxation of the ionic van Hove functions is described by diffusional motion. That is, we ignore the frequency dependence of $D_\alpha(\omega)$ in Eq. (18) and replace it by its zero-frequency value D_α and solve the resultant equation in the time domain to obtain

$$[G(k,t)] = [S(k)]\exp(-[D]k^2t[S(k)]^{-1}). \tag{38}$$

where $[D]$ is the diagonal matrix of self-diffusion coefficients. When Eqs. (36)–(38) are substituted in Eq. (34), the resultant integral over the wave vector $\mathbf{k}$ can be evaluated analytically[35] and the final result of the time-dependent microscopic electrolyte friction is given by

$$\zeta_{s,\text{mic}}(t) = \frac{q_s^2\kappa_D^2}{3\epsilon}\left[\frac{e^{-D\kappa_D^2 t}}{\sqrt{2\pi Dt}} + \kappa_D e^{D\kappa_D^2 t}\{\Phi(\sqrt{2\kappa_D^2 Dt})-1\}\right], \tag{39}$$

where $\Phi(x)$ is the error function and it is assumed that all ions have the same diffusion coefficient D. We note that Eq. (39) of time-dependent electrolyte friction becomes identical with the one derived by de Leon et al.[35] when the diffusion coefficient D in the right-hand side of Eq. (39) is replaced by D^0, which is the value of the ion diffusion coefficient in the limit of infinite dilution.

The Laplace transform of Eq. (39) can be carried out analytically[36] to obtain the following expression of the frequency-dependent friction:

$$\zeta_{s;\text{mic}}(\omega) = \frac{q_s^2\kappa}{6\epsilon D}\frac{1}{1+\frac{1}{\sqrt{2}}[1-i\omega/D\kappa^2]^{1/2}}. \tag{40}$$

The zero-frequency microscopic electrolyte friction is given by[13]

$$\zeta_{s;\text{mic}}(0) = \frac{q_s^2 \kappa}{6 \epsilon D}(2 - \sqrt{2}), \tag{41}$$

We next substitute Eq. (41) in Eq. (40) and rewrite the resultant expression of the frequency-dependent friction in the following form:

$$\zeta_{s;\text{mic}}(\omega) = \zeta_{s;\text{mic}}(0) \frac{1 + \sqrt{q}}{1 + \sqrt{q}[1 - i\omega\tau_{\text{atm}}]^{1/2}}, \tag{42}$$

where q and τ_{atm} are defined in Sec. I. Equation (42) is identical to the DF expression [Eq. (2)]. Thus, it is clear from the above-mentioned 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.

It may be noted that the DF theory incorporates the cross dynamical coupling of ions at the level of ion atmosphere relaxation (or the ionic van Hove functions) and not at the level of ionic velocity or current relaxation. Thus, the DF expression of ion atmosphere friction does not include the effects of the so-called current cross terms. The DF expression is treated as the limiting expression of ion atmosphere friction when current cross terms are ignored and it is shown that the present microscopic theory correctly goes over to this limiting expression at the limit of very low ion concentration. Also, the contribution of the cross correlation is expected to be minimal at very low ion concentration where the DF theory is valid.

IV. DERIVATION OF THE CONDUCTIVITY EXPRESSIONS OF CHANDRA, WEI, AND PATEY

In this section we describe how the CWP expressions of the frequency-dependent conductivity can be recovered from the present theory. To recover the expression of model I [Eq. (5)], we ignore the frequency dependence of $\zeta_s(\omega)$ in Eq. (11) and replace it by the zero-frequency value ζ_s so that

$$D_s(\omega) = \frac{k_B T}{m_s} \frac{1}{-i\omega + \zeta_s} = \frac{D_s}{1 - i\omega D_s m_s / k_B T}, \tag{43}$$

where, in deriving the second equality, we have used the Einstein relation $\zeta_s = k_B T / D_s m_s$. On combining Eq. (43) with the Nernst–Einstein relation [Eq. (12)], one gets Eq. (5), 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,[19]

$$\sigma(\omega) = \frac{\sigma}{1 - i\omega D m / k_B T}, \tag{44}$$

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 $\sigma(\omega)$.[15]

