Brownian Model Theory of Nonequilibrium Liquid Structure and Hydrodynamics of Strong Binary Electrolyte Solutions in an External Field

Byung Chan Eu and Hui Xu

Department of Chemistry, McGill University,
801 Sherbrooke St. West, Montreal, QC H3A 0B8, Canada

Kyunil Rah

IT and Electronic Materials R & D, LG Chem Research Park,
104-1 Moonji-dong, Yuseung-gu, Daejeon 305-380, Korea

(Date: May 2, 2014)

Abstract

In this paper, on the basis of the Onsager–Wilson theory of strong binary electrolyte solutions we completely work out the solutions of the governing equations (Onsager–Fuoss equations and Poisson equations) for nonequilibrium pair correlation functions and ionic potentials and the solutions for the Stokes equation for the velocity and pressure in the case of strong binary electrolyte solutions under the influence of an external electric field of arbitrary strength. The solutions are calculated in the configuration space as functions of coordinates and reduced field strength. Thus the axial and transversal components of the velocity and the accompanying nonequilibrium pressure are explicitly obtained. Computation of velocity profiles makes it possible to visualize the movement and distortion of ion atmosphere under the influence of an external electric field. In particular, it facilitates tracking the movement of the center \((x_c, 0)\) of the ion atmosphere along the \(x\) axis, as the field strength increases. Thus it is possible to imagine a spherical ion atmosphere with its center displaced to \((x_c, 0)\) from the origin. On the basis of this picture we are able to formulate a computation-based procedure to unambiguously select the values of \(x\) and \(r\) in the electrophoretic factor for \(\xi > 0\) and thereby calculate the ionic conductance. This procedure facilitates to overcome the mathematical divergence difficulty inherent to the method used by Wilson in his unpublished dissertation on the ionic conductance theory (namely, the Onsager–Wilson theory) for strong binary electrolytes. We thereby define divergence-free electrophoretic and relaxation time factors which would enable us to calculate equivalent conductance of strong binary electrolytes subjected to an external electric field in excellent agreement with experiment. We also investigate the nature of approximations that yield Wilson’s result from the exact divergence-free electrophoretic and relaxation time coefficients. In the sequels, the results obtained in this work are applied to study ionic conductivity and nonequilibrium pressure effects in electrolyte solutions.
I. INTRODUCTION

Linear and nonlinear transport processes and nonequilibrium phenomena in dilute non-ionic (neutral) fluids have been known adequately treatable by means of singlet distribution functions obeying, for example, the Boltzmann equations and related kinetic equations\[1\] for singlet distribution functions. Relying on the experience gained from the theories of neutral dilute fluids, theories of ionized gases\[2\], plasmas, and charge carriers in semiconductors\[3–5\] often rely on singlet distribution functions obeying Boltzmann-like kinetic equations and their suitable modifications. However, since ions in ionized fluids interact through long-ranged Coulombic interactions, even if the ionized species are dilute in concentration, their spatial correlations are significant, lingering on to manifest their effects even in the infinitely dilute regime of concentration as the thermodynamic properties (e.g., activity coefficients) of ionic solutions demonstrate. Therefore it would be very important to find a way, and learn, to incorporate long-range correlations into the theory of nonequilibrium phenomena and transport processes in ionized fluids and therein lies the significance of the limiting theory of conductivity in ionized liquids in the external field of arbitrary strength described in this work.

Interestingly, in the subject fields of nonlinear phenomena in ionic liquids, the Wien effect\[6\] was one of the earliest experimental examples that exhibited a marked nonlinear deviation from the Coulombic law of conduction and, as such, it attracted considerable attention theoretically and experimentally. Being a nonlinear effect in ionic conductance which shows a strongly nonlinear, non-Coulombic field-dependence of ionic conductance, the phenomenon was studied actively in physical chemistry until several decades ago to understand ionic solutions and their physical properties\[7, 8\]. Recently, there appears to be a revival of experimental studies on Wien effect and related aspects in ionic conductance of ionic liquids in the presence of high external electric fields\[9–11\]. There are other many fascinating aspects of physical properties of ionic liquids recently being studied actively and reported in the recent literature\[12, 13\], although they are mostly in the field of equilibrium phenomena. In the present series of work, we are interested in nonlinear transport processes and, in particular, learning about the theories of the Wien effect on ionic conductance in electrolyte solutions in order to gain insights and theoretical approaches to treat the currently studied properties of ionic fluids. As a first step to this aim, we will study strong binary (symmetric) electrolytes because of the relative simplicity of the subject matter. More complicated systems of asymmetric electrolytes, in which the charges in a molecule are asymmetric, will be treated in the sequels\[14, 15\] to this work in preparation.
The ideas of physical mechanisms underlying the Wien effect, which might also encompass nonlinear phenomena in general in ionic fluids, proceed as follows. It is founded on the idea of ion atmosphere in Debye’s theory of electrolyte solutions. According to his theory, ion atmosphere is formed around ions in the solution, which is spherically symmetric if the ions are spherical and the system is in equilibrium. When the external electric field is applied to the ionic fluid, the ions of opposite charges begin to move in directions opposite to each other. Thus the basic physical mechanisms involved in the ionic movements under the external field are believed to be due to a distortion of the spherically symmetric ion atmosphere into a non-spherical form and its subsequent tendency to relax to a spherically symmetric form. The former effect gives rise to the electrophoretic effect and the latter to the relaxation time effect. It should be emphasized here that the aforementioned effects are on the ionic atmosphere, but not on the ion of attention situated at the center of ion atmosphere.

This idea can be translated into a qualitative mathematical form as given below: In experiments, we measure migration of ions and accompanying flow of medium. If the external electric field is denoted \( X \), the force \( k_j \) on ion \( j \) of charge \( e_j \) is then given by

\[
k_j = e_j X \quad (j = 1, \ldots, s).
\]

Since the ion of charge \( e_j \) in the solution creates an ion atmosphere of charge \(-e_j\), which is distributed in the ion atmosphere to balance the charge in the solution, and this atmosphere is subjected to a force of \(-e_j X\). This force tends to move the ion atmosphere in the direction of force \(-e_j X\), while the central ion \( j \) of atmosphere is carried by force \( e_j X \) in the medium in the direction opposite to the motion of ion atmosphere in order to balance the momentum. The velocity of the countercurrent generated thereby may be readily calculated if it is assumed that the entire countercharge \(-e_j\) of the atmosphere is distributed in a spherical shell of radius \( \kappa^{-1} \), where \( \kappa^{-1} \) is the Debye radius of ion atmosphere from the central ion, and that the motion of this sphere of radius \( \kappa^{-1} \) surrounding the central charge is governed by the Stokes law holding for the motion of a sphere in a viscous fluid. Thus, this velocity of the countercurrent is estimated to be

\[
\Delta v_j = \frac{k_j \kappa}{6 \pi \eta_0} = \frac{e_j X \kappa}{6 \pi \eta_0},
\]

where \( \Delta v_j \) is the velocity of the shell of radius \( \kappa^{-1} \) and \( \eta_0 \) is the viscosity of the medium. We are thus led to the result that the medium in the interior of the shell travels with this velocity, and that the central ion migrates against a collective current of the medium in the shell. The deduction of this expression qualitatively elucidates the most important part of the effect of electrophoresis.
Clearly, this effect has to do with hydrodynamic motion of the solvent around the center ion enclosed by the ion atmosphere of radius $\kappa^{-1}$ that moves against the former. One may therefore quantify this qualitative description by means of a hydrodynamic method using the Navier–Stokes equation [19–21], but the Navier–Stokes equation requires a local body-force—local mean external force—as an input. This local body-force cannot be obtained through a purely phenomenological consideration, but, for example, must be calculated by means of statistical mechanics combined with classical electrodynamics. Before proceeding to the remaining effect, it is important to point out that Eq. (2) gives the velocity of a physical object of radius $\kappa^{-1}$ (i.e., the radius of ion atmosphere) in the direction of $\mathbf{X}$.

The second effect, that is, the relaxation time effect, is seen as follows: If the central ion possessed no atmosphere, it would simply migrate with a velocity $k_j/\zeta_j$, where $\zeta_j$ is the friction constant, but owing to its ion atmosphere, the ion is subject to a net force, $k_j - \Delta k_j$, where $\Delta k_j$ is the force arising from the dissymmetry of the ion atmosphere created by the movement of the ions in the external field, and hence it will move, relative to its environment, with a velocity of a magnitude, $(k_j - \Delta k_j)/\zeta_j$. This $\Delta k_j$ is due to the effect arising from the relaxation of the asymmetric ion atmosphere.

Consequently, the net velocity $v_j$ of ion $j$ is given by

$$v_j = \frac{(e_j X - \Delta k_j)}{\zeta_j} - \frac{e_j X \kappa}{\zeta_j 6\pi \eta_0}. \tag{3}$$

Here $\Delta k_j \zeta_j^{-1}$ represents the relaxation time effect on relaxation to a spherically symmetric form of the distorted ion atmosphere, and the last term the electrophoretic effect.

The aforementioned two effects making up the velocity given in Eq. (3) are believed to underlie in charge conduction in electrolytic solutions. In fact, the mobility of ions induced by an external electric field can be calculated on the basis of the aforementioned two effects, for example, by using Eq. (3).

As we can see from this heuristic discussion, the aforementioned two effects require the velocity of the fluid (medium), which obviously obeys the hydrodynamic equations for the system subjected to an external electric field. Since such velocity solutions can be obtained from the Stokes equation, more generally, Navier–Stokes equation, we may apply the solutions thereof to calculate the charge conductance and the countercurrent of the medium to learn the mode of charge conductance in electrolyte solutions subjected to an external field. The hydrodynamic equations, however, contain external body-forces, which in the present case are the external electric field. The external electric field or body-force is generally local and depends on the local distribution of charges. The local
charge distributions require molecular distributions in the system and a statistical mechanical theory for them—a molecular theory.

To answer this question, Onsager\[22\] with Fuoss formulated a formal framework of theory in which a Fokker–Planck-type differential equations for nonequilibrium pair distribution functions are derived on the assumption of a Brownian motion model for ions in a continuous medium of dielectric constant $D$ and viscosity $\eta_0$. We will refer to these differential equations for pair correlation functions as the Onsager–Fuoss (OF) equations henceforth. They are coupled to the Poisson equations\[24\] of classical electrodynamics for the ionic potentials. These two coupled systems of differential equations will be referred to as the governing equations in the present work. The governing equations were applied to study the ionic conductance of binary strong electrolytes in an external electric field by Wilson in his dissertation\[25\]. This theory will be referred to as the Onsager–Wilson (OW) theory. Wilson solved the governing equations and obtained analytic formulas for the electrophoretic and relaxation time coefficients and the equivalent ionic conductance qualitatively displaying the Wien effect in the regime of strong electric fields. Unfortunately, his dissertation has never been published in public domain, but only important results, such as the electrophoretic and relaxation time coefficients, had been excerpted in the well-known monograph\[7\] by Harned and Owen on electro-physical chemistry. Tantalized by the possibility of the utility of the theory for recent experimental results for ionic fluids and charge carrier mobilities in semiconductors referred to earlier, we have thoroughly examined the OW theory to learn the details of it. Surprisingly, we have discovered that the velocity solution of the Stokes (hydrodynamic) equation in the OW theory can give rise to a divergent result rendering into question the electrophoretic coefficient calculated by Wilson’s procedure described in his dissertation\[25\]. We believe that the basic framework of governing equations—the OF equations and Poisson equations—should be correct, but the way the solutions are evaluated by him may be called into question. Therefore, it is our principal aim of this work to analyze the solutions of the governing equations in the case of binary strong electrolytes in an external electric field and obtain physically reasonable and thus acceptable theoretical results that can be made use of to study experimental data on conductivity and other transport phenomena in the high field regime.

This paper is organized as follows. In Sec. II, we present the governing differential equations, which consist of the OF equations for the ionic pair distribution functions and the Poisson equations for the potentials of ionic interaction. We note that Kirkwood\[26\] also derived a similar equation for non-ionic liquids in his kinetic theory of liquids. One (BCE) of the present authors also derived\[27\] the OF equations from the generalized Boltzmann equation.\[28, 29\] Since Wilson’s dissertation\[25\]
has not been published anywhere in a journal, the governing equations and their solutions are discussed to the extent that the present paper can be followed intelligibly.

In Sec. III, the solutions of the governing equations—the pair distribution functions and potentials of ionic interaction—are presented in the case of a strong binary electrolyte solution subjected to an external field. These solutions are given in one-dimensional Fourier transforms in an axially symmetric coordinate system, namely, a cylindrical coordinate system whose axial coordinate is parallel to the applied external electric field. The Fourier transform is with respect to the axial coordinate. The distribution functions obtained are nonequilibrium pair distribution functions which describe the nonequilibrium ionic liquid structure, and the nonequilibrium ionic potentials of interaction in the external field. Since they should be of considerable interest to help us learn about the nonequilibrium ionic liquid properties we study the solutions of the governing equations in detail and obtain, especially, their spatial profiles, indicating how ions and their nonequilibrium part of the potentials are distributed in the external electric field. It should be noted that the distribution functions are the nonequilibrium corrections to the Boltzmann distribution function predicted by the Debye–Hückel theory[17] of electrolytes, and similarly for the potentials.

In Sec. IV, we then discuss the solutions of the Stokes equation, which replaces the Navier–Stokes equation in the case of incompressible fluids that we assume the ionic solution of interest is. Solving the Stokes equation, we obtain the axial and transversal velocity components as well as the nonequilibrium pressure from the solutions of the Stokes equation. We present the solution procedure for the Stokes equation in detail, because, firstly, Wilson’s thesis contains only the symmetric part of the solution, leaving out the antisymmetric part that turns out to be comparable to the former in magnitude and, secondly, we believe that the solution procedure of the Stokes equations, which combines statistical mechanics and hydrodynamics in a rather intriguing manner, appears to be very much worth learning, especially, if one is interested in nonequilibrium theories of ionic liquids in an external electric field. In this section we also discuss the connection with the electrophoretic and relaxation time coefficients originally obtained by Wilson, who evaluated them at the position of the center ion of ion atmosphere, namely, at the coordinate origin. This discussion would show that one of his integrals evaluated at the coordinate origin is divergent. Therefore we evaluate explicitly the solutions to explore a way to make the OW theory of ionic conductance unencumbered by such a divergence difficulty.

In Sec. IV, we also compute numerically the spatial profiles of the axial velocity, and study them to guide us to avoid the divergence difficulty mentioned in connection with Wilson’s result and choose the optimum position coordinates at which to calculate the relaxation time and
electrophoretic coefficients. To this aim we have either evaluated analytically or reduced to one-dimensional quadratures, by means of contour integration methods, the Fourier transform integrals making up the solutions of the Stokes equations obtained earlier before computing their spatial profiles. The contour integration methods are described in Appendix A. Since they, however, do not cover the entire coordinate space owing to the condition imposed by Jordan’s lemma\cite{30} on applicability of contour integration methods involving integrations along a circle of infinite radius, the integrals must be numerically computed outside the region where the aforementioned condition is violated. The details of the condition are discussed in Sec. IV and also in Appendix A. These numerical studies reveal the manner in which the ions flow subject to the applied external electric field provide insight into the behavior of the velocity and valuable clues to formulate an empirical rule to select the position parameters \((x, r)\) in the electrophoretic factor, so that a physically sensible and non-divergent electrophoretic coefficient and the corresponding relaxation time coefficient can be defined and ionic conductance correctly predicted. This problem is addressed in the companion paper. Sec. V is for discussion and concluding remark.

II. GOVERNING EQUATIONS

Let \(\mathbf{r}_j\) denote the position vector of ion \(j\) in a fixed coordinate system and \(\mathbf{r}_{ji}\) the relative coordinate of ion \(i\) from ion \(j\):
\[
\mathbf{r} \equiv \mathbf{r}_{ji} = \mathbf{r}_i - \mathbf{r}_j = \mathbf{r}_j - \mathbf{r}_i = -\mathbf{r}_{ij} \equiv -\mathbf{r}, \tag{4}
\]
and let \(f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})\) denote the concentration of ion \(i\) in the atmosphere of ion \(j\) located at position \(\mathbf{r}_j\)—in other words, the distribution function to find ion \(i\) at distance \(\mathbf{r}_{ij}\) from ion \(j\) located at \(\mathbf{r}_j\). At equilibrium it is given by the Boltzmann distribution function times the density of ion \(j\). Let us also denote by \(\mathbf{v}_{ji}\) the velocity of ion \(i\) in the neighborhood of ion \(j\). Therefore this velocity also depends on positions of ions \(i\) and \(j\) in the following manner:
\[
\mathbf{v}_{ji} = \mathbf{v}_{ji}(\mathbf{r}_j, \mathbf{r}_{ij}), \quad \mathbf{v}_{ij} = \mathbf{v}_{ij}(\mathbf{r}_i, \mathbf{r}_{ji}). \tag{5}
\]
The equation of continuity for ion pair \((j, i)\) is then given by
\[
- \frac{\partial f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})}{\partial t} = \nabla_j \cdot (\mathbf{v}_{ij} f_{ij}) + \nabla_i \cdot (\mathbf{v}_{ji} f_{ji}) = - \frac{\partial f_{ij}(\mathbf{r}_i, \mathbf{r}_{ji})}{\partial t}, \tag{6}
\]
where \(\nabla_j = \partial/\partial \mathbf{r}_j\). Hence, at a steady state \(\partial f_{ji}/\partial t = 0\) the steady-state equation of continuity is given by
\[
\nabla_j \cdot (\mathbf{v}_{ij} f_{ij}) + \nabla_i \cdot (\mathbf{v}_{ji} f_{ji}) = 0. \tag{7}
\]
Assuming that the ions, being randomly bombarded by molecules of the continuous medium (solvent) of dielectric constant $D$ and viscosity $\eta_0$, move randomly, namely, execute random Brownian motions, in the presence of an applied external field, the velocities $v_{ji}$ and $v_{ij}$ may be assumed given by the Brownian motion model

$$v_{ji} = V(\mathbf{r}_i) + \omega_i(K_{ji} - k_BT \nabla_i \ln f_{ji}),$$  
(8)

$$v_{ij} = V(\mathbf{r}_j) + \omega_j(K_{ij} - k_BT \nabla_j \ln f_{ij}),$$  
(9)

where $V(\mathbf{r}_k)$ is the velocity of solution at position $\mathbf{r}_k$ ($k = i, j$); $\omega_k$ is the inverse of the friction coefficient $\zeta_k$ of ion $k$, which is related to the diffusion coefficient $D_k$ of ion $k$ of charge $e_k$ in the medium of viscosity $\eta_0$

$$D_k = k_BT \omega_k = \frac{k_BT}{\zeta_k}.$$  
(10)

Here $k_B$ is the Boltzmann constant and $T$ the absolute temperature; $K_{ji}$ is the total force acting on ion $i$. We assume that forces on ions $K_{ji}$ are linear with respect to charge numbers

$$K_{ji} = k_i - e_i \nabla_i \psi_j(\mathbf{r}_j, \mathbf{r}_{ij}),$$  
(11)

so that the superposition principle of fields is preserved. Here $k_i$ is the applied external force on ion $i$. Under the assumptions for $v_{ji}$ and for $K_{ji}$ stated earlier, the steady-state equation of continuity (7) becomes a coupled set of differential equations (12) satisfied by ion pair distribution functions $f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})$ of the ionic liquid:

$$k_BT \left(\omega_i + \omega_j\right) \nabla \cdot \nabla f_{ji}(\mathbf{r}) + (\omega_j e_j - \omega_i e_i) \mathbf{X} \cdot \nabla f_{ji}(\mathbf{r})$$

$$+ n_i n_j \left[e_i \omega_i \nabla \cdot \nabla \psi_j(\mathbf{r}) + e_j \omega_j \nabla \cdot \nabla \psi_i(-\mathbf{r})\right] = 0,$$  
(12)

$$\quad (i, j = 1, 2, \ldots, s).$$

We will call this set of differential equations the Onsager–Fuoss (OF) equations. Here for simplicity of notation we have omitted the first position variables in the distribution functions and potentials and typeset them as follows: $f_{ji}(\mathbf{r}) \equiv f_{ji}(\mathbf{r}_j, \mathbf{r}_{ij})$, etc. and $\psi_j(\mathbf{r}) \equiv \psi_j(\mathbf{r}_j, \mathbf{r})$ and $\psi_i(-\mathbf{r}) \equiv \psi_i(\mathbf{r}_i, -\mathbf{r})$. In fact, for Eq. (12) the coordinate origin may be regarded as fixed on position of ion $j$. These are Fokker–Planck-type equations for $f_{ji}(\mathbf{r})$ and $\psi_j(\mathbf{r})$ and $\psi_i(-\mathbf{r})$. In Eq. (12), $n_i$ is density of ion $i$ and $\mathbf{X}$ is the external (electric) field. The potentials $\psi_k$ ($k = i, j$) appearing in this set of differential equations, Eq. (12), obey the Poisson equations of classical electrodynamics (13),

$$\nabla \cdot \nabla \psi_j(\mathbf{r}) = -\frac{4\pi}{Dn_j} \sum_{i=1}^{s} e_i f_{ji}(\mathbf{r}).$$  
(13)

The two sets (12) and (13) are coupled to each other and will be henceforth referred to as the governing equations in this work.
A. Boundary Conditions

The two sets of equations (12) and (13) are subject to the boundary conditions stated below.