To recover the expression of model II [Eq. (6)], we ignore the hydrodynamic effects so that $\zeta_s(t) = \zeta_{s;\text{mic}}(t)$ and we write the total friction as

$$\zeta_s(t) = \frac{1}{3 k_B T} \int d\mathbf{r} \langle F(\mathbf{r},t) F(\mathbf{r},0) \rangle, \tag{45}$$

where $F(\mathbf{r},t)$ is the total force (including the solvent contribution) acting on the tagged ion at time t. Clearly, $\zeta_s(t=0)$ is described by the zero-time force–force correlation

$$\zeta_s(t=0) = \frac{1}{3 k_B T} \int d\mathbf{r} \langle F(\mathbf{r},0) F(\mathbf{r},0) \rangle = \Omega_s^2, \tag{46}$$

where Ω_s is the Einstein frequency[21] of the tagged ion. We next assume an exponential decay of $\zeta_s(t)$ so that

$$\zeta_s(t) = \Omega_s^2 e^{-t/\tau_s}. \tag{47}$$

where relaxation time τ_s can be eliminated in favor of the diffusion coefficient D_s by using the above-described Einstein relation and the resultant expression after Laplace transformation gives

$$\zeta_s(\omega) = \frac{\Omega_s^2}{-i\omega + D_s m_s \Omega_s^2 / k_B T}. \tag{48}$$

Equation (48), on combining with Eqs. (11) and (12), gives Eq. (6), which is the CWP 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. We also note that although the hydrodynamic effects such as electrophoretic contributions are not explicitly included in this model, such effects can be implicitly included to some extent by using proper experimental values of the zero-frequency diffusion coefficients.

V. NUMERICAL RESULTS AND DISCUSSION

We present numerical results of the frequency dependence of friction and conductivity for solutions of varying ion concentration. In the numerical calculations, all ions of the solutions are assumed to be of equal diameter σ and equal mass m for simplicity. The solutions are considered to be of a symmetric salt such that the charge of each positive ion is q_1 and that of each negative ion is $-q_1$ and $\rho_1 = \rho_2$ and also $D_1 = D_2$. The solutions can be completely specified by specifying the values of 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 values of ϵ and q_1^* for all the solutions are 80 and 14.1, respectively. The above-mentioned value of the reduced charge corresponds to the charge of a univalent ion of diameter 2.82 Å at $T = 298$ K.

In the numerical calculations, the self-consistent equations of the microscopic and electrophoretic frictions are solved iteratively. We first calculate the zero-frequency electrolyte friction and the zero-frequency diffusion coefficient D. This zero-frequency diffusion coefficient is then used as the initial guess for the frequency-dependent diffusion coefficient $D(\omega)$ and we calculate the frequency-dependent ionic van Hove [Eqs. (20)–(23)] and self van Hove [Eq. (28)] functions. The time dependence of these van Hove functions are then calculated through numerical inverse Laplace trans-
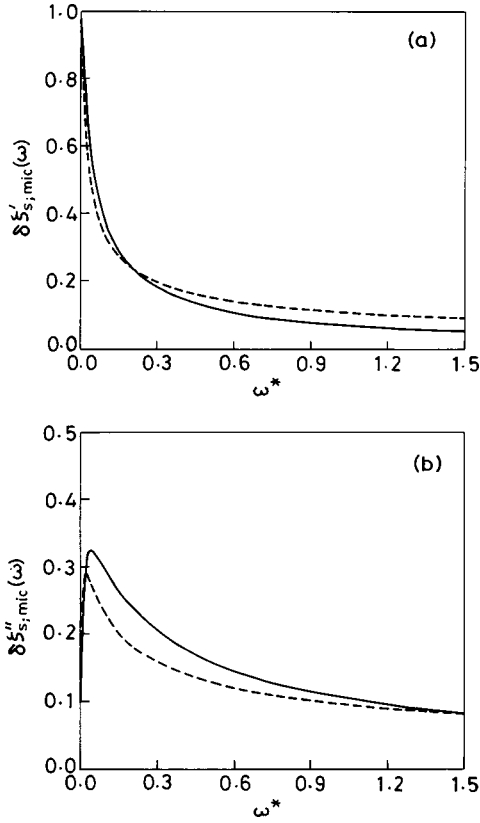
FIG. 1. The frequency dependence of the (a) real and (b) imaginary parts of the microscopic electrolyte friction on an ion in a 0.01 M solution of a 1:1 electrolyte. The solid and the dashed curves represent, respectively, the results of the present theory and of Debye–Falkenhagen expression [Eq. (2)].
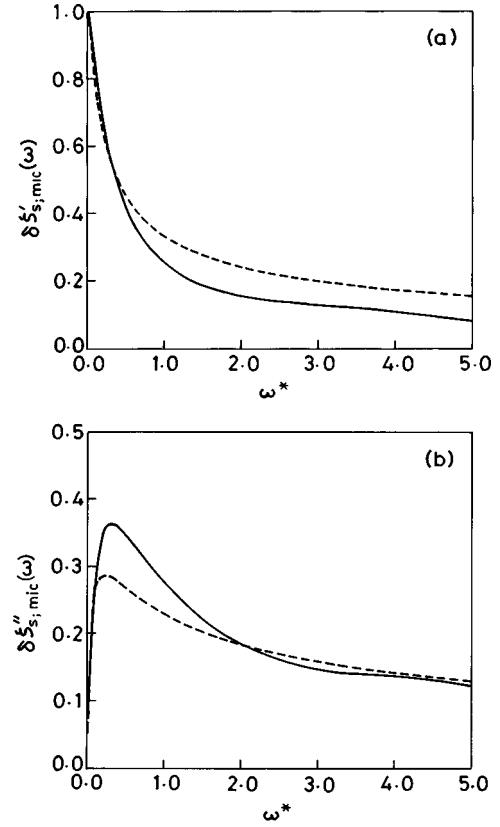

FIG. 2. The frequency dependence of the (a) real and (b) imaginary parts of the microscopic electrolyte friction on an ion in a 0.1 M solution. The different curves are as in Fig. 1.

formation. This leads to the calculation of the time-dependent microscopic friction $\zeta_{s;\text{mic}}(t)$ [Eq. (16)], which is then numerically Laplace transformed to obtain $\zeta_{s;\text{mic}}(\omega)$. The electrophoretic friction is calculated from Eq. (33). These two frequency-dependent frictions are then combined to obtain the new values of $D(\omega)$ from Eq. (11). The entire process is repeated several times until convergence is achieved.

We decompose the frequency-dependent microscopic electrolyte friction into its real and imaginary parts as follows:

$$\delta\zeta_{s;\text{mic}}(\omega) = \delta\zeta'_{s;\text{mic}}(\omega) + i\,\delta\zeta''_{s;\text{mic}}(\omega). \qquad (49)$$

Similar decomposition is also made for the electrophoretic friction and the conductivity functions as these are all complex quantities at finite frequencies. In Figs. 1(a) and 1(b), we have shown the frequency dependence of the real and imaginary parts of the microscopic electrolyte friction for $\rho_1^* = 0.000\,135$. The above-mentioned value of the reduced ion density corresponds to a 0.01 M solution for $\sigma = 2.8\,\text{Å}$. Thus, this solution corresponds to 0.01 M solution of a 1:1 electrolyte at room temperature. The corresponding results for a 0.1 molar solution are shown in Figs. 2(a) and 2(b). The values of the friction at different frequencies are normalized by its zero-frequency value and the reduced frequency $\omega^* = \omega\sigma^2/D$. In the present calculations, we have used $\eta = 8.95 \times 10^{-3}\,\text{g cm}^{-1}\,\text{s}^{-1}$, $D^0 = 2.0 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ and $m = 40\,\text{amu}$ where D^0 is the ionic diffusion coefficient at infi-

nite dilution. In Figs. 1 and 2, the results of DF friction [Eq. (2)] are also included for comparison. At low concentration and at low frequency, the results of the present theory are found to be quite close to the DF results. 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.