1. No Flux Conditions

The number of ions, leaving and entering the interior, \( \Omega \), of a surface \( S \) should be balanced, because no ions are created or destroyed. Therefore \( f_{ji}(\mathbf{r}) [\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] \) is sourceless in \( \Omega \). This fact may be expressed as

\[
\int_S dS f_{ji}(\mathbf{r}) \{ \mathbf{e}_n \cdot [\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] \} = \int_\Omega d\Omega \nabla \cdot \{ f_{ji}(\mathbf{r}) [\mathbf{v}_{ji}(\mathbf{r}) - \mathbf{v}_{ij}(-\mathbf{r})] \} = 0,
\]

where \( \mathbf{e}_n \) is the vector normal to the surface \( S \). This will be henceforth called no flux condition.

2. Boundary Conditions on Potentials

If the charge \( e_j \) is within \( \Omega \), we obtain

\[
\lim_{\Omega \to 0} \int_\Omega d\Omega \rho_j(\mathbf{r}) = e_j \delta,
\]

where \( \rho_j(\mathbf{r}) \) is the charge density. Therefore, the space charge within \( \Omega \) must be such that

\[
-\frac{D}{4\pi} \int_\Omega d\Omega \nabla^2 \psi_j(\mathbf{r}) = \int_\Omega d\Omega \rho_j(\mathbf{r}),
\]

or alternatively

\[
\lim_{\Omega \to 0} \int_S dS \mathbf{S} \cdot \nabla \psi_j(\mathbf{r}) = -\frac{4\pi e_j}{D} \delta,
\]

for the boundary condition on the ionic potentials. Here

\[
\delta = \begin{cases} 
1 & \text{if ion } j \text{ is located at } \mathbf{r} = 0 \\
0 & \text{otherwise}
\end{cases}.
\]

The boundary condition (17) corresponds to the fact that the charge \( e_j \) at the origin (i.e., at the center of the ion atmosphere) must balance the net charge of the rest of the ion atmosphere.

B. Symmetric and Antisymmetric Parts of Governing Equations

Since it is convenient to work with dimensionless variables, we first reduce position variable \( \mathbf{r} \) with respect to the Debye parameter \( \kappa \)

\[
\mathbf{r} = \kappa \mathbf{r},
\]
where the Debye parameter is defined by
\[ \kappa = \sqrt{\frac{4\pi T_0}{Dk_BT}}; \quad \Gamma_0 = \sum_{k=1}^{s} n_k e_k^2. \] (19)

The distribution functions and potentials change the sign of argument if particle indices \( j \) and \( i \) are interchanged. Therefore they are expected to consist of symmetric and antisymmetric components. Consequently, it is convenient to distinguish the symmetric and antisymmetric components \( f_{ji}^{\pm}(\mathbf{r}) \) and \( \psi_{ji}^{\pm}(\mathbf{r}) \), etc. of distribution functions and potentials. They are defined in reduced forms as follows:

\[
\begin{align*}
\frac{k_{\text{B}} n_i e_j e_i}{Dk_BT} f_{ji}^{+}(\mathbf{r}) &= \frac{1}{2} [f_{ji}(\mathbf{r}) + f_{ji}(-\mathbf{r})] - n_i n_j, \\
\frac{k_{\text{B}} n_j e_i e_j}{Dk_BT} f_{ji}^{-}(\mathbf{r}) &= \frac{1}{2} [f_{ji}(\mathbf{r}) - f_{ji}(-\mathbf{r})], \\
\frac{k e_j}{D} \psi_{ji}^{+}(\mathbf{r}) &= \frac{1}{2} [\psi_{ji}(\mathbf{r}) \pm \psi_{ji}(-\mathbf{r})].
\end{align*}
\] (20, 21)

Since the distribution functions tend to \( n_i n_j \) as \( r = |\mathbf{r}| \) tends to infinity, \( f_{ji}^{\pm}(\mathbf{r}) \) vanishes as \( r \to \infty \). According to the definitions (20) and (21), the following symmetry properties can be deduced for them as the ion positions are interchanged:

\[
\begin{align*}
f_{ji}^{+}(-\mathbf{r}) &= f_{ji}^{+}(\mathbf{r}) = f_{ij}^{+}(-\mathbf{r}), \\
f_{ji}^{-}(-\mathbf{r}) &= -f_{ji}^{-}(\mathbf{r}) = -f_{ij}^{-}(-\mathbf{r}), \\
\psi_{ji}^{+}(-\mathbf{r}) &= \psi_{ji}^{+}(\mathbf{r}), \\
\psi_{ji}^{-}(-\mathbf{r}) &= -\psi_{ji}^{-}(\mathbf{r}).
\end{align*}
\] (22, 23)

The differential equations of the symmetric and antisymmetric components of \( f_{ji} \) and \( \psi_{ji} \) in Eqs. (12) and (13) then can be separated as follows:

\[
\begin{align*}
\nabla^2 f_{ji}^{+}(\mathbf{r}) - (\omega_{ij}\mu_i + \omega_{ji}\mu_j) f_{ji}^{+}(\mathbf{r}) - \omega_{ji}\mu_j f_{jj}^{+}(\mathbf{r}) - \omega_{ji}\mu_i f_{ii}^{+}(\mathbf{r}) + \mu_{ji}^{+} \nabla_x f_{ji}^{-}(\mathbf{r}) &= 0, \\
\nabla^2 f_{ji}^{-}(\mathbf{r}) - [\mu_i f_{ji}^{+}(\mathbf{r}) + \mu_j f_{jj}^{+}(\mathbf{r})] &= 0, \\
\nabla^2 f_{ii}^{+}(\mathbf{r}) - [\mu_i f_{ii}^{+}(\mathbf{r}) + \mu_j f_{jj}^{+}(\mathbf{r})] &= 0,
\end{align*}
\] (24)

\[
\begin{align*}
\nabla^2 f_{ji}^{-}(\mathbf{r}) - (\omega_{ij}\mu_i + \omega_{ji}\mu_j) f_{ji}^{-}(\mathbf{r}) - \omega_{ji}\mu_j f_{jj}^{-}(\mathbf{r}) + \omega_{ji}\mu_i f_{ii}^{-}(\mathbf{r}) + \mu_{ji}^{-} \nabla_x f_{ji}^{+}(\mathbf{r}) &= 0, \\
\nabla^2 f_{jj}^{-}(\mathbf{r}) &= 0, \\
\nabla^2 f_{ii}^{-}(\mathbf{r}) &= 0,
\end{align*}
\] (25)
where $\nabla^2$ now stands for Laplacian operator of reduced variable $r$, 

$$\mu_i = \frac{\nu_i z_i^2}{\nu_i z_i^2 + \nu_j z_j^2}, \quad \omega_{ji} = \frac{\omega_i}{\omega_i + \omega_j}, \quad (26)$$

$$\mu_{ji}' = \frac{X}{\kappa k_B T} \left( \omega_j e_j - \omega_i e_i \right) \left( \omega_j + \omega_i \right) \quad (X = \text{external electric field strength}), \quad (27)$$

with $\nu_i$ denoting the stoichiometric coefficient of ion $i$ in the $(j,i)$ electrolyte and $z_k$ the charge number of ion $k$: $e_k = e z_k \quad (k = j, i)$. Henceforth the indices $j$ and $i$ refer to ions of the binary electrolyte $(j,i)$, but also may dually refer to other ions belonging to species $j$ or $i$. This notational device prevents proliferation of subscripts distinguishing ionic particles. The 10 differential equations of Eqs. (24) and (25) will be referred to as the governing equations, the set (24) as the Onsager–Fuoss (OF) equations, and the set (25) as the Poisson equations. The solutions of the governing equations provide the information on the nonequilibrium ionic liquid structure and ionic potentials of the electrolyte solutions subjected to an external electric field of arbitrary strength.

A theory of transport processes in ionic solutions can be developed by making use of them.

### III. NONEQUILIBRIUM IONIC LIQUID STRUCTURE AND POTENTIALS OF BINARY ELECTROLYTES

#### A. Complete Solutions of the Governing Equations

We now limit our study to strong binary electrolyte solutions as in the theory of Wilson and Onsager. If the electrolyte is binary and strong, then $|e_j| = |e_i| = e z$ with $z = |z_i| = |z_j|$, and

$$\mu_i = \mu_j = \frac{1}{2}, \quad \mu_{ji}' = \frac{z e X}{\kappa k_B T} \equiv \xi.$$ 

Wilson in his unpublished PhD thesis obtained formal solutions of the governing equations in the forms of Fourier transforms under the assumption that $\omega_i = \omega_j$, which means $\omega_{ji} = \omega_{ij} = \frac{1}{2}$; that is, the diffusivities of the constituent ions are equal. (As it will turn out, the difference in the diffusivities has only a minor effect that can be ignored without much effect on the solutions.) And therewith he formulated a theory of ionic conductance of binary electrolytes under the influence of external electric field. However, Wilson’s thesis unfortunately has not been published in a journal in public domain, nor have the nonequilibrium ionic liquid structures and accompanying potentials been explicitly evaluated and studied. In fact, neither were the velocity profiles completely calculated in the full configuration space since he limited the study to the velocity of the center ion of the ion atmosphere located at the coordinate origin in his calculation of the electrophoretic
effect. Moreover, the particular velocity formula made use of by Wilson had a divergence difficulty at the origin, but he argued it away on the ground that the divergent term would not contribute to the ionic conductance. We will show his argument was mathematically groundless and would not hold true. For these reasons, in this work we will first evaluate the velocity formulas explicitly by applying analytic methods or methods of contour integrations or numerical computation methods for wide ranges of position coordinates, and then will explore a way to overcome or get around the divergence difficulty. The results obtained thereby for the nonequilibrium ionic liquid structure and potentials as well as the velocity profiles would be principal contributions of the present work, which are not available in the literature on ionic liquids at present. In the subsequent paper[31], the solutions of the present paper will be applied to study the Wien effect on equivalent ionic conductance as a function of the applied field strength.

Since Wilson’s dissertation is not only not readily accessible as mentioned earlier, but also his solution procedure is difficult to follow, on the basis of our understanding of his solution procedure we will reconstruct the solutions for the governing equations (24) and (25). The solution procedure presented below is not exactly the same as his except in spirit, but most of the final results agree with his in the main. Under the assumptions on $\omega_{ij} = \omega_{ji}$ mentioned earlier, the governing equations (24) and (25) are given as follows:

\[
\nabla^2 f_{ji}^+ (\mathbf{r}) - \frac{1}{2} f_{ji}^+ (\mathbf{r}) - \frac{1}{4} f_{jj}^+ (\mathbf{r}) - \frac{1}{4} f_{ii}^+ (\mathbf{r}) + \xi \nabla_x f_{ji}^- (\mathbf{r}) = 0,
\]
\[
\nabla^2 f_{jj}^+ (\mathbf{r}) - \frac{1}{2} \left[ f_{jj}^+ (\mathbf{r}) + f_{jj}^- (\mathbf{r}) \right] = 0,
\]
\[
\nabla^2 f_{ii}^+ (\mathbf{r}) - \frac{1}{2} \left[ f_{ii}^+ (\mathbf{r}) + f_{jj}^- (\mathbf{r}) \right] = 0,
\]
\[
\nabla^2 f_{ji}^- (\mathbf{r}) - \frac{1}{2} f_{ji}^- (\mathbf{r}) - \frac{1}{4} f_{jj}^- (\mathbf{r}) + \frac{1}{4} f_{ii}^- (\mathbf{r}) + \xi \nabla_x f_{ji}^+ (\mathbf{r}) = 0,
\]
\[
\nabla^2 f_{jj}^- (\mathbf{r}) = 0,
\]
\[
\nabla^2 f_{ii}^- (\mathbf{r}) = 0,
\]

\[
\nabla^2 \psi_{ji}^+ (\mathbf{r}) = -\frac{1}{2} \left[ f_{ji}^+ (\mathbf{r}) + f_{jj}^+ (\mathbf{r}) \right],
\]
\[
\nabla^2 \psi_{ij}^+ (\mathbf{r}) = -\frac{1}{2} \left[ f_{ii}^+ (\mathbf{r}) + f_{ji}^+ (\mathbf{r}) \right],
\]
\[
\nabla^2 \psi_{ji}^- (\mathbf{r}) = -\frac{1}{2} \left[ f_{ji}^- (\mathbf{r}) + f_{jj}^- (\mathbf{r}) \right],
\]
\[
\nabla^2 \psi_{ij}^- (\mathbf{r}) = -\frac{1}{2} \left[ f_{ij}^- (\mathbf{r}) + f_{ji}^- (\mathbf{r}) \right].
\]

Owing to the fact that the solution of the Laplace equation is constant, the solutions of the
fifth and sixth equations of the set (28) are constant:

\[ f_{jj}^-(\mathbf{r}) = C_j, \quad f_{ii}^- (\mathbf{r}) = C_i, \]

but by the boundary conditions that they must vanish as \( r \to \infty \). Therefore, the constants \( C_j \) and \( C_i \) must be equal to zero. Hence

\[ f_{jj}^- (\mathbf{r}) = 0, \quad f_{ii}^- (\mathbf{r}) = 0. \]  

Consequently, the governing equations reduce to the following 8 differential equations:

\[
\left( \nabla^2 - \frac{1}{2} \right) f_{ji}^+ (\mathbf{r}) - \frac{1}{4} \left[ f_{jj}^+ (\mathbf{r}) + f_{ii}^+ (\mathbf{r}) \right] + \xi \nabla_x f_{jj}^- (\mathbf{r}) = 0, \tag{31}
\]

\[
\left( \nabla^2 - \frac{1}{2} \right) f_{ji}^+ (\mathbf{r}) - \frac{1}{2} f_{jj}^+ (\mathbf{r}) = 0, \tag{32}
\]

\[
\left( \nabla^2 - \frac{1}{2} \right) f_{ii}^+ (\mathbf{r}) - \frac{1}{2} f_{ji}^+ (\mathbf{r}) = 0, \tag{33}
\]

\[
\left( \nabla^2 - \frac{1}{2} \right) f_{jj}^- (\mathbf{r}) + \xi \nabla_x f_{ji}^+ (\mathbf{r}) = 0, \tag{34}
\]

\[
\nabla^2 \psi_j^+ (\mathbf{r}) = -\frac{1}{2} \left[ f_{ji}^+ (\mathbf{r}) + f_{jj}^+ (\mathbf{r}) \right], \tag{35}
\]

\[
\nabla^2 \psi_i^+ (\mathbf{r}) = -\frac{1}{2} \left[ f_{ii}^+ (\mathbf{r}) + f_{ji}^+ (\mathbf{r}) \right], \tag{36}
\]

\[
\nabla^2 \psi_j^- (\mathbf{r}) = -\frac{1}{2} f_{ji}^- (\mathbf{r}), \tag{37}
\]

\[
\nabla^2 \psi_i^- (\mathbf{r}) = -\frac{1}{2} f_{jj}^- (\mathbf{r}). \tag{38}
\]

These two sets, (31)–(34) and (35)–(38), suggest that having obtained the solutions of the first set (31)–(34) we can look for the solutions of the second set (35)–(38), inhomogeneous differential equations. We will follow this strategy by applying the method of Fourier transform.