In Fig. 3, we have shown the frequency dependence of the electrophoretic term for the 0.1 M solution. The disper-
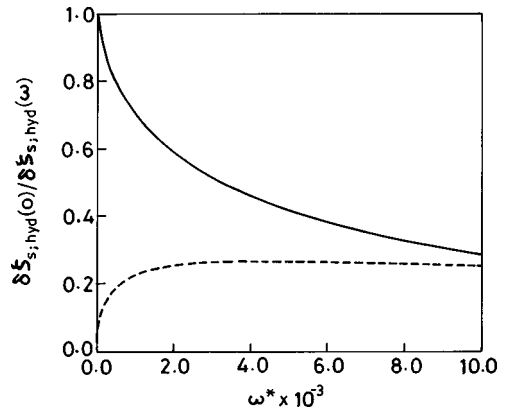

FIG. 3. The frequency dependence of the electrophoretic friction on an ion in a 0.1 M solution. The solid and the dashed curves represent, respectively, the real and the imaginary parts.
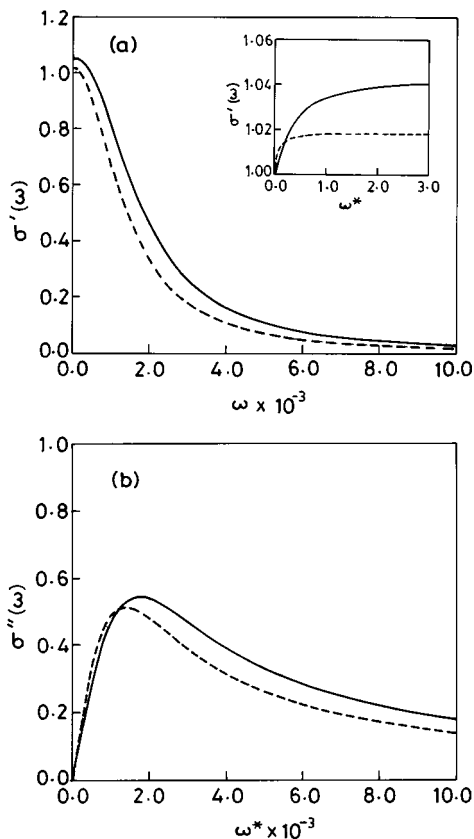
FIG. 4. The frequency dependence of the (a) real and (b) imaginary parts of the conductivity of solutions of a 1:1 electrolyte. The dashed and the solid curves correspond to the 0.01 and 0.1 M solutions, respectively.

FIG. 5. The Cole–Cole plots of the frequency-dependent conductivity. The imginary part is plotted against the real part calculated at different frequencies. The dashed and the solid curves are for 0.01 and 0.1 M solutions, respectively. The dotted curve represents the simple Debye behavior.

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 for the two solutions are shown in Fig. 5. Significant non-Debye behavior is observed at higher ion concentration. This is not unexpected as the Debye form of $\sigma(\omega)$ [Eq. (44)] is valid only in limiting situations as discussed in Sec. V and, in general, the dispersion of the conductivity shows a more complex behavior.

VI. SUMMARY AND CONCLUSIONS

We have presented a self-consistent theory of the frequency-dependent friction on a moving ion and the conductivity of electrolyte solutions. The theory is based on a combination of the mode coupling theory and time-dependent density functional approach and it incorporates the details of the static and dynamic ion–ion correlations and also the effects of self-motion of the ions. Both the ion atmosphere relaxation and the electrophoretic effects are included which are now frequency dependent and the results of the two effects are combined to obtain the frequency-dependent electrolyte friction and the conductivity. It is shown that the present theory correctly reduces to the well-known Debye–Falkenhagen expression of the frequency-dependent electrolyte friction in the limit of very low ion concentration. It is also shown how the expressions of the frequency-dependent conductivity derived earlier by Chandra, Wei, and Patey[19] can be recovered from the present theory. Numerical results are obtained for the real and imaginary parts of the friction and the conductivity at various frequencies. It is found that at high concentration the frequency dependence of the friction can be quite different from that given by the Debye–Falkenhagen expression. With increase of concentration, the dispersion of the electrolyte friction is found to occur at a higher frequency because of faster relaxation of the ion atmosphere. The real part of the conductivity is found to change rather weakly at low frequency. In fact, at

sion of the electrophoretic contribution is seen to occur at a much higher frequency as one would expect. In fact, any noticeable change in the electrophoretic term is found only above $\omega^* = 10^3$, which corresponds to a frequency well above the gigahertz 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 Figs. 4(a) and 4(b) for the 0.01 and 0.1 M solutions. The ionic charges are the same as in Fig. 1. 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 other hand, 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 [Eq. (11)]
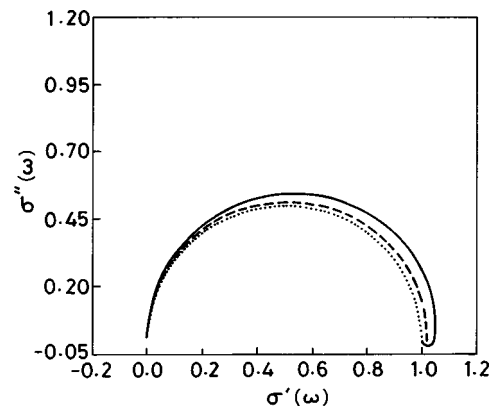
low concentration, a slight increase of the real part of the conductivity is observed at low frequency which can be attributed to the so-called Debye–Falkenhagen effect. The dispersion of the conductivity is found to occur at a much higher frequency than that of the ion atmosphere friction. Also, significant non-Debye behavior is observed in the Cole–Cole plots of the conductivity of concentrated solutions.

The theory of the frequency-dependent conductivity developed here can be used to study the dynamics of many interesting chemical phenomena such as solvation dynamics,[37–40] dielectric relaxation,[5,41,42] and chemical reactions in electrolyte solutions.[43–46] In all these chemical problems, the motion of ions in response to a time-dependent electric field or to a changing charge distribution inside the solution plays an important role and the theory developed here can be applied or generalized to study such problems. Also, in the present theory, the solvent is considered to be a dielectric continuum. Thus, although the present theory incorporates the static and dynamic ion–ion correlations and the screening effects, the molecular details of the ion–solvent and solvent–solvent correlations are missing. Also, since the conductivity is calculated by using the generalized Nernst–Einstein relation [Eq. (12)], the dynamical cross correlations between velocities of distinct ions or the collective effects in the current–current correlation are not included in the present theory. Because of these approximations, the present theory is limited to solutions of not too high concentration (say, less than 0.1 M). In fact, recent computer simulations have shown that for highly concentrated solutions, the dynamic ion–solvent correlations and the cross velocity correlations are responsible for much of the complex behavior of the conductivity at finite frequencies.[19] Thus, it would certainly be worthwhile to generalize the present self-consistent theory to include the molecularity of the solvent and also the collective effects in the current-current correlation.

The theoretical formulation developed here, and in our previous work, can be extended to understand some aspects of the conductivity of dilute polyelectrolyte solutions. This is a problem where dynamical cross correlations can be rather important. The large polyion, with very low mobility, can exert considerable amount of friction on the more mobile counterions and can in fact lead to a partial immobilization of those counterions which are in the proximity of the polyion. This immobilization occurs as a consequence of the slow decay of the polyion–counterion cross-correlation function. Note that this immobilization or the quenching of motion of the counterions is mostly dynamical in origin and is different from the more traditional static view of the ''Manning condensation.''[47] Another problem of interest is the diffusion of charged colloids. While a detailed treatment of a tagged ion is still difficult because of the inhomogeneity, an average behavior can be obtained by following the procedure outlined in this paper. The basic aspect of the problem can be captured in the following fashion. The force on a counterion due to the polyion at a distance $\mathbf{r}$ from the polyelectrolyte center of mass can be given by