Since there exists an axial symmetry present in the system owing to the fact that a uniform external electric field is applied in a direction, we choose a cylindrical coordinate system whose axial coordinate axis is parallel to the external field direction. The cylindrical coordinates will be denoted \((x, \rho, \theta)\) where \( x \) is the axial coordinate, \( \rho \) the radial coordinate transversal to the axis \( x \), and \( \theta \) the azimuthal angle; see Fig. 1. Then the distribution functions and potentials have axial symmetry around the \( x \) axis, and hence they are independent of angle \( \theta \). Now Fourier transforms
are taken with respect to the axial coordinate $x$:

\[
\begin{bmatrix}
 f^+_{ji}(x, \rho) \\
 f^-_{ji}(x, \rho)
\end{bmatrix}
= \frac{2}{\pi} \int_0^\infty d\alpha \begin{bmatrix}
 \cos(\alpha x) \hat{f}^+_{ji}(\alpha, \rho) \\
 \sin(\alpha x) \hat{f}^-_{ji}(\alpha, \rho)
\end{bmatrix}, \\
\begin{bmatrix}
 \psi^+_{ji}(x, \rho) \\
 \psi^-_{ji}(x, \rho)
\end{bmatrix}
= \frac{2}{\pi} \int_0^\infty d\alpha \begin{bmatrix}
 \cos(\alpha x) \hat{\psi}^+_{ji}(\alpha, \rho) \\
 \sin(\alpha x) \hat{\psi}^-_{ji}(\alpha, \rho)
\end{bmatrix},
\]

(39)

(40)

Here $\alpha$ is a dimensionless wave number in units of $\kappa$. When Fourier transformed in this manner, the governing equations (31)–(34) and (35)–(38) become sets of coupled second-order ordinary differential equations with respect to the reduced radial coordinate $\rho$ (perpendicular to the $x$ axis) given below:

\[
\left( D^2_{\rho} - \frac{1}{2} \right) \hat{f}^+_{ji}(\alpha, \rho) - \frac{1}{4} \left[ \hat{f}^+_{jj}(\alpha, \rho) + \hat{f}^+_i(\alpha, \rho) \right] + \alpha \xi \hat{f}^-_{ji}(\alpha, \rho) = 0,
\]

(41)

\[
\left( D^2_{\rho} - \frac{1}{2} \right) \hat{f}^+_{jj}(\alpha, \rho) - \frac{1}{2} \hat{f}^+_{ji}(\alpha, \rho) = 0,
\]

(42)

\[
\left( D^2_{\rho} - \frac{1}{2} \right) \hat{f}^+_i(\alpha, \rho) - \frac{1}{2} \hat{f}^+_{ji}(\alpha, \rho) = 0,
\]

(43)

\[
\left( D^2_{\rho} - \frac{1}{2} \right) \hat{f}^-_{ji}(\alpha, \rho) - \alpha \xi \hat{f}^+_{ji}(\alpha, \rho) = 0,
\]

(44)

\[
D^2_{\rho} \hat{\psi}^+_j(\rho) = -\frac{1}{2} \left[ \hat{f}^+_j(\rho) + \hat{f}^+_j(\rho) \right],
\]

(45)

\[
D^2_{\rho} \hat{\psi}^+_i(\rho) = -\frac{1}{2} \left[ \hat{f}^+_i(\rho) + \hat{f}^+_i(\rho) \right],
\]

(46)

\[
D^2_{\rho} \hat{\psi}^-_j(\rho) = -\frac{1}{2} \hat{f}^-_j(\rho),
\]

(47)

\[
D^2_{\rho} \hat{\psi}^-_i(\rho) = -\frac{1}{2} \hat{f}^-_j(\rho).
\]

(48)

Here symbol $D^2_{\rho}$ is defined by the differential operator

\[
D^2_{\rho} = \frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} - \alpha^2.
\]

(49)

Because the zeroth-order Bessel function $K_0(\alpha \rho)$ of second kind is an irregular solution of the differential equation $[32, 33]

\[
D^2_{\rho} K_0(\alpha \rho) = \left( \frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} - \alpha^2 \right) K_0(\alpha \rho) = 0,
\]

(50)

the coupled inhomogeneous differential equations (41)–(44) are expected to be solved by linear combinations of zeroth-order Bessel functions but of different arguments $\lambda_k \rho$, where $\lambda_k$ ($k = 1, 2, 3, 4$) are characteristic values of the differential equation system. Unfortunately, two of the characteristic values turn out to be degenerate. Therefore it is not possible to apply the method of linear
algebra to solve the system in the conventional manner in which the solutions are expanded in characteristic vectors. This difficulty is overcome if Eqs. (41)–(44) are solved in the following manner.

Operating \((D^2_{\rho} - \frac{1}{4})\) on Eq. (41) and eliminating resulting \((D^2_{\rho} - \frac{1}{4}) \hat{f}_{ji}^+, (D^2_{\rho} - \frac{1}{4}) \hat{f}_{ii}^+,\) and \((D^2_{\rho} - \frac{1}{4}) \hat{f}_{ji}^-\) using Eqs. (42)–(44), we obtain the fourth-order differential equation

\[
\left(D^2_{\rho} - \frac{1}{2} + \frac{1}{2} R\right) \left(D^2_{\rho} - \frac{1}{2} - \frac{1}{2} R\right) \hat{f}_{ji}^+ (\alpha, \rho) = 0, \tag{51}
\]

where

\[
R = \sqrt{1 - 4 (\alpha \xi)^2}. \tag{52}
\]

This fourth-order differential equations can be solved by Bessel function \(K_0 (\lambda_1 \rho)\) and \(K_0 (\lambda_2 \rho)\), where \(\lambda_1\) and \(\lambda_2\) are two characteristic values

\[
\lambda_1 = \sqrt{\frac{1}{2} + \alpha^2 + \frac{1}{2} R}, \quad \lambda_2 = \sqrt{\frac{1}{2} + \alpha^2 - \frac{1}{2} R}. \tag{53}
\]

These are non-degenerate. Therefore the general solution for Eq. (51) may be written as a linear combination of the Bessel functions

\[
\hat{f}_{ji}^+ (\alpha, \rho) = A_1 K_0 (\lambda_1 \rho) + A_2 K_0 (\lambda_2 \rho), \tag{54}
\]

where \(A_1\) and \(A_2\) are constant coefficients that must be determined by the boundary conditions, Eqs. (14) and (17), or the equivalent conditions, for the symmetric and antisymmetric parts. Note that this solution satisfies the boundary condition as \(\rho \to \infty\) since the Bessel functions \(K_0 (\lambda_k \rho)\) vanish at \(\rho = \infty\). Upon substituting this expansion into Eqs. (41)–(44) we obtain

\[
-\frac{1}{4} \hat{f}_{ji}^+ (\alpha, \rho) - \frac{1}{4} \hat{f}_{ii}^+ (\alpha, \rho) + \alpha \xi \hat{f}_{ji}^+ (\alpha, \rho) = -\frac{1}{2} R A_1 K_0 (\lambda_1 \rho) + \frac{1}{2} R A_2 K_0 (\lambda_2 \rho), \tag{55}
\]

\[
\left(D^2_{\rho} - \frac{1}{2}\right) \hat{f}_{ji}^+ (\alpha, \rho) = \frac{1}{2} A_1 K_0 (\lambda_1 \rho) + \frac{1}{2} A_2 K_0 (\lambda_2 \rho), \tag{56}
\]

\[
\left(D^2_{\rho} - \frac{1}{2}\right) \hat{f}_{ii}^+ (\alpha, \rho) = \frac{1}{2} A_1 K_0 (\lambda_1 \rho) + \frac{1}{2} A_2 K_0 (\lambda_2 \rho), \tag{57}
\]

\[
\left(D^2_{\rho} - \frac{1}{2}\right) \hat{f}_{ji}^- (\alpha, \rho) = \alpha \xi A_1 K_0 (\lambda_1 \rho) + \alpha \xi A_2 K_0 (\lambda_2 \rho). \tag{58}
\]

This inhomogeneous set may be also solved by expansion. Let

\[
\hat{f}_{ji}^+ (\alpha, \rho) = B_1 K_0 (\lambda_1 \rho) + B_2 K_0 (\lambda_2 \rho) + B_3 K_0 (\lambda_3 \rho), \tag{59}
\]

\[
\hat{f}_{ii}^+ (\alpha, \rho) = C_1 K_0 (\lambda_1 \rho) + C_2 K_0 (\lambda_2 \rho) + C_3 K_0 (\lambda_3 \rho), \tag{59}
\]

\[
\hat{f}_{ji}^- (\alpha, \rho) = D_1 K_0 (\lambda_1 \rho) + D_2 K_0 (\lambda_2 \rho) + D_3 K_0 (\lambda_3 \rho),
\]
where $B_k$, $C_k$, and $D_k$ are expansion coefficients to be determined and $\lambda$ is the degenerate characteristic value to be determined self-consistently. Inserting these expansions into Eqs. (55)–(58) we find relations between the coefficients and also the as-yet undetermined characteristic value $\lambda$. We find

$$\lambda = \sqrt{\alpha^2 + \frac{1}{2}} \equiv \lambda_3$$

(60)

which is the degenerate third characteristic value of the governing OF equations for binary electrolytes. It is independent of the external field strength $X$ or $\xi$ unlike $\lambda_1$ and $\lambda_2$. The relations between the coefficients are also obtained as follows:

$$B_1 = \frac{2\alpha\xi}{R} A_1, \quad B_2 = -\frac{2\alpha\xi}{R} A_2,$$

$$C_1 = \frac{1}{R} A_1, \quad C_2 = -\frac{1}{R} A_2,$$

$$D_1 = \frac{1}{R} A_1, \quad D_2 = -\frac{1}{R} A_2.$$  

(61)

Thus the distribution functions $\widehat{f}_{ji}^+, \widehat{f}_{jj}^+, \widehat{f}_{ii}^+, \widehat{f}_{ji}^-$ are given as linear combinations of Bessel functions $K_0(\lambda k \rho)$ ($k = 1, 2, 3$):

$$\widehat{f}_{ji}^+(\alpha, \rho) = A_1 K_0(\lambda_1 \rho) + A_2 K_0(\lambda_2 \rho),$$

$$\widehat{f}_{jj}^+(\alpha, \rho) = -\frac{2\alpha\xi}{R} A_1 K_0(\lambda_1 \rho) - \frac{2\alpha\xi}{R} A_2 K_0(\lambda_2 \rho) + B_3 K_0(\lambda \rho),$$

$$\widehat{f}_{ii}^+(\alpha, \rho) = \frac{1}{R} A_1 K_0(\lambda_1 \rho) - \frac{1}{R} A_2 K_0(\lambda_2 \rho) + C_3 K_0(\lambda \rho),$$

$$\widehat{f}_{ji}^-(\alpha, \rho) = \frac{1}{R} A_1 K_0(\lambda_1 \rho) - \frac{1}{R} A_2 K_0(\lambda_2 \rho) + D_3 K_0(\lambda \rho).$$

(62)–(65)

The solutions of Poisson equations (45)–(48) can be similarly obtained as linear combinations of Bessel functions $K_0(\lambda k \rho)$:

$$\widehat{\psi}_{j}^+(\alpha, \rho) = -\frac{1}{R} A_1 K_0(\lambda_1 \rho) + \frac{1}{R} A_2 K_0(\lambda_2 \rho) - C_3 K_0(\lambda \rho),$$

$$\widehat{\psi}_{i}^+(\alpha, \rho) = -\frac{1}{R} A_1 K_0(\lambda_1 \rho) + \frac{1}{R} A_2 K_0(\lambda_2 \rho) - (4\alpha\xi B_3 - C_3) K_0(\lambda \rho),$$

$$\widehat{\psi}_{i}^-(\alpha, \rho) = -\frac{2\alpha\xi}{R(1 + R)} A_1 K_0(\lambda_1 \rho) + \frac{2\alpha\xi}{R(1 - R)} A_2 K_0(\lambda_2 \rho) - B_3 K_0(\lambda \rho),$$

$$\widehat{\psi}_{i}^-(\alpha, \rho) = -\frac{2\alpha\xi}{R(1 + R)} A_1 K_0(\lambda_1 \rho) + \frac{2\alpha\xi}{R(1 - R)} A_2 K_0(\lambda_2 \rho) - B_3 K_0(\lambda \rho).$$

(66)–(69)

The coefficients $A_1$, $A_2$, $B_3$, and $C_3$ in these expansions are determined by imposing the boundary conditions (14) and (17), which for the symmetric and antisymmetric parts become

$$\lim_{\rho \to 0} \left( \rho \frac{d}{d\rho} \widehat{f}_{ji}^\pm + \frac{1}{2} \rho \frac{d}{d\rho} \widehat{\psi}_{j}^\pm + \frac{1}{2} \rho \frac{d}{d\rho} \widehat{\psi}_{i}^\pm \right) = 0,$$

$$\lim_{\rho \to 0} \left( \rho \frac{d}{d\rho} \widehat{f}_{kk}^\pm + \rho \frac{d}{d\rho} \widehat{\psi}_{k}^\pm \right) = 0 \quad (k = j, i),$$

(70)–(71)
\[
\lim_{\rho \to 0} \rho \frac{d}{d\rho} \psi^+ (\rho) = -\delta \quad (k = i, j), \quad (72)
\]
\[
\lim_{\rho \to 0} \rho \frac{d}{d\rho} \psi^- (\rho) = 0 \quad (k = i, j). \quad (73)
\]

We note that the behavior of \( K_0(\lambda_k\rho) \) near \( \rho = 0 \) has the property
\[
\lim_{\rho \to 0} \rho \frac{d}{d\rho} K_0 (\lambda_k\rho) = -\lim_{\rho \to 0} \rho \frac{d}{d\rho} \ln \rho = -1. \quad (74)
\]

Imposing the boundary conditions, we obtain the linear algebraic relations of coefficients, which can be easily solved upon reducing them to independent linear equations. To save the space we simply present the final results only:

\[
A_1 = -\frac{(R + 1)}{2R}, \quad A_2 = -\frac{(R - 1)}{2R}, \quad (75)
\]
\[
B_1 = \frac{(R + 1)\alpha\xi}{R^2}, \quad B_2 = -\frac{(1 - R)\alpha\xi}{R^2}, \quad B_3 = \frac{2\alpha\xi}{R^2}, \quad (76)
\]
\[
C_1 = -\frac{(R + 1)}{2R^2}, \quad C_2 = \frac{(R - 1)}{2R^2}, \quad C_3 = \frac{16 (\alpha\xi)^2}{R^2}, \quad (77)
\]
\[
D_1 = -\frac{(R + 1)}{2R^2}, \quad D_2 = \frac{(R - 1)}{2R^2}, \quad D_3 = \frac{4 (\alpha\xi)^2}{R^2}. \quad (78)
\]

The Fourier components \( \hat{f}^\pm_{\pm k} \) and \( \hat{\psi}^\pm_k \) in Eqs. (85) and (86) are finally given by

\[
\hat{f}^+_{ji} (\alpha, \rho) = -\frac{1}{2R} \left[ (R + 1) K_0 (\lambda_1\rho) + (R - 1) K_0 (\lambda_2\rho) \right], \quad (79)
\]
\[
\hat{f}^+_{jj} (\alpha, \rho) = -\frac{\xi\alpha}{R^2} \left[ (R + 1) K_0 (\lambda_1\rho) + (R - 1) K_0 (\lambda_2\rho) - 2K_0 (\lambda\rho) \right], \quad (80)
\]
\[
\hat{f}^+_{ii} (\alpha, \rho) = -\frac{1}{2R^2} \left[ (R + 1) K_0 (\lambda_1\rho) - (R - 1) K_0 (\lambda_2\rho) - 8 (\alpha\xi)^2 K_0 (\lambda\rho) \right], \quad (81)
\]
\[
\hat{f}^+_{ji} (\alpha, \rho) = -\frac{\xi\alpha}{R^2} \left[ (R + 1) K_0 (\lambda_1\rho) + (1 - R) K_0 (\lambda_2\rho) - 2K_0 (\lambda_3\rho) \right], \quad (82)
\]
\[
\hat{\psi}^+_{k} (\alpha, \rho) = \frac{1}{2R^2} \left[ (R + 1) K_0 (\lambda_1\rho) + (1 - R) K_0 (\lambda_2\rho) - 8 (\alpha\xi)^2 K_0 (\lambda_3\rho) \right], \quad (83)
\]
\[
\hat{\psi}^-_{k} (\alpha, \rho) = \frac{\xi\alpha}{R^2} \left[ K_0 (\lambda_1\rho) + K_0 (\lambda_2\rho) - 2K_0 (\lambda_3\rho) \right] \quad (k = j, i). \quad (84)
\]

We summarize the Fourier transforms of the solutions for the distribution functions and potentials.
we set out to find:

\[ f_{ji} (r) - n_i n_j = -\frac{2\kappa^2 n_i n_j e_j e_i}{D\pi k_B T} \int_0^\infty \frac{d\alpha}{R} \cos \left( \frac{\alpha x}{R} \right) \left[ (R + 1) K_0 (\lambda_1 \rho) + (R - 1) K_0 (\lambda_2 \rho) \right] \]

\[ -\frac{2\kappa^2 n_i n_j e_j e_i \xi}{D\pi k_B T} \int_0^\infty \frac{d\alpha}{R^2} \sin \left( \frac{\alpha x}{R} \right) \times \left[ (R + 1) K_0 (\lambda_1 \rho) + (R - 1) K_0 (\lambda_2 \rho) - 2K_0 (\lambda_3 \rho) \right] \]

\[ \psi_k (\alpha, \rho) = \frac{e_k}{2D} \int_0^\infty \frac{d\alpha}{R} \cos \left( \frac{\alpha x}{R} \right) \times \left[ (R + 1) K_0 (\lambda_1 \rho) + (R - 1) K_0 (\lambda_2 \rho) - 8 (\alpha \xi)^2 K_0 (\lambda_3 \rho) \right] \]

\[ + \frac{e_k \xi}{D} \int_0^\infty \frac{d\alpha}{R^2} \sin \left( \frac{\alpha x}{R} \right) \left[ K_0 (\lambda_1 \rho) + K_0 (\lambda_2 \rho) - 2K_0 (\lambda_3 \rho) \right] \quad (k = j, i), \quad \text{(86)} \]

and similarly for \( f_{jj} (x, \rho) \) and \( f_{ii} (x, \rho) \) to \( f_{ji} (x, \rho) \) in Eq. (85). It should be noted that the variables in the integrals are reduced variables in the units of the Debye parameter \( \kappa \); see Eq. (87) below.

The solutions presented in Eqs. (85) and (86) are the nonequilibrium parts of the pair distribution functions and potentials in the ionic liquid in the external field \( X \) (or \( \xi \) in reduced form) at arbitrary strength. Therefore they represent the nonequilibrium ionic liquid structure and potentials when the ions are moving subjected to the external field at a steady-state condition. If the full potential is desired, \( \psi_k (\alpha, \rho) \) must be combined with the equilibrium Debye potential—the Yukawa-type potential. Therefore it would be of great interest to see how the nonequilibrium liquid structure and potentials vary with respect to spatial positions and the field strength. We will investigate these aspects (i.e., profiles) in the following.

**B. Evaluation of Nonequilibrium Ionic Liquid Structure and Potentials**

The Fourier integrals in Eqs. (85) and (86) contain three parameters, position coordinates \( x \) and \( \rho \) and the reduce field strength \( \xi \). Although looking complicated, they can be evaluated analytically in the region where the transversal (radial) coordinate \( \rho \) satisfies a certain condition with respect to the axial coordinate \( x \), as will be stated more precisely later; see Eq. (90) below. In the rest of the \((x, \rho)\) plane where the condition is not met, they can be evaluated numerically, provided that the singular behavior of the integrands is properly handled by using the method of principal values used for singular integrals [34].

For the evaluation of the integrals, it is convenient to scale further the variables as follows:

\[ t = \sqrt{2\alpha}, \quad r = \rho/\sqrt{2}, \quad \hat{x} = x/\sqrt{2}, \quad \omega_k = \sqrt{2} \lambda_k. \quad \text{(87)} \]
Thus
\[ \omega_1 = \sqrt{1 + t^2 + \sqrt{1 - 2\xi^2 t^2}}, \quad \omega_2 = \sqrt{1 + t^2 - \sqrt{1 - 2\xi^2 t^2}}, \quad \omega_3 = \sqrt{1 + t^2}. \] (88)

It is also convenient to define
\[ \overline{\omega}_1 = \sqrt{1 - y^2 + \sqrt{1 + 2\xi^2 y^2}}, \quad \overline{\omega}_2 = \sqrt{1 - y^2 - \sqrt{1 + 2\xi^2 y^2}} \]
\[ \overline{\omega}_3 = \sqrt{1 - y^2}, \quad \omega = \frac{\sqrt{1 + 2\xi^2}}{\sqrt{2\xi}}. \] (89)

Notice that \( \overline{\omega}_k = \omega_k |_{t=iy} \) \((k = 1, \ldots)\) with the complex variable \( t \) taken along the imaginary axis. As shown in Appendix A, if the condition
\[ \frac{x}{r} + \frac{\text{Re} \omega_k (t)}{\text{Im} t} > 0 \] (90)
for \( \hat{x}, r > 0 \) in the complex plane of variable \( t \), the integrals in Eqs. (85) and (86) can be evaluated analytically or reduced to simple one-dimensional quadratures, if methods of contour integration are employed. As a matter of fact, the one-dimensional quadratures thus obtained can be analytically evaluated term by term in series if the series representation for Bessel functions \( I_0(z) \) is used. Condition (90) means that the region in question is roughly within a conical domain surrounding the \( x \) axis. Outside this region the integrals must be computed numerically by applying methods of principal integrations for singular integrals [34]. In this exterior region the integrals vanish uniformly as \( \hat{x}, r \to \infty \).

In his dissertation [25], Wilson did not evaluated either \( f_{ji} \) or \( \psi_k \), but only the axial velocity at the special position of \( \hat{x} = r = 0 \), namely, the coordinate origin. Henceforth for notational brevity the reduced variable \( \hat{x} \) will be simply typeset \( x \) without the caret \(^\wedge\).

The integrals in Eqs. (85) and (86), reduced as described above, are evaluated by means of the contour integration methods described in Appendix A. They are given by the expressions
\[ f_{ji} (\pm r) = n^2 - \frac{\kappa z n^2 \xi^2}{8 \pi D k_B T} \left\{ \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-xy} \left( 1 + \frac{1}{\sqrt{1 + 2\xi^2 y^2}} \right) I_0 (\overline{\omega}_1 r) \right. \]
\[ \left. \pm \xi \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-xy} y \left( 1 + \sqrt{1 + 2\xi^2 y^2} \right) \frac{1}{(1 + 2\xi^2 y^2)} I_0 (\overline{\omega}_1 r) \right) \]
\[ \mp 2\xi \int_0^1 dy \frac{ye^{-xy}}{1 + 2\xi^2 y^2} I_0 (\overline{\omega}_3 r) \}, \] (91)
\( \psi_j (\pm r) = -\psi_i (\mp r) \)

\[
= -\frac{ze}{8\pi \sqrt{2} D} \left\{ \int_0^1 dy \frac{e^{-xy} \left( 1 + \sqrt{1 + 2\xi^2 y^2} \right)}{1 + 2\xi^2 y^2} I_0 (\omega_1 r) \\
-4\xi^2 \int_0^1 dy \frac{e^{-xy} y^2}{1 + 2\xi^2 y^2} I_0 (\omega_3 r) \right\} \pm \sqrt{2\xi} \left[ \int_0^1 dy \frac{ye^{-xy} I_0 (\omega_1 r)}{1 + 2\xi^2 y^2} - 2 \int_0^1 dy \frac{ye^{-xy} I_0 (\omega_3 r)}{1 + 2\xi^2 y^2} \right].
\]

(92)

Here \( I_0 (\omega_k r) \) \((k = 1, 3)\) are the regular Bessel functions of zeroth order of second kind. In these expressions the range of position variables \( x \) and \( r \) must be such that \( \sqrt{2(1 + \xi^2)} x > r \) for the integrals involving \( \omega_1 \), and \( x > r \) for the integrals involving \( \omega_3 \). These conditions, related to Condition (90) stemming from Jordan's lemma on contour integrals, ensure the boundary conditions for the distribution functions and the potentials, which vanish as \( x \) and \( r \) tend to infinity.

The results presented in Eqs. (91) and (92) for the reduced nonequilibrium part of pair distribution function \( \Delta f_{ji} \) and the reduced nonequilibrium part of ionic potential \( \Delta \psi_j \), respectively, defined by

\[
\Delta f_{ji} = \frac{\pi D k_B T}{\sqrt{2\kappa e^2}} (f_{ji} - n^2), \quad \Delta \psi_j = \frac{\sqrt{2\pi D}}{\kappa e} \left( \psi_j - \psi^0_j \right)
\]

(93)

are graphically depicted in the case of \( \xi = 1 \) in Figs. 2–3 to give pictorial representations for the nonequilibrium parts of the ionic liquid structure and the mean ionic potential in the Brownian motion model. They vanish as \( x \) and \( r \) increase to infinity from a finite value at the origin. The choice of the value of the reduced field strength \( \xi \) is arbitrary; it could be as large as desired.

Fig. 2 displays an important feature most distinguishable from the equilibrium pair distribution function for ion pair \((j, i)\) that should be spherically symmetric and peaked at the coordinate origin \((x, r) = (0, 0)\). Instead, the nonequilibrium part of the pair distribution function \( \Delta f_{ji} (x, r, \xi) \) at \( \xi > 0 \) has a peak displaced from the coordinate origin. This means that the spherical symmetry originally present at equilibrium (i.e., at \( \xi = 0 \)) not only has been destroyed with its peak position displaced to a point \((x, r) \neq (0, 0)\) from the coordinate origin, but also the ion atmosphere is no longer spherically symmetric if \( \xi > 0 \). This means that the center of ion atmosphere has also been displaced by the external field along the \( x \) axis. As a matter of fact, the present exact solutions of the governing equations provide the details of the state of distortion of the spherical ionic atmosphere and its migration as \( \xi \) increases from \( \xi = 0 \). We will see in the next section how this mode of distortion in the ion atmosphere is further modified in a manner of feedback process by the hydrodynamic motion of medium induced by the motions of ions under the influence of the
external field. Fig. 3 for $\Delta \psi_j$ illustrates the molecular cause for the distortion of the spherical ionic atmosphere through the nonequilibrium change in the ionic potentials.

If the series representations for the Bessel functions $I_0(\omega_1 r)$ and $I_0(\omega_3 r)$ are used, the integrals can be evaluated in terms of elementary functions of $\xi$, $x$, and $r$, but since these series converges slowly, such series representations would have a limited practical value for precise evaluation of integrals. Nevertheless, such representation might be of some use for some theoretical study. Eqs. (91) and (92) contain the information on the nonequilibrium ionic liquid structure and the mean potentials for the ionic liquid subjected to the external electric field. They are new results for ionic solutions in an external field examined here. The distribution functions and ionic potentials could be made use of to develop a theory of transport processes in binary electrolyte solutions. In this sense, they would be potentially very useful, especially, for calculating transport coefficients of the ionic solution in the electric field.

IV. HYDRODYNAMIC EQUATION AND FLOW PROFILES

In the conventional ionic conductance experiments the flow velocity of the medium is usually not large. Therefore flow may be regarded as laminar. Under this condition the nonlinear inertial term can be neglected in the Navier–Stokes equation. Moreover, the liquid may be considered incompressible to a good approximation. Under these conditions the Navier–Stokes equation becomes the Stokes equation \[19–21\] for an incompressible fluid. We therefore use the Stokes equation to calculate the flow velocity of the medium around the moving ions pulled by the external field. It may be helpful to point out that the flow field generated would be schematically reminiscent of the flow field around a moving object submerged in a medium.

We assume that there are no body-forces other than an applied electric field. However, because ions are strongly correlated by long-range Coulomb forces and also interacting with the applied external electric field, it is necessary to calculate the mean local electric field. For the purpose of calculating it we may use the solutions of the OF equations and the Poisson equations presented in the previous section. Therefore the mean local electric field is expected to depend on the spatial position and the external field strength $\xi$. 
A. Local Electric Field

Since the field is aligned along the $x$ axis and the charge density is given by the Poisson equation, the local force due to the field $X$ on charge density $\rho$ is given by

$$F_x = -\frac{DX}{4\pi} \nabla^2 \psi_j (r). \quad (94)$$

Since $\psi_j (r)$ is given by

$$\psi_j (r) = \frac{k \epsilon_j}{\pi D} \int_0^\infty d\alpha \cos (\alpha x) \left[ (R+1) K_0 (\lambda_1 \rho) + (1-R) K_0 (\lambda_2 \rho) - 2 (1-R^2) K_0 (\lambda_3 \rho) \right]$$

$$+ \frac{8 \kappa \epsilon_j \xi}{D} \int_0^\infty d\alpha \sin (\alpha x) \left[ \frac{\alpha}{R^2} [K_0 (\lambda_1 \rho) + K_0 (\lambda_2 \rho) - 2K_0 (\lambda_3 \rho)] \right], \quad (95)$$

we obtain the mean local body-force

$$F_x = -\frac{X e_j \kappa^3}{2\pi^2} \int_0^\infty d\alpha \cos (\alpha x) \left[ \frac{(R+1) \left( \lambda_1^2 - \alpha^2 \right)}{2R^2} K_0 (\lambda_1 \rho) 
+ (1-R) \frac{\left( \lambda_2^2 - \alpha^2 \right)}{2R^2} K_0 (\lambda_2 \rho) 
- \frac{(1-R^2) \left( \lambda_3^2 - \alpha^2 \right)}{R^2} K_0 (\lambda_3 \rho) \right]$$

$$- \frac{X e_j \kappa^3 \xi}{2\pi^2} \int_0^\infty d\alpha \sin (\alpha x) \left[ \frac{\alpha \left( \lambda_1^2 - \alpha^2 \right)}{R^2} K_0 (\lambda_1 \rho) 
+ \frac{\alpha \left( \lambda_2^2 - \alpha^2 \right)}{R^2} K_0 (\lambda_2 \rho) - 2 \frac{\alpha \left( \lambda_3^2 - \alpha^2 \right)}{R^2} K_0 (\lambda_3 \rho) \right], \quad (96)$$

This expression shows that the external force $e_j X$ is dressed up by the long-range correlations between the ions interacting through Coulomb forces and the interaction of ions and ion atmosphere with the external field. The effects of long-range correlations are described by the governing equations, and their feedback effect manifests itself in the form of dressed external force. This aspect is an important characteristic of the present theory of ionic solutions not usually seen in theories of charge carrier mobilities and their transport processes in recent literatures [3–5].

It is convenient to write Eq. (96) in a compact form to solve the Stokes equation:

$$F_x = \frac{X e_j \kappa^3}{2\pi^2} \sum_{l=1}^{3} \left[ C_l \cos (\alpha x) K_0 (\lambda_l \rho) + S_l \sin (\alpha x) K_0 (\lambda_l \rho) \right], \quad (97)$$
where integral operators $C_l$ and $S_l$ are defined by

$$
C_l = - \int_0^\infty d\alpha \left\{ \begin{array}{ll}
\frac{(1+R^2)(\lambda^2_1-\alpha^2)}{2R^2} & \text{for } l = 1 \\
\frac{(1-R^2)(\lambda^2_2-\alpha^2)}{2R^2} & \text{for } l = 2 \\
\frac{(1-R^2)(\lambda^4_1-\alpha^2)}{R^2} & \text{for } l = 2
\end{array} \right.,
$$

(98)

$$
S_l = - \int_0^\infty d\alpha \left\{ \begin{array}{ll}
\frac{\xi\alpha(\lambda^2_1-\alpha^2)}{R^2} & \text{for } l = 1 \\
\frac{\xi\alpha(\lambda^2_2-\alpha^2)}{R^2} & \text{for } l = 2 \\
-\frac{2\xi\alpha(\lambda^4_1-\alpha^2)}{R^2} & \text{for } l = 3
\end{array} \right.,
$$

(99)

This mean local force $F_x$ is an input for the Stokes equation of the flow problem under consideration.

**B. Stokes Equation and its Equivalent Form**

At an arbitrary Reynolds number the steady Navier–Stokes equation must be used:

$$
\overline{\rho} \nabla \cdot \mathbf{v} - \eta_0 \nabla^2 \mathbf{v} - \eta_b \nabla (\nabla \cdot \mathbf{v}) = -\nabla p + \mathbf{F},
$$

(100)

where $\overline{\rho}$ is the fluid density, $\eta_0$ is the shear viscosity of the electrolyte solution, $\eta_b$ is its bulk viscosity, $p$ is the pressure, and $\mathbf{F}$ is the body (external) force density. For an incompressible fluid $\nabla \cdot \mathbf{v} = 0$. For a fluid undergoing laminar flow of low Reynolds number (typically $Re = O(10^{-6})$ at the field gradient of 1 kVolt/m in aqueous solution) the inertial term can be neglected. Thus the Navier–Stokes equation for velocity $\mathbf{v}$ becomes the Stokes equations for divergenceless flow

$$
-\eta_0 \nabla^2 \mathbf{v} = -\nabla p + \mathbf{F},
$$

(101)

$$
\nabla \cdot \mathbf{v} = 0.
$$

(102)

Note that the presence of an external field makes the pressure nonuniform in space. As is well known, if $\text{curl}$ of Eq. (101) is taken, the $\nabla p$ term vanishes and Eq. (101) takes the form

$$
\eta_0 \nabla \times \nabla \times \nabla \times \mathbf{v} = \nabla \times \mathbf{F}.
$$

(103)

Since $\nabla \times \nabla \times \mathbf{v} = \nabla (\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v}$ by vector algebra, the two equations (101) and (102) may be combined into a single equation

$$
\eta_0 \nabla \times \nabla \times \mathbf{v} = -\nabla p + \mathbf{F}.
$$

(104)

For the present problem $\mathbf{F} = \delta_x F_x$, where $\delta_x$ is the unit vector along the $x$ axis.
To solve Eq. (103) for $\mathbf{v}$, we observe $\nabla \cdot \mathbf{v} = 0$, which means that there exists an axial vector $\mathbf{A}$ such that $\mathbf{v} = \nabla \times \mathbf{A}$, where $\mathbf{A}$ must depend on position vector $\mathbf{r}$ and field vector $\mathbf{X}$, both of which are ordinary vectors. Thus we may transform the solution $\mathbf{v}$ of Eq. (104) into the form

$$\mathbf{v} = \nabla \times \nabla \times \mathbf{a} + \mathbf{v}^0,$$

(105)

where $\mathbf{v}^0$ is a constant satisfying the appropriate boundary conditions of the velocity. Since $\mathbf{a} \to 0$ and also $\mathbf{v}$ should vanish as $|\mathbf{r}| \to \infty$, it follows $\mathbf{v}^0 = 0$. Thus we will set $\mathbf{v}^0 = 0$ henceforth.

In the first step to formally solve Eq. (104), substitute Eq. (105) with $\mathbf{v}^0 = 0$ into Eq. (104) to obtain the equation

$$\eta_0 \nabla \times \nabla \times \nabla \times \nabla \times \mathbf{a} = -\nabla \mathbf{p} + \mathbf{F},$$

(106)

By the identities of vector algebra

$$\nabla \times \nabla \times \mathbf{a} = \nabla (\text{div} \mathbf{a}) - \nabla^2 \mathbf{a},$$

(107)

$$\nabla \times \nabla \times (\nabla \cdot \mathbf{a}) = 0,$$

(108)

and

$$\nabla \times \nabla \times (\nabla^2 \mathbf{a}) = \nabla (\nabla^2 \text{div} \mathbf{a}) - \nabla^2 (\nabla^2 \mathbf{a}),$$

(109)

it follows that

$$\nabla \times \nabla \times \nabla \times \nabla \times \mathbf{a} = \nabla \times \nabla \times \nabla (\nabla \cdot \mathbf{a}) - \nabla \times \nabla \times (\nabla^2 \mathbf{a})$$

$$= -\nabla \times \nabla \times (\nabla^2 \mathbf{a}).$$

(110)

Upon using Eq. (110) in Eq. (106) and substituting the result into Eq. (104), we obtain a fourth-order differential equation of vector $\mathbf{a}$:

$$\eta_0 \nabla^2 \nabla^2 \mathbf{a} - \mathbf{F} = \nabla (\eta_0 \nabla^2 \text{div} \mathbf{a} - \mathbf{p}).$$

(111)

This equation is equivalent to Eq. (101) or the Stokes equations. Because the left and right hand sides of Eq. (111) are of two different kinds of vectors the equation may be separated into two equations:

$$\eta_0 \nabla^2 \nabla^2 \mathbf{a} = \mathbf{F},$$

(112)

$$p = p_0 + \eta_0 \nabla^2 \text{div} \mathbf{a}.$$
The solution of the Stokes equations is now reduced to that of Eq. (112), a fourth-order differential equation with $F$ given by the solutions of the OF equations and the Poisson equations—namely, the governing equations. In summary, we have for the velocity and pressure the expressions

$$v = \nabla \times \nabla \times a + v^0 = \nabla \times \nabla \times a,$$

$$p = p_0 + \eta_0 \nabla^2 (\nabla \cdot a).$$

Vector $a$ is determined by solving Eq. (112) in terms of the local force density given by Eq. (96) or (97), a compact abbreviation of the former. In Eq. (61) $p_0$ is a homogeneous pressure uniform in space, that is, the equilibrium pressure consisting of the osmotic pressure of the solution. This equilibrium pressure must be either supplied phenomenologically by using thermodynamics or from the statistical mechanics of the electrolyte solution. Therefore, given the solution for vector $a$, both velocity and pressure can be determined from the Stokes equation.