$$\mathbf{F},(r,t) = k_B T \nabla \int dr' c_{ic}(\mathbf{r}-\mathbf{r}') \delta \rho_c(\mathbf{r}',t)$$
$$+ k_B T \nabla \int dr' c_{ij}(\mathbf{r}-\mathbf{r}') \delta \rho_j(\mathbf{r}',t), \qquad (50)$$

where $c_{ci}(\mathbf{r},t)$ is the colloid-ion direct correlation function, $\delta \rho_c(\mathbf{r}',t)$ is the density fluctuation of the colloids, c_{ij} is the ion–ion direct correlation function, and $\delta \rho_j(\mathbf{r}',t)$ is the fluctuation in the density of ion type j. Equation (50) naturally leads to an expression for the friction which depends on the dynamic structure factor of the colloids. A similar expression can be written for the friction on the colloids which would involve the dynamic structure factor of the ions. These equations need to be solved self-consistently. While this method is well-known, one can carry out such detailed calculations now with the availability of the desired pair and direct correlation functions. In this context, we note the work of Leon et al.[35] where similar equations have been derived for the time-dependent friction on a charged colloidal particle from an approach of contracted description through generalized Langevin equation.[48] The resultant equations were, however, solved without incorporating the inherent self-consistency required in the problem. It would certainly be worthwhile to carry out full self-consistent calculations of the frequency-dependent friction on such charged macroparticles. Work in these areas is in progress.

[1] H. S. Harned, *The Physical Chemistry of Electrolyte Solutions* (Reinhold, New York, 1958).
[2] H. Falkenhagen, *Theorie der Elektrolyte* (Hirzel, Leipzig, 1971).
[3] J. Koryta and J. Dvorak, *Principles of Electrochemistry* (Wiley, New York, 1987).
[4] P. M. V. Resibois, *Electrolyte Theory: An Elementary Introduction to Microscopic Theory* (Harper and Row, New York, 1968).
[5] J. M. G. Barthel, H. Krienke, and W. Kunz, *Physical Chemistry of Electrolyte Solutions: Modern Aspects* (Steinkopff, New York, 1998).
[6] B. Bagchi and R. Biswas, Acc. Chem. Res. **31**, 181 (1998), and references therein; B. Bagchi and R. Biswas, Adv. Chem. Phys. **109**, 207 (1999).
[7] P. Debye and H. Huckel, Z. Phys. **25**, 49 (1924).
[8] L. Onsager, Z. Phys. **27**, 388 (1926); **28**, 277 (1927).
[9] A. R. Altenberger and H. L. Friedman, J. Chem. Phys. **78**, 4162 (1983); E. C. Zhong and H. L. Friedman, J. Phys. Chem. **92**, 1685 (1988).
[10] O. Bernard, W. Kunz, P. Turq, and L. Blum, J. Phys. Chem. **96**, 398 (1992); **96**, 3833 (1992); M. Jardat, O. Bernard, P. Turq, and G. R. Kneller, J. Chem. Phys. **110**, 7993 (1999).
[11] A. P. Lyubartsev and A. Laaksonen, J. Phys. Chem. **100**, 16410 (1996).
[12] A. Chandra, R. Biswas, and B. Bagchi, J. Am. Chem. Soc. **121**, 4082 (1999).
[13] A. Chandra and B. Bagchi, J. Chem. Phys. **110**, 10024 (1999).
[14] P. Debye and H. Falkenhagen, Z. Phys. **29**, 121 (1928); **29**, 401 (1928). See also Ref. 45.
[15] J. E. Anderson, J. Non-Cryst. Solids **172–174**, 1190 (1994).
[16] J. M. Caillol, D. Levesque, and J. J. Weis, J. Chem. Phys. **85**, 6645 (1986); **91**, 5544 (1989); **91**, 5555 (1989).
[17] D. Wei and G. N. Patey, J. Chem. Phys. **94**, 6795 (1991).
[18] I. M. Svishchev and P. G. Kusalik, Physica A **192**, 628 (1993).
[19] A. Chandra, D. Wei, and G. N. Patey, J. Chem. Phys. **99**, 2083 (1993).
[20] A. Samanta and S. K. Ghosh, J. Mol. Liq. **77**, 165 (1998).