To solve Eq. (112) for $a$, substitute Eq. (97) into the former, which then reads

$$\nabla^2 (\nabla^2 a) = \frac{X e_j \kappa^2}{2 \pi^2 \eta_0} \delta_x \left[ C_l \cos (\alpha x) K_0(\lambda_l \rho) + S_l \sin (\alpha x) K_0(\lambda_l \rho) \right],$$

where the repeated index $l$ means a sum over $l = 1, 2, 3$. Since Eq. (115) suggests that $\nabla^2 a$ must be a linear combination of the Bessel functions in the right hand side of the equation, recalling Eqs. (49) and (50) we find

$$\nabla^2 a = \frac{X e_j \kappa^2}{2 \pi^2 \eta_0} \delta_x \left[ C_l \cos (\alpha x) K_0(\lambda_l \rho) + S_l \sin (\alpha x) K_0(\lambda_l \rho) \right] + \delta_x A^*,$$

where $A^*$ is the homogeneous solution obeying the equation

$$\nabla^2 (\nabla^2 A^*) = 0$$

with $A^* = \delta_x A^*$. The solution $A^*$ must satisfy the boundary conditions at infinite $\rho$. Thus we choose

$$A^* = -\frac{X e_j \kappa}{2 \pi^2 \eta_0} \delta_x \left[ C_l \cos (\alpha x) \frac{K_0(\lambda_l \rho) - K_0(\alpha \rho)}{\lambda_l^2 - \alpha^2} + S_l \sin (\alpha x) \frac{K_0(\lambda_l \rho) - K_0(\alpha \rho)}{\lambda_l^2 - \alpha^2} \right],$$

since this satisfies Eq. (117). Therefore we obtain the equation

$$\nabla^2 a = \frac{X e_j \kappa}{2 \pi^2 \eta_0} \delta_x \times \left\{ C_l \frac{\cos (\alpha x) [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{\lambda_l^2 - \alpha^2} + S_l \frac{\sin (\alpha x) [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{\lambda_l^2 - \alpha^2} \right\}. \quad (119)$$
Since the solution of this inhomogeneous second-order differential equation must be a linear combination of the Bessel functions making up the inhomogeneous term on the right, it is sought in the form
\[ a = \frac{X e^j}{2\pi^2 \eta_0 \kappa} \delta_x \left[ C_l \cos (\alpha x) + S_l \sin (\alpha x) \right] \times \]
\[ \{ b_1 [K_0(\lambda_t \rho) - K_0(\alpha \rho)] + b_2 [K_0(\beta_t \rho) - K_0(\alpha \rho)] \}, \quad (120) \]
where \( b_1, b_2, \) and \( \beta_t \) are constants determined as follows: On inserting this expansion into Eq. (119) we find
\[ [b_1 (\lambda_t^2 - \alpha^2) - 1] K_0(\lambda_t \rho) + b_2 (\beta_t^2 - \alpha^2) K_0(\beta_t \rho) + K_0(\alpha \rho) = 0. \quad (121) \]
The expansion coefficients \( b_1 \) and \( b_2 \) and the parameter \( \beta_t \) are determined below. Since Bessel functions \( K_0(\lambda_t \rho), K_0(\beta_t \rho), \) and \( K_0(\alpha \rho) \) not only do not vanish everywhere in \( \rho, \) but also their arguments are arbitrary, we may choose \( b_1 \) and \( b_2 \) such that
\[ b_1 = \frac{1}{\lambda_t^2 - \alpha^2} \quad (122) \]
and
\[ \lim_{\beta_t \to \alpha} b_2 (\beta_t^2 - \alpha^2) K_0(\beta_t \rho) = -K_0(\alpha \rho). \quad (123) \]
Then Eq. (121) is satisfied and hence Eq. (120) is a solution of Eq. (119). Eq. (123) therefore implies
\[ b_2 = -\frac{1}{(\beta_t^2 - \alpha^2)}. \quad (124) \]
Finally, we obtain for the solution of Eq. (119)
\[ a = \frac{X e^j}{2\pi^2 \eta_0 \kappa} \delta_x \left[ C_l \cos (\alpha x) + S_l \sin (\alpha x) \right] \times \]
\[ \left\{ \frac{[K_0(\lambda_t \rho) - K_0(\alpha \rho)]}{(\lambda_t^2 - \alpha^2)^2} + \frac{\alpha \rho K_1(\alpha \rho)}{2(\lambda_t^2 - \alpha^2) \alpha^2} \right\}. \quad (125) \]
For the solution (125) for \( a, \) we have used Eq. (107) and the recurrence relations of the Bessel functions [32, 33]
\[ \frac{d}{dz} K_0(z) = -K_1(z), \]
\[ \frac{d}{dz} K_1(z) = -K_0(z) - \frac{1}{z} K_1(z), \quad (126) \]
\[ \left( \frac{1}{z} \frac{d}{dz} - \frac{dz}{dz} - 1 \right) z K_1(z) = -2K_0(z), \]
as well as \( \text{div} \ a = \partial a_x / \partial x \) owing to the fact that \( F = \delta_x F_x \) and hence \( a_\rho = a_\theta = 0 \) identically.
C. Fourier Transform Solution for the Axial Velocity

It is now possible to obtain the Fourier transform solution for the axial component of the velocity. Since

\[(\nabla \times \nabla \times a)_x = \nabla_x (\text{div} a) - \nabla^2 a_x,\]

by using the formulas for \(\nabla_x (\text{div} a)\) and \(\nabla^2 a_x\) it follows from Eq. (113) the Fourier transform solution for the axial velocity component for all values of \(x\) and \(\rho\):

\[
v_x(x, \rho; \xi) = -\frac{Xe_j}{2\pi^2\eta_0\kappa} \sum_{l=1}^{3} C_l \cos (\alpha x) \left\{ \frac{\lambda_l^2 [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{(\lambda_l^2 - \alpha^2)^2} + \frac{\alpha \rho K_1(\alpha \rho)}{2(\lambda_l^2 - \alpha^2)} \right\} - \frac{Xe_j}{2\pi^2\eta_0\kappa} \sum_{l=1}^{3} S_l \sin (\alpha x) \left\{ \frac{\lambda_l^2 [K_0(\lambda_l \rho) - K_0(\alpha \rho)]}{(\lambda_l^2 - \alpha^2)^2} + \frac{\alpha \rho K_1(\alpha \rho)}{2(\lambda_l^2 - \alpha^2)} \right\},
\]

(127)

Here we now have restored the summation sign over index \(l\). For a more explicit expression the sum over \(l\) may be expanded. This formula does not exactly agree with Wilson’s expression\[25\] for the axial velocity because of some missing terms and typographical errors in his formula.

The Fourier transform integrals in Eq. (127) may be expressed by using the reduced variables defined in Eqs. (87) and (88) to cast them into as simple forms as possible. We will also define the reduced velocity

\[
\hat{v} = \left(2\sqrt{2}\pi^2\eta_0/zeX\kappa\right)v.
\]

(128)

Then the axial velocity \(v_x(x, \rho; \xi)\) is given by

\[
v_x(x, \rho; \xi) = \frac{zeX\kappa}{2\sqrt{2}\pi^2\eta_0} \hat{v}_x(x, r, \xi),
\]

(129)

where the reduced axial velocity is now given by components made up of cosine and sine Fourier transforms:

\[
\hat{v}_x(x, r, \xi) = \frac{1}{2} K^B_{c} + \frac{\xi}{\sqrt{2}} K^S_{c} - K^S_{e} + \frac{1}{2} r K^c_{5} - \frac{1}{\sqrt{2} \xi} K^c_{1},
\]

(130)

Various components in Eq. (130) are defined by the Fourier transforms

\[
K^B_{c}(x, r, \xi) = \int_{0}^{\infty} dt \frac{\cos (xt)}{(1 - 2\xi^2 t^2)} \left[ \frac{\omega_1^2 K_0(\omega_1 r) + \omega_2^2 K_0(\omega_2 r) - 4\xi^2 t^2 \omega_3^2 K_0(\omega_3 r)}{(1 + \sqrt{1 - 2\xi^2 t^2}) + (1 - \sqrt{1 - 2\xi^2 t^2}) - 2\omega_3^2 K_0(\omega_3 r)} \right],
\]

(131)

\[
K^B_{s}(x, r, \xi) = \int_{0}^{\infty} dt \frac{t \sin (xt)}{(1 - 2\xi^2 t^2)} \times \left[ \frac{\omega_1^2 K_0(\omega_1 r)}{(1 + \sqrt{1 - 2\xi^2 t^2})} + \frac{\omega_2^2 K_0(\omega_2 r)}{(1 - \sqrt{1 - 2\xi^2 t^2})} - 2\omega_3^2 K_0(\omega_3 r) \right],
\]

(132)
\begin{align*}
K_4^c &= \int_0^\infty dt \cos (xt) \omega_0^2 K_0(rt), \\
K_5^c &= \int_0^\infty dt \cos (xt) tK_1(rt), \\
K_4^s &= \int_0^\infty dt \sin (xt) K_0(rt).
\end{align*}

Integrals $K_4^c$, $K_5^c$, and $K_4^s$ can be evaluated analytically in closed algebraic forms. On the other hand, the Brownian motion part of the integrals $K_4^c(x,r,\xi)$ and $K_5^s(x,r,\xi)$ can be evaluated by methods of contour integration in the region satisfying Condition \[90\] required by the Jordan lemma\[30\] for the contour integrals. Outside the region, they are computed by using straightforward numerical integration methods employing a method of principal values.

1. Evaluation of Integrals $K_4^c$, $K_5^c$, and $K_4^s$

All the integrals appearing in the expression for $\hat{v}_x(x,r,\xi)$ do not appear simple at first glance. Presumably, for this reason Wilson evaluated the integrals for the case of $x = r = 0$ only. However, the integrals $K_4^c$, $K_5^c$, and $K_4^s$ are indeed amenable to analytic evaluations in closed form. We explicitly illustrate the method by using $K_4^c$ as an example. Other integrals can be evaluated similarly.

a. $K_4^c$ On substitution of the integral representation\[32\] of the Bessel function $K_\nu(rt)$ of integer order

\[K_\nu(z) = \int_0^\infty ds e^{-z \cosh s} \cosh (\nu s) \quad (\text{arg } z < \frac{\pi}{2}),\]

the integral $K_4^c$ can be written as

\[K_4^c = \frac{1}{2} \int_0^\infty dt \int_0^\infty ds \left[ e^{-t(r \cosh s - ix)} + e^{-t(r \cosh s + ix)} \right].\]

It is legitimate to interchange the order of integrals. Then the integration over $t$ is trivial; changing variable to $z = \sinh s$, we obtain elementary integrals with respect to $z$, which can be easily integrated:

\[K_4^c = \frac{\pi}{2 (x^2 + r^2)^{1/2}} - \frac{\pi (2x^2 - r^2)}{2 (r^2 + x^2)^{5/2}}.\]

It reminds us of Coulombic and dipole contributions, which are purely mechanical.

b. $K_5^c$ Upon using the integral representation of $K_1(rt)$ and the same procedure as for integral $K_4^c$, we obtain $K_5^c$,

\[K_5^c = \frac{\pi r}{2 (x^2 + r^2)^{3/2}}.\]
This integral appears in Wilson’s formulation as the divergence-causing term. We will return to it again when we compare the present result with Wilson’s \cite{25} in more detail.

c. $K_s^4$ This integral also can be evaluated in the same manner as for $K_c^4$. We obtain

$$K_s^4 = \frac{\pi x}{2 (x^2 + r^2)^{3/2}}.$$  \hfill (139)

The three integrals $K_c^4$, $K_s^4$, and $K_s^5$ make up purely mechanical contributions to the axial velocity $v_x$. They may be interpreted as either Coulombic or dipolar contributions of the ion atmosphere, which acts as if it is a dipole toward the external field. The collection of the three integrals evaluated up to this point will be collectively referred to as a mechanical velocity $(\bar{v}_x)_{me}$, which is a countercurrent induced by Coulomb and dipole interactions of ion atmosphere interacting with the applied external field:

$$(\bar{v}_x)_{me} \equiv -K_c^4 + \frac{r}{2} K_s^5 - \frac{1}{\sqrt{2\xi}} K_s^4$$

$$= -\frac{\pi}{2\sqrt{2\xi}} \frac{x}{(x^2 + r^2)^{3/2}}$$

$$- \frac{\pi r^2}{4 (x^2 + r^2)^{1/2}} + \frac{\pi (2x^2 - r^2)}{2 (x^2 + r^2)^{5/2}}.$$  \hfill (140)

This contribution of $(\bar{v}_x)_{me}$ to $\bar{v}_x$ represents the fully deterministic part of the hydrodynamic velocity that is not associated with the Brownian motion of particles giving rise to the dissipative part of the local body-force. In fact, one of these terms [i.e., the first term in the second equality of Eq. (140)], when inserted into the velocity formula (129), becomes field-independent and, consequently, does not contribute to the mobility or electrophoretic coefficient. Moreover, $(\bar{v}_x)_{me}$ is negatively divergent at the coordinate origin, and its manner of divergence is clearly direction-dependent, that is, depending on whether the zero of $x$ or $r$ is approached first. Note that when converted to the axial velocity in real units, the last three terms in $(\bar{v}_x)_{me}$ in Eq. (140) are proportional to the reduced field strength $\xi$.

2. \textbf{Evaluation of $K_c^B (x, r, \xi)$ and $K_s^B (x, r, \xi)$ Arising from Brownian Motions}

The remaining integrals (131) and (132) can be calculated by means of contour integration methods described in Appendix A. We collect them in the form

$$\frac{1}{2} k_c^B + \frac{\xi}{\sqrt{2}} K_s^B = -\frac{\pi}{4} [\mathcal{C}_1 (x, r, \xi) - \mathcal{S}_1 (x, r, \xi)] - \frac{\pi}{2} [\mathcal{C}_2 (x, r, \xi) - \mathcal{S}_2 (x, r, \xi)],$$  \hfill (141)
where

\[
\mathcal{C}_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{1 - y^2 + \sqrt{1 + 2\xi^2 y^2}}{1 + 2\xi^2 y^2} e^{-xy I_0(\omega_1 r)},
\]

(142)

\[
\mathcal{C}_2(x, r; \xi) = \int_0^{1} dy \frac{2\xi^2 y^2 (1 - y^2)}{1 + 2\xi^2 y^2} e^{-xy I_0(\omega_3 r)},
\]

(143)

\[
\mathcal{S}_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \sqrt{2\xi y (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})} \left(1 + 2\xi^2 y^2\right) e^{-xy I_0(\omega_1 r)},
\]

(144)

\[
\mathcal{S}_2(x, r; \xi) = \int_0^{1} dy \sqrt{2\xi y (1 - y^2)} \left(1 + 2\xi^2 y^2\right) e^{-xy I_0(\omega_3 r)}.
\]

(145)

The parameters \((x, r)\) in integrals (142) and (144) are subject to the condition

\[
x\sqrt{1 + \xi^2} > r
\]

(146)

and integrals (143) and (145) to the condition

\[
x > r,
\]

(147)

both of which arise from the condition to satisfy the Jordan lemma on the contour integrals involving an infinite semicircle in the complex plane; see contours in Figs. 11–13 in Appendix A:

\[
x/r + \text{Re} \omega_l (t) / \text{Im} t > 0 \quad (t = \text{complex}; \ l = 1, 2, 3).
\]

(148)

These conditions also have been mentioned in connection with the pair distribution functions and potentials in Sec. II. If these conditions are not met, the contour integration methods cannot be applied because the integrals along curve \(C_\infty\) of infinite radius diverge. In the region of \((x, r)\) plane not satisfying these conditions (i.e., exterior to the region) the integrals must be evaluated numerically by using the method of principal values. Note that as in the contour integration methods used for Eqs. (142)–(145) the contributions from the singular points cancel in the end, leaving only the principal value parts. It is also important to note the sine transform terms make significant contributions comparable in magnitude to the cosine transform terms, as will be found later in the numerical analysis. On the other hand, if \(x\) were set equal to zero, the sine integral would identically vanish and thus have made no contribution to the velocity. Consequently, the final velocity values would be different depending on whether setting \(x\) and \(r\) equal to zero before or after integration. This subtle, but important point should be kept in mind when we handle this kind of integrals or the result obtained could be misleading.
In summary for the axial velocity, we obtain

\[
\mathbf{v}_x (x, r, \xi) = -\frac{\kappa^2 k_B T}{8\pi\eta_0} \frac{x}{(x^2 + r^2)^{3/2}} - \frac{ze\kappa X}{4\sqrt{2}\pi\eta_0} \left[ \frac{1}{(x^2 + r^2)^{3/2}} - \frac{r^2}{2(x^2 + r^2)^{5/2}} - \frac{2x^2 - r^2}{(x^2 + r^2)^{5/2}} \right] - \frac{ze\kappa X}{4\sqrt{2}\pi\eta_0} \left[ C_1 (x, r, \xi) + 2C_2 (x, r, \xi) - S_1 (x, r, \xi) - 2S_2 (x, r, \xi) \right].
\]  (149)

The axial velocity obtained here contains a term independent of the external field—i.e., the first term on the right, whereas the rest of terms are led by terms proportional to \(X\) (or \(\xi\) in reduced units); they are in fact rather complicated functions of the field strength \(\xi\). Physically, the velocity calculated from the Stokes equation represents the flow profile of the countercurrent induced by the moving center ion and its ion atmosphere in response to the external electric field.

3. Electrophoretic Factor

The mobility of ions in the \(x\) direction is associated with the field-dependent terms of the axial velocity, and the mobility or electrophoretic coefficient can be defined as the coefficient in the axial velocity vs. electric field according to the thermodynamic force-flux relations in thermodynamics of irreversible processes\[35, 36\]. Therefore, according to the usual practice in the theory of ionic conductance\[7\] within the framework of irreversible thermodynamics, we define the electrophoretic factor \(f(x, r; \xi)\) as follows:

\[
\mathbf{v}_x (x, r, \xi) = -\frac{\kappa^2 k_B T}{8\pi\eta_0} \frac{x}{(x^2 + r^2)^{3/2}} - \frac{zeX\kappa}{6\sqrt{2}\pi\eta_0} f(x, r; \xi).
\]  (150)

In fact, the factor \(f(x, r; \xi)\) is generally dependent on position coordinates \(x\) and \(r\) as well as \(\xi\). Note that the second term on the right of Eq. (150) is reminiscent of the velocity formula in Eq. (3), which was obtained by a heuristic argument on the basis of the Stokes law in contrast to the hydrodynamic derivation of Eq. (150). Then upon comparison with the axial velocity formula (149) the electrophoretic factor \(f(x, r; \xi)\) is identified with the expression

\[
f(x, r; \xi) = \frac{3}{2} \left( \frac{3r^2}{(r^2 + x^2)^{1/2}} - \frac{3r^2}{4(r^2 + x^2)^{3/2}} - \frac{3(2x^2 - r^2)}{2(r^2 + x^2)^{5/2}} \right) + \frac{3}{2} \left[ C_1 (x, r, \xi) + 2C_2 (x, r, \xi) - S_1 (x, r, \xi) - 2S_2 (x, r, \xi) \right].
\]  (151)

Since it generally depends on coordinates as does the axial velocity, the factor \(f(x, r; \xi)\), in fact, describes the electrophoretic profile in \((x, r)\) plane as is evident from the figure shown below.
4. **Numerical Evaluation of the Axial Velocity**

Since it is important to learn about the axial velocity profiles we have plotted them in the \((x,r)\) plane in the case of \(\xi = 1\). In the region satisfying Conditions (148) the formula given in Eq. (149) is used with the integrals (142)–(145), and in the exterior to the region defined by the conditions the velocity integrals for the Brownian motion contributions—i.e., Eqs. (131) and (132)—are calculated by applying methods of principal integration because the integrals have singularities on the real axis. Thus computed axial velocity profiles are summarized in Figs. 4–6.

In Fig. 4 the axial velocity is plotted in \((x,r)\) plane in 3D with the vertical axis indicating the magnitude (color coded) of the axial velocity. It is seen negative in a semi-elliptic region enclosing the \(r\) axis beginning from \(r = 0\) (yellow-green color) as predicted by Formula (149), it being negative principally because of the mechanical part of the axial velocity \((\mathbf{\hat{v}}_x)_m\), which becomes dominant over the Brownian motion contributions—the last group of terms in Eq. (149). According to Fig. 4, the maximum of the axial velocity in the positive \(x\) direction (dark red region) is located in the neighborhood of the coordinate origin, but displaced from the origin \((x,r) = (0,0)\). The axial velocity decreases gradually and eventually vanishes as \(x\) and \(r\) values increase to infinity. To gain a better idea of the electrophoretic factor \(f(x,r,\xi)\) it is plotted 3-dimensionally in \((x,r)\) plane in Fig. 5 with the magnitude in the similar color coding used for Fig. 4. Its shape is rather similar to the velocity profile in Fig. 4, but its sign is opposite to that of \(\mathbf{\hat{v}}_x\) owing to the way it is defined. To have a better idea of the behavior of the electrophoretic factor we have plotted the projection of the level curves of the \(f(x,r,\xi)\) surface onto the \((x,r)\) plane in Fig. 6. It displays two sets of roughly elliptical contours, one with the major axis on the \(x\) axis and the other with the major axis on the \(r\) axis excluding the coordinate origin. The former set of contours corresponds to the negative portion of \(f(x,r,\xi)\), whereas the latter to the positive portion of \(f(x,r,\xi)\) but transversal to the \(x\) axis. The outermost level curve denoted \(C_p\) in fact represents the locus of zero of \(f(x,r,\xi)\), that is, \(f(x,r,\xi) = 0\). These two sets of quasi-elliptical contours, and particularly, curve \(C_p\) (i.e., the quasi-ellipse above the \(x\) axis) indicates how the spherical ion atmosphere at equilibrium with its center located at the coordinate origin when \(\xi\) was equal to zero drifts away from the origin along the \(x\) axis and the spherical form is, at the same time, distorted to a non-spherical (quasi-elliptical) form with its center at \(x > 0\) as the external field strength increases—i.e., a nonequilibrium state. For example, in the present reduced variables employed, the equilibrium radius of the ion atmosphere \((\xi = 0)\) is \((1/\sqrt{2})\ \kappa^{-1} \simeq 0.7\kappa^{-1}\) with the center at the coordinate origin, but if \(\xi = 1\), not only the center of the quasi-ellipse has migrated to \(x \simeq 0.6\kappa^{-1}\) and the curve \(C_p\) is no longer spherical with
the major axis reduced to approximately $1.2\kappa^{-1} = 2(0.6\kappa^{-1})$ instead of $2(1/\sqrt{2})\kappa^{-1} \approx 1.4\kappa^{-1}$ in the case of $\xi = 0$. This trend persists with increasing $\xi$. This behavior is numerically examined in Fig. 7, where the position of the center $(x_c,0)$ of the quasi-ellipse is plotted against $\xi$. It gradually and significantly diminishes with increasing $\xi$ after having reached a maximum. Since this position $(x_c,0)$ is at the center of displaced ion atmosphere that is simultaneously distorted by the external field it is natural to choose $x$ in $f(x,r,\xi)$ with the $x$ coordinate of the center $x_c$ of the quasi-ellipse as the center of the ion atmosphere at $\xi$. Since the electrophoretic coefficient may be regarded as the force on the imaginary spherical ion atmosphere with its center at $(x_c,0)$, then it is reasonable to choose $r$ in $f(x,r,\xi)$ with $r = x_c$. With this choice of the $x$ and $r$ values in the electrophoretic factor $f(x,r,\xi)$ we have verified that the electrophoretic coefficient thus calculated invariably produces the correctly behaved equivalent ionic conductance over a wide range of the external field strength, provided that the relaxation time coefficient [see Eqs. (192) and (193) below] is calculated with the same set of $(x,r)$. Thus, in this manner we have been able to formulate a procedure based on computation result for selecting the position parameters $(x,r)$ in the electrophoretic and relaxation time factors and therewith the ionic conductance unambiguously. We now state this procedure as follows: The values of the coordinates $x$ and $r$ in the electrophoretic factor $f(x,r,\xi)$ are selected to be the $x$ coordinate of the center of the quasi-elliptic level curve $C_P$ and the corresponding value for $r$ of the imaginary spherical ion atmosphere $r_c = x_c$ centered at $(x_c,0)$. The relaxation time factor is similarly calculated. In retrospect, this procedure—which may be called a rule—seems natural since the center of the ion atmosphere drifts along the $x$ axis as $\xi$ increases and the electrophoretic coefficient must be reckoned with respect to the center of ion located at the $(x_c,0)$ of the spherical ion atmosphere of radius $x_c$, namely, $(1/\sqrt{2})\kappa^{-1}$ in the actual units, which means $r_c = x_c$.

With this identification of the coordinate parameters $(x,r)$ in the electrophoretic and relaxation time factors the electrophoretic and relaxation time coefficients are rendered unambiguous and unique. They are also divergence-free because the center of the displaced and distorted ion atmosphere does not occur at the coordinate origin for all values of $\xi$ and the OW theory becomes free from the divergence difficulty inherent to Wilson’s procedure of selecting $x = r = 0$.

5. **Comparison with Wilson’s Result for the Electrophoretic Coefficient**

Having defined the electrophoretic factor based on the full formula (149) for the axial velocity obtained from the Stokes equation, we investigate how Wilson’s result for the electrophoretic coefficient can be recovered. He observed that since the ion of interest in conductance experiment
is the center ion of the ion atmosphere, which is located at the coordinate origin, the axial velocity must be considered at \( x = r = 0 \). He then noticed that the Fourier transform integrals comprising the axial velocity could be analytically evaluated at \( x = r = 0 \), because in the Bessel function \( K_0(z) \) represented in power series as

\[
K_0(z) = -\left[ \ln \left( \frac{1}{2} z \right) + \gamma \right] \sum_{k=0}^{\infty} \frac{(\frac{1}{2})^{2k}}{(k!)^2} z^{2k} + \frac{z^2}{2^2 (1!)^2} + \frac{(1 + \frac{1}{2} + \frac{1}{2}) z^4}{2^4 (2!)^2} + \cdots ,
\]

where \( \gamma \) is Euler’s constant, if \( x = r = 0 \), only the leading term of \( K_0(z) \) contributes. Therefore, at \( x = r = 0 \) Formula (129) for the axial velocity can be written as a sum of simple integrals

\[
\hat{v}_x(0, 0; \xi) = -\frac{1}{2} \int_{0}^{\infty} dt \frac{1}{(1 - 2\xi^2 t^2)} \times \left[ \omega_1^2 \ln \left( \frac{2\omega_1}{t} \right) + \omega_2^2 \ln \left( \frac{2\omega_2}{t} \right) - 2 \left( 1 - R^2 \right) \omega_3^2 \ln \left( \frac{2\omega_3}{t} \right) \right] + \int_{0}^{\infty} dt \frac{1}{2},
\]

(153)

The logarithmic integrals can be exactly evaluated by means of contour integrations by using contours similar to Figs. 10–12 in Appendix A. (Note, however, his contours used are not exactly the same as Figs. 10–12 we have employed in Appendix A except for the locations of simple poles and branch cuts.) With so evaluated integrals and the electrophoretic coefficient defined by the relation

\[
v_x(0, 0; \xi) = -\frac{zeX \kappa}{6\sqrt{2\pi} \eta_0} f(\xi),
\]

(154)

the electrophoretic coefficient \( f(\xi) \) could be shown given by the expression

\[
f(\xi) = 1 + \frac{3}{4\sqrt{2\xi^3}} \left\{ 2\xi^2 \sinh^{-1} \xi + \sqrt{2\xi - \xi \sqrt{1 + \xi^2}} \right.
\]

\[
- (1 + 2\xi^2) \tan^{-1} \left( 2\sqrt{\xi} \right) + (1 + 2\xi^2) \tan^{-1} \left( \frac{\xi}{\sqrt{1 + \xi^2}} \right) \left\},
\]

(155)

provided that the last integral in Eq. (153) is ignored. For this formula for \( f(\xi) \) we have used the identities:

\[
\frac{1}{2} \tan^{-1} \left( 2\xi \sqrt{1 + \xi^2} \right) = \tan^{-1} \left( \xi / \sqrt{1 + \xi^2} \right) ; \quad \sinh^{-1} \left( 2\xi \sqrt{1 + \xi^2} \right) = 2 \sinh^{-1} \xi.
\]

As a matter of fact, for the last integral in Eq. (153) for \( \hat{v}_x(0, 0; \xi) \) Wilson argued that the integral of \( \frac{1}{2} \) contributes nothing to the electrophoretic coefficient because its contour integral vanishes. This argument is fallacious because although the contour integral in question certainly vanishes, it is composed of two integrals which are manifestly infinite, but opposite in sign:

\[
\int_{C} \frac{1}{2} dz = \int_{-\infty}^{\infty} \frac{1}{2} dx + \int_{C_{\infty}} \frac{1}{2} dz = 0,
\]

(156)
As a matter of fact, according to the analysis leading to Eq. (149) the last integral in Eq. (153) originates from the integral \( K_5 \), which we have already evaluated analytically for all values of \( x \) and \( r \), and it is equal to zero at \( r = 0 \) only if \( x \neq 0 \), as is obvious from the following consideration:

\[
K_5 = \frac{\pi r}{2 (x^2 + r^2)^{3/2}} = \begin{cases} 
0 & \text{as } r \to 0, \ x \neq 0 \\
\frac{\pi}{2r} & \text{for } x \to 0, \ r \neq 0 
\end{cases}.
\] (157)

However, if \( x \) and \( r \) simultaneously tend to 0 at the same rate, \( K_5 \) is manifestly divergent. Therefore rigorously speaking, Wilson’s electrophoretic coefficient cannot be defined upon evaluation of \( v_x (0, 0; \xi) \) with preset values of \( x = r = 0 \) unless we simply abandon the divergent term. It now appears that his procedure of setting \( x = r = 0 \) in the velocity integrals before evaluating the integrals is the cause for the divergence difficulty to obtain a finite electrophoretic coefficient, or the position \( x = r = 0 \) should not have been taken in the electrophoretic coefficient defined through the thermodynamic force–flux relation for mobility or the Stokes law. This divergence difficulty and our desire to obtain physically sensible mobility coefficient was the principal motivation that we have evaluated and examined the velocity profiles in the \((x, r)\) plane to understand how the velocity varies in space and to find out what would be the most probable or reasonable velocity that should be used to calculate ionic conductance if the Wilson–Onsager theory of conduction is adopted as the theory to rely on. We believe that OW theory is a correct approach to the ionic conduction problem, but the solutions must be evaluated more carefully for a wider range of \((x, r)\), because the ion atmosphere, and therefore its center, migrates under the influence of an external field.

We now would like to show in what manner the Wilson formula for \( f (\xi) \) would emerge from Eq. (151). First of all, the potentially divergent mechanical contribution \( (\tilde{v}_x)_{\text{me}} \) should be ignored to obtain a finite numerical value for \( f(x, r; \xi) \) at \( x = r = 0 \), although neglecting \( (\tilde{v}_x)_{\text{me}} \) would result in a significant error to the axial velocity, and integrals \( \mathcal{C}_1 (x, r, \xi), \ldots, \mathcal{S}_2 (x, r, \xi) \) should be approximated as follows. First, let the Brownian motion contributions be denoted by

\[
\tilde{v}_{\text{Brown}} (x, r, \xi) = \mathcal{C}_1 (x, r, \xi) + 2\mathcal{C}_2 (x, r, \xi) - \mathcal{S}_1 (x, r, \xi) - 2\mathcal{S}_2 (x, r, \xi) .
\]

Then if the Bessel functions \( I_0(z) \) in the integrals for \( \mathcal{C}_1 (x, r, \xi) \), etc. are expanded in series

\[
I_0(z) = \sum_{k=0}^{\infty} \frac{(\frac{1}{4}z^2)^k}{k!\Gamma(k+1)}, \quad \text{(158a)}
\]

they can be evaluated analytically in closed form (at least, for quite a few leading order terms) at \( x = 0 \). Especially, at \( x = 0 \) the zeroth-order term, namely, the \( k = 0 \) term in Eq. \( (158a) \), gives rise
to exactly the same \( f(\xi) \) as in Wilson’s, Eq. (155):

\[
\hat{v}_{\text{Brown}}(0, 0, \xi) = -\frac{zeX\kappa}{6\sqrt{2\pi\eta_0}} f_{\text{Brown}}(\xi),
\]

(159)

where \( f_{\text{Brown}}(\xi) \) is then given by the expression

\[
f_{\text{Brown}}(\xi) = \frac{3}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{1}{1 + 2\xi^2 y^2} \left( 1 - y^2 + \sqrt{1 + 2\xi^2 y^2} \right) + 3 \int_0^1 dy \frac{2\xi^2 y^2 (1 - y^2)}{1 + 2\xi^2 y^2} - \frac{3}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{\sqrt{2}\xi y \left( 1 - y^2 + \sqrt{1 + 2\xi^2 y^2} \right)}{(1 + 2\xi^2 y^2) \left( 1 + \sqrt{1 + 2\xi^2 y^2} \right)} - 3 \int_0^1 dy \frac{\sqrt{2}\xi y (1 - y^2)}{1 + 2\xi^2 y^2},
\]

(160)

which can be shown identical with \( f(\xi) \) in Eq. (155). This process of arriving at \( f(\xi) \) from \( f(x, r; \xi) \), as a matter of fact, indicates that the electrophoretic coefficient \( f(\xi) \) obtained by Wilson [25] must be regarded as an approximation to the more precisely defined exact electrophoretic factor (or mobility coefficient) \( f(x, r; \xi) \) through the mobility [35] of ions on the basis of the irreversible thermodynamic force–flux relation between the external electric field and flow velocity. Recall that for \( f(\xi) \) it is necessary to leave out \((\hat{v}_x)_{\text{me}}\) from the axial velocity \( v_x(x, r, \xi) \) in Eq. (149). It is of course necessary also to leave out the field independent term—the first term on the right in Eq. (149)—for both \( f(\xi) \) and \( f(x, r; \xi) \) because the term has nothing to do with the mobility of ions in the external electric field.

The axial velocity profiles presented in Eq. (149) arise from the presence of ion atmosphere and its interaction with the center ion itself and the external electric field. We must recognize that dynamics of ions in a solution and their interactions with the external field is not like that of an isolated single ion in the external field. Moreover, the center ion of the ion atmosphere does not directly contribute to the ionic conduction because of the countercurrent of the medium produced by the ion atmosphere, and the electrophoretic coefficient must be appropriately calculated taking this fact and the interaction of ion atmosphere with the external field into account. Therefore the position coordinate values should be taken with those of a point other than the coordinate origin, preferably, exterior to the curve \( C_p \), to calculate the electrophoretic coefficient because the center ion of the ion atmosphere moves with \( \xi \) increasing; see Fig. 6 and the rule for choosing \((x, r)\) in \( f(x, r; \xi) \) proposed. In this regard, recall that \( f(x, r; \xi) = 0 \) on \( C_p \).

D. Fourier Transform Solution for the Transversal Velocity

By using the relation

\[
(\nabla \times \nabla \times \mathbf{a})_\rho = \nabla_\rho (\text{div} \mathbf{a}) - \nabla^2 a_\rho = \nabla_\rho (\text{div} \mathbf{a})
\]

(161)
in the case of \( a_\rho = a_\theta = 0 \) we find the transversal velocity component in the form

\[
\hat{v}_\rho(x, r, \xi) = \frac{\xi}{2\sqrt{2}} J_c^B - \frac{1}{2} J_s^{B} - \frac{1}{\sqrt{2} \xi} J_4^c + J_4^s - \frac{1}{2} r J_5^s,
\]

where \( \hat{v}_\rho(x, r, \xi) \) is the reduced transversal velocity defined by Eq. (\ref{eq:128}),

\[
J_c^B = \int_0^\infty dt \frac{\cos (tx)}{(1 - 2\xi^2 t^2)} \left[ \frac{t^2 \omega_1 K_1(\omega_1 r)}{1 + \sqrt{1 - 2\xi^2 t^2}} + \frac{2t^2 \omega_1 K_1(\omega_2 r)}{1 - \sqrt{1 - 2\xi^2 t^2}} - 2t^2 \omega_3 K_1(\omega_3 r) \right],
\]

\[
J_s^B = \int_0^\infty dt \frac{\sin (tx)}{(1 - 2\xi^2 t^2)} [t\omega_1 K_1(\omega_1 r) + t\omega_2 K_1(\omega_2 r) - 4\xi^2 t^3 \omega_3 K_1(\omega_3 r)],
\]

The integrals \( J_4^c, J_4^s, \) and \( J_5^s \) are analytically evaluated by using the integral representations of the Bessel functions in the same manner as for \( K_4^c, K_4^s, \) and \( K_5^s \):

\[
J_4^c = \int_0^\infty dt \cos (tx) t K_1(tr),
\]

\[
J_4^s = \int_0^\infty dt \sin (tx) t^2 K_1(rt),
\]

\[
J_5^s = \int_0^\infty dt \sin (tx) t K_0(rt).
\]

The integrals \( J_c^B \) and \( J_s^B \) can be evaluated by using the contour integration methods similarly for the integrals \( K_c^B \) and \( K_s^B \). Jordan’s lemma gives rise to the same conditions as Inequalities (\ref{eq:148}). In the region outside the validity of Ineq. (\ref{eq:148}) the method of principal value integration is numerically employed.