[21] H. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[22] B. Bagchi, J. Chem. Phys. **109**, 3989 (1998).

[23] J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946).

[24] P. Colonomos and P. G. Wolynes, J. Chem. Phys. **71**, 2644 (1979).

[25] B. Bagchi, J. Chem. Phys. **95**, 467 (1991); R. Biswas, S. Roy, and B. Bagchi, Phys. Rev. Lett. **75**, 1098 (1995); R. Biswas and B. Bagchi, J. Am. Chem. Soc. **119**, 5946 (1997).

[26] L. Sjogren and A. Sjolander, J. Phys. C **12**, 4369 (1979).

[27] T. Gaskell and S. Miller, J. Phys. C **11**, 3749 (1978).

[28] S. Bhattacharyya and B. Bagchi, J. Chem. Phys. **106**, 1757 (1996).

[29] J. Hubbard and L. Onsager, J. Chem. Phys. **67**, 4850 (1977).

[30] R. Zwanzig, J. Chem. Phys. **38**, 1603 (1963).

[31] B. Bagchi and A. Chandra, Adv. Chem. Phys. **80**, 1 (1991).

[32] A. Chandra, D. Jana, and S. Bhattacharjee, J. Chem. Phys. **104**, 8662 (1996).

[33] P. Attard, Phys. Rev. E **48**, 3604 (1993).

[34] P. Debye and E. Huckel, Z. Phys. **24**, 185 (1923); **24**, 305 (1923).

[35] G. C. de Leon, M. Medina-Noyola, O. Alarcon-Waess and H. Ruiz-Estrada, Chem. Phys. Lett. **207**, 294 (1993); H. Ruiz-Estrada, A. Vizcarra-Rendon, M. Medina-Noyola, and R. Klein, Phys. Rev. A **34**, 3446 (1986).

[36] G. E. Roberts and H. Kaufman, *Table of Laplace Transforms* (Saunders, Philadelphia, 1966).

[37] A. Chandra and G. N. Patey, J. Chem. Phys. **100**, 1552 (1994).

[38] E. Neria and A. Nitzan, J. Chem. Phys. **100**, 3855 (1994).

[39] C. C. Chapman and M. Maroncelli, J. Phys. Chem. **95**, 9095 (1991); D. Huppert, V. Ittah, and E. M. Kosower, Chem. Phys. Lett. **159**, 267 (1989).

[40] A. Chandra, Chem. Phys. Lett. **244**, 314 (1995); Chem. Phys. **208**, 1 (1996); K. Mahajan and A. Chandra, J. Chem. Phys. **106**, 2360 (1997).

[41] J. B. Hasted, *Aqueous Dielectrics* (Chapman and Hall, London, 1973).

[42] A. Chandra, D. Wei, and G. N. Patey, J. Chem. Phys. **98**, 4959 (1993); A. Chandra, and G. N. Patey, *ibid.* **100**, 8385 (1994).

[43] J. T. Hynes, in *The Theory of Chemical Reactions*, edited by M. Baer (Chemical Rubber, Boca Raton, FL, 1985), Vol. 4; G. van der Zwan and J. T. Hynes, Chem. Phys. **152**, 169 (1991).

[44] S. Sridharan, J. A. McCammon, and J. B. Hubbard, J. Chem. Phys. **90**, 237 (1989).

[45] K. Ibuki and M. Nakahara, J. Chem. Phys. **92**, 7323 (1990).

[46] A. Chandra, Chem. Phys. Lett. **253**, 456 (1996); J. Mol. Struct.: THEOCHEM **422**, 49 (1998); J. Chem. Phys. **110**, 1569 (1999).

[47] G. S. Manning, J. Chem. Phys. **99**, 477 (1993).

[48] M. Medina-Noyola, Faraday Discuss. Chem. Soc. **83**, 21 (1987).