In summary, we obtain the transversal velocity component \( v_\rho(x, r, \xi) \) in the form

\[
v_\rho(x, r, \xi) = -\frac{\kappa^2 k_B T}{8\pi \eta_0} \frac{r}{(x^2 + r^2)^{3/2}}
\]

\[
- \frac{\kappa z e X}{4\sqrt{2}\pi \eta_0} \left[ \frac{r}{2(x^2 + r^2)^{3/2}} + \frac{3x(x^4 - x^2 r^2 - r^4)}{r^3(x^2 + r^2)^{5/2}} \right] + \frac{\kappa z e X}{8\sqrt{2}\pi \eta_0} \left[ |\mathcal{C}_3(x, r, \xi) + \mathcal{S}_3(x, r, \xi) + 4\mathcal{C}_4(x, r, \xi) - 4\mathcal{S}_4(x, r, \xi)| \right],
\]
where

\[ C_3(x,r,\xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{y\sqrt{1-y^2 + \sqrt{1+2\xi^2y^2}}}{(1+2\xi^2y^2)} e^{-xy} I_1(\omega_1 r), \]  
(172)

\[ C_4(x,r,\xi) = \int_0^{1} dy \frac{\xi^2y^3\sqrt{1-y^2}}{1+2\xi^2y^2} e^{-xy} I_1(\omega_3 r), \]  
(173)

\[ G_3(x,r,\xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{\xi y^2\sqrt{1-y^2 + \sqrt{1+2\xi^2y^2}}}{\sqrt{2}(1+2\xi^2y^2)} e^{-xy} I_1(\omega_1 r), \]  
(174)

\[ G_4(x,r,\xi) = \int_0^{1} dy \frac{\sqrt{2\xi^3}y^2\sqrt{1-y^2}}{1+2\xi^2y^2} e^{-xy} I_1(\omega_3 r). \]  
(175)

These integrals can be analytically evaluated term by term by using the series expansion of the Bessel function \( I_1(z) \) or numerically by a fairly straightforward procedure. The profiles of \( v_\rho(x,r,\xi) \) look quite similar to those of the axial velocity \( v_x(x,r,\xi) \) in Figs. 4–6.

E. Fourier Transform Solution for Pressure

Since for the present system the (nonequilibrium) pressure is given by

\[ p = p_0 + \eta_0 \nabla^2 \left( \frac{\partial a_x}{\partial x} \right), \]  
(176)

it is easy to calculate it from Eq. (125):

\[ p - p_0 = \frac{zeX}{4\pi^2} \int_0^\infty d\alpha \frac{\sin(\alpha x)}{2R^2} \left[ (1+R) K_0(\lambda_1 \rho) + (1-R) K_0(\lambda_2 \rho) - 2(1-R^2) K_0(\lambda_3 \rho) \right] \]

\[ - \frac{zeX}{4\pi^2} \int_0^\infty d\alpha \sin(\alpha x) K_0(\alpha \rho) \]

\[ - \frac{zeX}{4\pi^2} \xi \int_0^\infty d\alpha \frac{\alpha^2 \cos(\alpha x)}{R^2} \left[ K_0(\lambda_1 \rho) + K_0(\lambda_2 \rho) - 2K_0(\lambda_3 \rho) \right]. \]  
(177)

The formula presented above represents a nonequilibrium part of pressure \( \Delta p = p - p_0 \) consistent with the velocity components obtained as the solution of the Stokes equation for a fluid in an external electric field. It also can be decomposed into the mechanical and Brownian motion parts as for the axial and transversal velocity components. They can be evaluated by the same methods as for the axial velocity, for example. With the reduced nonequilibrium pressure \( \Delta \hat{p} \) defined by the formula

\[ \Delta \hat{p} = \Delta p \left( \frac{zeX\kappa^2}{4\pi^2} \right)^{-1} \]  
(178)
we obtain the nonequilibrium pressure profile in the form

\[ \Delta \hat{p} = -\frac{\pi x}{2(x^2 + r^2)^{3/2}} - \frac{\pi}{4} \int_0^{\sqrt{2}(1+\xi^2)} dy \frac{e^{-xy}y(1 + \sqrt{2}\xi y + \sqrt{1 + 2\xi^2}y^2)}{1 + 2\xi^2 y^2} I_0(\sqrt{2}y) + \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy}\sqrt{2}\xi y^2 (1 - \sqrt{2}\xi y)}{1 + 2\xi^2 y^2} I_0(\sqrt{2}y), \]  

(179)

This shows that \( \Delta \hat{p} \) is also singular at the origin of the coordinates. It is significant to observe that the nonequilibrium pressure \( \Delta p \) is generally negative, that is, there is a tension that becomes negative infinite at the origin. This implies that the nonequilibrium pressure is compressional in the neighborhood of the origin. Moreover, it is proportional to the field strength \( X \). It seems to be a remarkable result, probably deserving a deeper consideration, because the degree of compression can be manipulated by the applied external electric field strength. We will report on a further study of this nonequilibrium pressure separately elsewhere[37].

F. Ionic Field and Relaxation Time Effect

Just as the velocity is induced by the mean local body-force which in turn is produced by interaction of the ion atmosphere[17] with the external field, the local ionic force field is modified by a feedback process of correlations arising from the Coulomb potentials and their interaction with the external field. Thus we may express the total electric field \( X_t \) acting on the ion in the \( x \) direction as

\[ X_t = X + \Delta X, \]  

(180)

where the local contribution \( \Delta X \) is the ionic field produced by the interaction of the ion atmosphere with the external force field. If the potential of ion \( j \) in the electrolyte solution is denoted by \( \psi_j(r) \) the force arising from the potential \( \psi_j(r) \) is given by

\[ e_j \Delta X(r) = -\nabla \psi_j(r). \]  

(181)

Upon using the solution for \( \psi_j(r) \), Eq. [92], we obtain the mean local ionic force

\[ e_j \Delta X(r) = \frac{e_j^r \mu}{\pi D r^2} \int_0^\infty d\alpha \cos(\alpha x) \frac{\alpha}{R^2} [K_0(\lambda_1 \rho) + K_0(\lambda_2 \rho) - 2K_0(\lambda_3 \rho)] + \frac{e_j^r^2}{\pi D} \int_0^\infty d\alpha \frac{\sin(\alpha x)}{2R^2} [(1 + R) K_0(\lambda_1 \rho) + (1 - R) K_0(\lambda_2 \rho) - 2(1 - R^2) K_0(\lambda_3 \rho)] \]  

(182)
in the notation already defined. It should be noted that the formula for $e_j\Delta X (r)$ in Eq. (182) is an exact result, although formal. The external field dependence $\xi$ enters the theory in a nonlinear manner through the arguments of the Bessel functions. We have shown that the Fourier transforms such as those in Eq. (182) can be reduced to finite quadratures consisting of regular Bessel functions of zeroth order of second kind $I_0(z)$ weighted by some algebraic functions.

The integrals in the expression for $\Delta X (r)$ were also evaluated by Wilson in his dissertation[25] for the case of $x = r = 0$ in the same manner as for the electrophoretic coefficient $f(\xi)$, Eq. (155). With the so-obtained result the relaxation time coefficient $g(\xi)$ was defined by the relation

$$ze\Delta X (0,0;\xi) = -\frac{e_j\mu'\kappa}{2D}g(\xi) = -\frac{e_j\kappa^2\xi}{2D}g(\xi),$$

for which he obtained $g(\xi)$ in a simple analytic form

$$g(\xi) = \frac{1}{2\xi^3} \left[ \xi \sqrt{(1 + \xi^2)} - \tan^{-1}\left(\frac{\xi}{\sqrt{1 + \xi^2}}\right) - \sqrt{2}\xi + \tan^{-1}\left(\sqrt{2}\xi\right) \right].$$

It is a nonlinear but well-behaved function of the reduced field strength $\xi$; its limiting values are $g(0) = \frac{1}{6} (2 - \sqrt{2})$ as $\xi \to 0$ and $g(\infty) = 0$ as $\xi \to \infty$. We will show presently under what condition this result, Eq. (184), is recovered from the exact formula for $e_j\Delta X (r)$, Eq. (182).

To obtain a complete formula for the local ionic field from Eq. (182) the Fourier transform integrals therein must be calculated without setting $x = r = 0$ before evaluating them. For this purpose we use the same contour integration methods described in Appendix A as for the velocity formulas. We thereby obtain $e_j\Delta X (r)$ in the form

$$e_j\Delta X (r) = -\frac{e_j\kappa^2}{2\sqrt{2}D} \left[ \int_0^{\sqrt{2}(1+\xi^2)} dy \frac{e^{-xy}y^2I_0(\omega_1 r)}{1 + 2\xi^2y^2} - 2 \int_0^{\sqrt{2}(1+\xi^2)} dy \frac{e^{-xy}y^2I_0(\omega_3 r)}{1 + 2\xi^2y^2} \right]$$

$$- \frac{e_j^2\kappa^2}{4D} \left[ \int_0^{\sqrt{2}(1+\xi^2)} dy \frac{e^{-xy}y(1 + \sqrt{1 + 2\xi^2y^2})I_0(\omega_1 r)}{1 + 2\xi^2y^2} \right]$$

$$+ 4\xi^2 \int_0^{\sqrt{2}(1+\xi^2)} dy \frac{e^{-xy}I_0(\omega_3 r)}{1 + 2\xi^2y^2},$$

The variables $x$ and $r$ as well as $\xi$ and $y$ appearing in the integrals in Eq. (185) are dimensionless reduced variables defined earlier. The integrals in Eq. (185), of course, are subject to conditions deduced from conditions (148) related to the Jordan lemma[30] for the contour integrals. Exterior to the region of $(x,r)$ satisfying Conditions (148) the method of principal values for singular integrals is used to numerically compute the Fourier transform integrals.

The first group of terms in Eq. (185) descends from the cosine transform terms in Eq. (185) whereas the second group originates from the sine transform terms. If $x$ and $r$ are set equal to
zero in Eq. (185) the first group exactly gives rise to Wilson’s result, Eq. (184), but the integrals in the second group do not vanish even if \( x = r = 0 \) is taken after their evaluation, but give rise to a field-independent term \(-e_j\kappa^2/2D\) in the limits of \( x \to 0 \) and \( r \to 0 \), in addition to \( \xi \)-dependent terms as shown below. However, if we took \( x = 0 \) in the sine transform integrals in Eq. (182) there would have been no contribution from it at all. This example, once again, manifestly demonstrates a need for caution to take in evaluating the Fourier transforms, especially, with regard to setting \( x = r = 0 \): We reiterate that the values obtained of the integrals are different, depending on whether particular parameter values, especially, \( x = r = 0 \), are taken before or after evaluation of the integrals, or even depending on the order of taking the limits \( x \to 0 \) and \( r \to 0 \); we have seen a similar situation in the previous section for velocity profiles. The fact that \( x \) and \( r \) must be set equal to zero to obtain Wilson’s formula for \( g(\xi) \) also suggests that his formula is an approximation to the full relaxation time factor defined below, as is \( f(\xi) \) an approximation to the full \( f(x, r; \xi) \) given in Eq. (151).

To define the appropriate relaxation time factor we split \( e_j \Delta X(r) \) in Eq. (185) into two parts

\[
e_j \Delta X(r) = -e_j\kappa^2/2D g_c(x, r; \xi) - e_j^2\kappa^2/2D g_s(x, r; \xi)
\]  

(186)

with the definitions

\[
g_c(x, r; \xi) = \frac{1}{\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy}y^2 I_0(\sqrt{2}r)}{1 + 2\xi^2 y^2} - \frac{1}{\sqrt{2}} \int_0^1 dy \frac{e^{-xy}y^2 I_0(\sqrt{3}r)}{1 + 2\xi^2 y^2},  
\]

(187)

\[
g_s(x, r; \xi) = \frac{1}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy}y \left(1 + \sqrt{1 + 2\xi^2 y^2}\right) I_0(\sqrt{2}r)}{1 + 2\xi^2 y^2}  
+ 2\xi^2 \int_0^1 dy \frac{y^3 e^{-xy} I_0(\sqrt{3}r)}{1 + 2\xi^2 y^2}.  
\]

(188)

The reason for the splitting made above is that the term \( g_s(x, r; \xi) \) tends to a value independent of \( \xi \) as \( \xi \to 0 \):

\[
g_s(x, r; 0) = \int_0^{\sqrt{2}} dy e^{-xy} I_0 \left( r\sqrt{2 - y^2} \right) \neq 0,  
\]

(189)

which contributes a field-independent term to \( e_j \Delta X(r) \):

\[
- e_j^2\kappa^2/2D \int_0^{\sqrt{2}} dy e^{-xy} I_0 \left( r\sqrt{2 - y^2} \right)  
\]

(190)

and this contribution would have nothing to do with the relaxation of ion atmosphere. Therefore
it is useful to define the field-dependent part of $g_\kappa(x, r; \xi)$ by the expression

$$\Delta g_\kappa(x, r; \xi) = \frac{1}{\xi} \left[ \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{y^2}{1+2\xi^2y^2} - \sqrt{2} \int_0^1 dy \frac{y^2}{1+2\xi^2y^2} \right] + 2\xi \int_0^1 dy \frac{y^3}{1+2\xi^2y^2}. \quad (191)$$

With this we are now able to cast $e_j \Delta X(r)$ into a more appropriate form

$$e_j \Delta X(r) = -\frac{e_j^2 \kappa^2}{2D} g_\kappa(x, r; 0) - \frac{e_j \xi \kappa^2}{2D} g_\kappa(x, r; \xi), \quad (192)$$

where the relaxation time factor $g_\kappa(x, r; \xi)$ in the cylindrical coordinate representation is defined by the formula

$$g_\kappa(x, r; \xi) = g_c(x, r; \xi) + \Delta g_\kappa(x, r; \xi). \quad (193)$$

It is easily verifiable that $\Delta g_\kappa(x, r; \xi)$ is indeed a constant in the limit of $\xi = 0$ and hence $\xi \Delta g_\kappa(x, r; \xi)$ vanishes as $\xi \to 0$. With this definition of relaxation time factor $g_\kappa(x, r; \xi)$, we are now ready to examine its relation to Wilson’s $g(\xi)$ formula.

If both $x$ and $r$ are set equal to zero in integrals in Eqs. (187), (190), and (191), it follows

$$g_c(0, 0; \xi) = \frac{1}{\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{y^2}{1+2\xi^2y^2} - \sqrt{2} \int_0^1 dy \frac{y^2}{1+2\xi^2y^2} = \frac{1}{4\xi^3} \left( 2\xi \sqrt{\xi^2 + 1} - \arctan 2\xi \sqrt{\xi^2 + 1} - 2\sqrt{2}\xi + 2\arctan \sqrt{2}\xi \right), \quad (194)$$

$$\Delta g_\kappa(0, 0; \xi) = \frac{1}{2\xi} \left( \int_0^{\sqrt{2(1+\xi^2)}} dy \left( \frac{1 + \sqrt{1+2\xi^2y^2}}{1+2\xi^2y^2} - 2 \right) + 2\xi \int_0^1 dy \frac{y^3}{1+2\xi^2y^2} \right)$$

$$= \frac{1}{4\xi^3} \left[ \left\{ \ln(2\xi^2 + 1) + (2\xi^2 + 1) - 1 \right\} - 4\xi^2 \right] + \frac{1}{4\xi^3} \left[ 2\xi^2 - \ln(2\xi^2 + 1) \right]$$

$$= 0, \quad (195)$$

$$g_\kappa(0, 0; 0) = 1. \quad (196)$$

Here $g_c(0, 0; \xi)$ is identical with Formula $g(\xi)$ in Eq. (184) for the relaxation time coefficient in Wilson’s method, whereas $\Delta g_\kappa(0, 0; \xi)$ together with $g_\kappa(0, 0; 0)$ represents extra terms not present in his result. We reiterate that in Wilson’s method $g_\kappa(0, 0; \xi)$ does not appear because the sin($\alpha x$) term in the sine transform integral vanishes if $x$ is set equal to zero before evaluating the sine transform integral. This shows under what condition Wilson’s $g(\xi)$ is recoverable from the present result for $g_\kappa(x, r; \xi)$. 42
In Fig. 8, \( g(x, r; \xi) \) computed, for example, at \( x = 0.5 \) and \( r = 0.5 \) is plotted as a function of the field strength \( \xi \) and compared with Wilson’s relaxation time coefficient \( g(\xi) \) in Eq. (184), the dotted curve. To better comprehend the profile of the ionic field graphically, we plot a 3D example of \( g(x, r; \xi) \) in the case of \( \xi = 1 \) in Fig. 9. A combination of formulas (193)–(196) and the method of principal values for integration is used to compute the relaxation time factor \( g(x, r; \xi) \) presented in Fig. 9. As does the electrophoretic factor, it also exhibits a singular behavior near the origin, although the details are different from the behavior of \( f(x, r; \xi) \) in Fig. 5. It also vanishes as \( x \) and \( r \) increase to infinity.

We give a short summary of this long section: The results of evaluation of \( v_x(x, r, \xi), v_\rho(x, r, \xi), \) and \( \Delta p(x, r, \xi) \) for all values of \( x \) and \( r \) and the related electrophoretic and relaxation time factors constitute some of the important contributions of this work to the hydrodynamics of strong binary electrolyte solutions in the external electric field. On extensively studying the velocity profiles we have been able to formulate a rule for selecting the position variable \((x, r)\) in the electrophoretic and relaxation time coefficients, which are finite everywhere. By using this rule and the profiles of velocities and nonequilibrium pressure as well as the distribution functions and mean potentials calculated, we will also be able to predict or deduce, in a well-defined manner, hydrodynamic consequences to transport properties, such as conductivity, and related nonequilibrium properties of ionic motions in the medium in an external electric field of arbitrary strength.

V. DISCUSSION AND CONCLUDING REMARKS

In this paper, we have shown that since ions interact with each other through long-range Coulombic interactions, ion atmosphere with ions, and both of them with the external electric field, the correlations of particles in the ionic liquids are quite complex and the whole body of an ionic solution collectively and cooperatively moves subjected to the external electric field. Consequently, even at a dilute ionic concentration the macroscopic behavior of electrolyte solutions under an external electric field is not simple, but rather complex and, therefore, exhibits an interesting feedback system. In this regard, the subject matter is interesting from not only the theoretical, but also practical standpoint to gain insights into the behavior of complex liquids. For this reason, we believe the ideas of the OW theory as a theory designed to treat ionic fluid systems in the external field are worth studying in depth for the insights they provide for dynamical theories of ionic matter in general. However, examining in detail the solutions of the Stokes equation for flow velocity obtained from the solutions of the governing equations in the OW theory, we find that
the velocity formula not only had a divergence difficulty that we have unexpectedly encountered while studying it, but also was incompletely treated mathematically in Wilson’s work\textsuperscript{25} because only the behavior of the center ion at the coordinate origin was examined despite the fact that the ion atmosphere moves in the external electric field and develops a non-simple spatial structure. Therefore, we felt that there still remained the task of fully implementing the theory in a mathematically satisfactory manner to make it serve as a complete theory of ion conductivity in the nonlinear regime of external field dependence.

To achieve the goal in mind, we have numerically studied the velocity profiles in the configuration space over a range of external field strength and, in particular, the movement and distortion of the ion atmosphere, as the external electric field strength is continuously varied over a wide range. Thereby we have numerically quantified the trajectory of the center ion of the ion atmosphere with respect to $\xi$, but also studied the manner of its distortion from a spherical form to a quasi-elliptical form, as the field strength $\xi$ is varied. The general picture we obtain of the electrophoretic factor $f(x, r; \xi)$ is as follows: within curve $C_P$ it is negative whereas outside $C_P$ it is positive. Moreover, $C_P$ is non-spherical. This implies that the ion atmosphere not only polarizes into a negative and a positive domain (typical of a dipolar distribution), but also the boundary curve (i.e., $C_P$) gets distorted to a quasi-ellipse from a spherically symmetric form, as $\xi$ increases from zero. On the basis of the body of numerical studies of the axial velocity profiles we have been able to formulate a procedure by which it is sufficient to calculate the center position of the moving ion atmosphere at every value of $\xi$ and therewith calculate the electrophoretic and relaxation time coefficients as functions of $\xi$.

The identified procedure is that: the electrophoretic coefficient at a value of $\xi$ is given by the electrophoretic factor $f(x, r; \xi)$ evaluated at the center of the displaced spherical ion atmosphere of radius $x_c$, whose center is located at $(x, r) = (x_c, 0)$, the center of the displaced quasi-elliptic curve $C_P$ that is the locus of $f(x, r; \xi) = 0$. Since the spherical ion atmosphere with its center at $(x_c, 0)$ has a radius $x_c$, the value of $r_c$ must be equal to $x_c$. Therefore the electrophoretic coefficient $f(\xi)$ is given by $f(\xi) \equiv f(x_c, r_c; \xi) = f(x_c, x_c; \xi)$ according to this finding. Since the center position of quasi-elliptic curve $C_P$ is unique for every $\xi$, the electrophoretic coefficient $f(\xi)$ defined is unique. The relaxation time coefficient $g(\xi)$ is then calculated by $g(\xi) \equiv g(x_c, r_c; \xi) = g(x_c, x_c; \xi)$ to be consistent with the electrophoretic coefficient defined.

This behavior (trajectory) of the center of ion atmosphere gives rise to non-divergent electrophoretic coefficients for all field strengths and hence the ionic conductance based on the Fokker–Planck equations employed is now rendered divergence-free. This is made possible by recognizing
that the electrophoretic coefficient must be calculated for the moving ionic atmosphere with the center of the displaced ion atmosphere at \((x_c, 0)\) when the external electric field is applied to the system.

The set of values for \(x\) and \(r\) obtained to use for \(f(x, r; \xi)\) and \(g(x, r; \xi)\) is \((x_c, r_c) = (x_c, x_c)\) which is in significant contrast to the values \(x = r = 0\) taken by Wilson to evaluate the integrals that gives rise to a divergence difficulty. In the companion paper [31], we apply this identification of \(x\) and \(r\) to compute the electrophoretic and relaxation time coefficients, and calculate therewith the equivalent ionic conductance and, in particular, the Wien effect of a binary electrolyte solution in comparison with experimental data available.

The velocity profiles graphically presented also suggest a skin effect by which the mobility of ions in solution is predominantly contributed by ions outside the curve \(C_P\). We have not suspected the existence of this effect before: that the conduction currents are mostly carried by ions in the periphery—i.e., in the shells of radius of \(O(\kappa^{-1})\)—of ion atmosphere, but not by the center ions, as is obvious from Fig. 4–Fig. 6.

The another important mathematical question we are answering in the present work is that variable parameters, such as \(x\), \(r\), and \(\xi\), in the Fourier transform solutions of the OF equations, Poisson equations, and Stokes equation should not be set equal to zero before fully evaluating them, since the results so obtained do not generally yield the same results as those obtained by setting them equal to zero after their complete evaluation. They would give identical results only if the results of the integrals are analytic everywhere in the space of \(x\), \(r\), and \(\xi\), but the examples we have studied definitely show that the evaluated results are not necessarily analytic everywhere in the aforementioned space, and as a consequence the results of evaluations by the aforementioned two different modes can be significantly different; that is, the results are not uniformly convergent to the same conclusion. This should be regarded as a significant point of the present analysis to keep in mind in the study of this line of theories for ionic solutions.

What we have shown in this work are the exact velocity and pressure profiles in space in a Brownian motion model, which we may apply to study other irreversible phenomena in the binary electrolyte solutions in the electric field than the Wien effect. Being full exact solutions without an approximation within the framework of the Brownian motion model, not only do they, at least in the low density regime, promise to provide a more complete picture of conduction phenomena, but also the insights gained therefrom should also help us develop theories of related transport phenomena in systems of current interest in science and engineering, such as plasmas [3, 38], semiconductors [4, 5, 39], small systems [40], etc. in electromagnetic fields. In any case, they repre-
sent new results in the subject field. In the sequels, we will also study asymmetric electrolyte solutions, in which charges of the cation and anion are not symmetric, and ionic conductance under an external electric field. Although more complicated than the present symmetric binary electrolyte solutions, we find that a similar mathematical analysis is possible to obtain for them. The results of the mathematical solutions will be reported in the near future, together with their numerical results in comparison with experimental data.

Acknowledgment

The present work has been supported in part by the Discovery grants from the Natural Sciences and Engineering Research Council of Canada.

Appendix A: Contour Integration Method

Some of the integrals in the formulas for the distribution functions, potentials, velocities, and pressure can be evaluated by applying the method of contour integration which yields formulas more readily amenable to analysis and further approximations giving rise to simple results which will make them possible to use for the purpose of assessing the existing results on the subject matter.

1. Axial Velocity

We consider the axial velocity first for the reason that it contains more experimentally direct features than the nonequilibrium structure and potentials. The integrals appearing in the formal Fourier transform solutions in the present theory all involve the Bessel functions $K_0(\lambda_l \rho)$ ($l = 1, 2, 3$) of argument $\lambda_l \rho$ with $\lambda_l$ being relatively complicated functions of the integration variable, the wave number; see Eq. (87) and Eq. (88) and also Eq. (89) for $\omega_l$. In reduced variables we have defined for the analysis they have the mathematical properties listed below.

(1) The zeros of the arguments of the Bessel function $K_\nu(\omega_l r)$ for $r \neq 0$ are found to be:

\[
\begin{align*}
t &= \pm i \sqrt{2 (1 + \xi^2)} & \text{for } \omega_1, \\
t &= 0 & \text{for } \omega_2, \\
t &= \pm i \frac{\kappa}{\sqrt{2}} & \text{for } \omega_3.
\end{align*}
\]

(A1)

(A2)

(A3)

The argument of $K_\nu(\omega_1 r)$ therefore has branch points at $tr = \pm i \sqrt{2 (1 + \xi^2)} r$, whereas the argument of $K_\nu(\omega_2 r)$ has branch points at $tr = 0 \times r$ and $-\infty \times r$ and the argument of
\( K_{\nu}(\omega_3 r) \) branch points at \( tr = \pm ir \).

Thus we may insert a branch cut on the imaginary axis of complex \( t \) plane between \( t = i \sqrt{2(1 + \xi^2)} \) and \( t = -i \sqrt{2(1 + \xi^2)} \) for the integral of \( K_{\nu}(\omega_1 r) \), while a branch cut may be inserted along the negative real axis for the integral of \( K_{\nu}(\omega_2 r) \), and on the imaginary axis between \( t = i \) and \( t = -i \) for the integral of \( K_{\nu}(\omega_3 r) \), respectively. See Figs 11–13 below.

(2) We recall that Bessel function \( K_{\nu}(z) \) of complex variable \( z \) is regular in \( z \) plane cut along the negative real axis\([32, 33]\). That is, it is a multi-valued function in the cut plane. Therefore, in the present case, \( K_0(\omega_1 r) \) changes discontinuously as the branch cut \( [-ir \sqrt{2(1 + \xi^2)}, ir \sqrt{2(1 + \xi^2)}] \) is crossed (\( r \) is a fixed parameter), whereas \( K_{\nu}(\omega_2 r) \) changes discontinuously as the negative real axis is crossed, and \( K_{\nu}(\omega_3 r) \) changes discontinuously as the branch cut \( [-ir, ir] \) is crossed on the imaginary axis of \( t \) plane. Note that the Bessel functions \( K_{\nu}(\omega_2 r) \) and \( K_{\nu}(tr) \) are defined in \( t \) plane cut along the negative real axis.

(3) We also observe that all the integrands of the singular integrals, for example, in \( K^B_c \) and \( K^B_s \) in Eqs. \(131 \) and \(132 \) are even with respect to \( t \).

(4) Moreover, for \( 0 < \arg t < \pi \) we find

\[
-\left( \frac{\pi}{2} - \delta \right) < \arg \omega_l < \left( \frac{\pi}{2} - \delta \right) \quad \left( \frac{\pi}{2} > \delta > 0; \ l = 1, 2, 3 \right). \tag{A4}
\]

Therefore in the upper half of complex \( t \) plane

\[
\lim_{|t| \to \infty} K_{\nu}(\omega_l r) = \lim_{|t| \to \infty} \sqrt{\frac{\pi}{2\omega_l r}} e^{-\omega_l r} \to 0. \tag{A5}
\]

(5) Lastly, all the integrands in Eqs. \(131 \)–\(132 \) have simple poles on the real axis at

\[
t = \pm \frac{1}{\sqrt{2\xi}}. \tag{A6}
\]

There is also a branch cut between \( t = -\frac{1}{\sqrt{2\xi}} \) and \( t = \frac{1}{\sqrt{2\xi}} \) because of the \( (1 \pm R) \) factor in the integrals, but this particular branch cut associated with \( \sqrt{1 - 2\xi^2 t^2} \) does not play a role in the contour integrals considered in the present work, because the real axis is not crossed by the contours in performing integrations. Therefore we may ignore this particular branch cut.

All these properties (1)–(5) together suggest it is possible to evaluate the integrals by using methods of contour integration\([30]\) along the closed contours of a semicircle as depicted in Figs.
8–10. However, in this approach the results obtained would not cover the entire region of the upper positive quadrant of plane \((x, r)\). In the region outside the domain defined by the inequalities, Ineq. (148) the Fourier transform integrals must be computed numerically because it is the region where Jordan’s lemma\([30]\) is violated; that is, the contour integral along the circle \(C_\infty\) does not vanish. In the exterior region their numerical values are small and hence of no importance. The practical advantage of this kind of contour integration method of evaluation is to isolate out the major part of contributions to the integrals and discuss the connection with the existing results where possible and with experimental data. It would be convenient to decompose \(K^B_c\) and \(K^B_s\) into component integrals as follows:

\[
K^B_c(x, r, \xi) = K^c_1 + K^c_2 - 4\xi^2K^c_3, \tag{A7}
\]

\[
K^B_s(x, r, \xi) = K^s_1 + K^s_2 - 2K^s_3, \tag{A8}
\]

where \(K^c_l\) and \(K^s_l\) are in the order of their appearance in Eqs. (131) and (132).

Since methods of integration will be similar for the integrals involved in \(K^c_l\) and \(K^s_l\) \((l = 1, 2, 3)\) we will illustrate them with the examples of integrals in \(K^c_1\) and \(K^s_1\) in the following. The results for the rest of integrals can be similarly obtained.

\[a. \quad \text{Contour integrations of } K^c_1 \text{ and } K^s_1\]

As prototypes of contour integrals appearing in the axial velocity formula, integrals \(K^c_1\) and \(K^s_1\) are explicitly evaluated below; see Eq. (130)–Eq. (135). Integrals \(K^c_1\) and \(K^s_1\) both have simple poles at \(t = \pm (\sqrt{2}\xi)^{-1}\). There is a branch cut along the imaginary axis between \(t = -i\sqrt{2}(1 + \xi^2)\) and \(+i\sqrt{2}(1 + \xi^2)\) and also a branch cut on the real axis between \(t = -1/\sqrt{2}\xi\) and \(t = +1/\sqrt{2}\xi\), but the latter branch cut plays no role in integration since the path of integration stays above the cut. For this reason the latter branch cut is not shown in Figs. 11–13. For evaluation of both \(K^c_1\) and \(K^s_1\) the contour in Fig. 12 is used.

Consider the contour integral denoted by \(C_1 K^c_1\) along the contour \(C_1\) in complex plane \(z\) depicted in Fig. 9:

\[
C_1 K^c_1 \equiv \int_{C_1} dz e^{izz} \frac{\omega_1^2}{1 - 2\xi^2 z^2} K_0(\omega_1 r), \tag{A9}
\]

where

\[
\omega_1 = \left[1 + z^2 + \sqrt{1 - 2\xi^2 z^2}\right]^{1/2}. \tag{A10}
\]
Since there is no singularity enclosed by contour $C_1$, this contour integral $C_1K_1^c$ is clearly equal to zero. Integral $C_1K_1^c$ can be decomposed into integrals along the paths $C_-, C_+, C, C_\infty$, and along the real axis $t$ in $C_1$. We thus may write it as

$$C_1K_1^c = \int_{-\infty}^{\infty} dt \frac{(1 + t^2 + \sqrt{1 - 2\xi^2 t^2})}{1 - 2\xi^2 t^2} e^{ixt} K_0(\omega_1(t)r) + \int_{C_-} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z)r) + \int_{C_+} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z)r) + \int_{C} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z)r) + \int_{C_\infty} dz \frac{(1 + z^2 + \sqrt{1 - 2\xi^2 z^2})}{1 - 2\xi^2 z^2} e^{ixz} K_0(\omega_1(z)r) = 0.$$  \hspace{1cm} (A11)

The first integral on the right, the integral along the real axis, can be shown to be equal to $2K_1^c$:

$$\int_{-\infty}^{\infty} dt \frac{(1 + t^2 + \sqrt{1 - 2\xi^2 t^2})}{1 - 2\xi^2 t^2} e^{ixt} K_0(\omega_1(t)r) = 2 \int_{0}^{\infty} dt \cos(t\pi) \frac{\omega_1^2}{(1 - 2\xi^2 t^2)} K_0(\omega_1r) = 2K_1^c.$$  \hspace{1cm} (A12)

The remaining integrals along contours $C_-, C_+, C, C_\infty$ will be denoted by $C_-K_1^c$, $C_+K_1^c$, $CK_1^c$, $C_0K_1^c$, respectively. By the theorem of residues \[30\] the integral $C_-K_1^c$ gives $\pi i$ times the residue of $C_-K_1^c$ at $t = -1/\sqrt{2}\xi$:

$$C_-K_1^c = i\frac{\sqrt{2}\pi}{8\xi^3} (2\xi^2 + 1) e^{-ix/\sqrt{2}\xi} K_0(\varpi_1r),$$

where

$$\varpi = \sqrt{\frac{1 + 2\xi^2}{\sqrt{2}\xi}}.$$  \hspace{1cm} (A13)

Similarly, we obtain

$$C_+K_1^c = -\pi i\frac{\sqrt{2}}{8\xi^3} (2\xi^2 + 1) e^{ix/\sqrt{2}\xi} K_0(\varpi_1r).$$

Thus combining the results for $C_-K_1^c$ and $C_+K_1^c$, we obtain

$$C_-K_1^c + C_+K_1^c = \frac{\sqrt{2}\pi}{4\xi^3} \sin \left(\frac{x}{\sqrt{2}\xi}\right) K_0(\varpi r).$$  \hspace{1cm} (A13)
To transform the contour integral $CK^c_1$ around the branch cut along the imaginary axis we observe that if the phase of the argument of $K_0(\omega_1 r)$ on the right hand lip of the cut is chosen equal to zero, the phase of the argument on the left hand lip is $\pi i$, so that the argument has the form $e^{\pi i} \omega_1 r$ for the Bessel function on the left side of contour $C$. In this connection, it must be recalled that only the relative phase across the branch cut is of importance. When traced along $C$ from the left to the right side of the cut, the Bessel function must be continued from the left side of the cut to the right side by the following continuation formula \cite{32,33}

\[ K_0(e^{i\pi} z) = K_0(z) - \pi i I_0(z), \quad (A14) \]

where $I_0(z)$ is the regular solution for the second kind of the Bessel function of order 0; $K_0(z)$ is irregular in contrast to $I_0(z)$. The irregular Bessel function $K_\nu(z) (\nu \geq 0)$ diverges logarithmically as $z \to 0$, whereas in series representation the Bessel function $I_0(z)$ is regular and given by the formula \cite{32,33}

\[ I_0(z) = \sum_{m=0}^{\infty} \frac{(\frac{1}{2}z)^{2m}}{(m!)^2}. \quad (A15) \]

This function is finite at $z = 0$, but it behaves asymptotically as

\[ I_0(z) \sim (2\pi z)^{-1/2} e^{z} [1 + O(z^{-1})] \quad (|\arg z| < \frac{1}{2} \pi). \quad (A16) \]

Using formula (A14) and changing variable from $iy$ to $y$, we obtain the integral along contour $C$:

\[ CK^c_1 = \pi \int_{0}^{\infty} \frac{\sqrt{\frac{1+\xi^2}{1+2\xi^2 y^2}}}{1+2\xi^2 y^2} e^{-xy} \left(1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right) I_0(\omega_1 r), \quad (A17) \]

where

\[ \overline{\omega}_1 = \left[1 - y^2 + \sqrt{1 + 2\xi^2 y^2}\right]^{1/2}. \quad (A18) \]

If the series form for $I_0(z)$ in Eq. (A15) is used, $CK^c_1$ can be computed in terms of quadratures of elementary functions—in fact, incomplete Laplace transforms. It should be recalled that this integral (A17) is subject to the condition (148) for the relation of $x$ to $r$ that is deducible from the Jordan lemma \cite{30}. To satisfy this lemma the integrands of integrals in $K_0^B$ and $K_1^B$ must satisfy the condition

\[ x \text{Im} t + r \text{Re} \omega_k > 0 \quad (k = 1, 2, 3) \quad (A19) \]

for $x, r > 0$. Thus values of $x$ and $r$ in the $(x, r)$ are limited to the region satisfying this condition plane, assuring the contour integrals along the curve $C_\infty$ vanishes as $x$ and $r$ tend to infinity. In
the case of integral $K^c_1$ the condition implies the inequality
\[ x\sqrt{1 + \xi^2} > r, \] (A20)
which in fact assures that the integral vanishes as $x$ and $r$ tend to infinity. Outside this region the contour integration method is not applicable. Therefore, integral (A18) does not hold and the Fourier transform integral $K^c_1$ must be evaluated numerically. However, the numerical values of the integral in the exterior region gets diminishingly smaller as $x$ and $r$ increase to infinity. The contour integral along the outer semicircle $C_\infty$ does vanish in the region satisfying Jordan’s lemma.

Collecting the results for the contour integrals obtained above into Eq. (A11), we obtain the integral $K^c_1$ in the form:
\[ K^c_1 = -\frac{\sqrt{2\pi}(1 + 2\xi^2)}{8\xi^3} \sin \left( \frac{x}{\sqrt{2\xi}} \right) K_0(\varpi r) \]
\[ - \frac{\pi}{2} \int_0^{2(1+\xi^2)} dy \frac{e^{-xy} \left( 1 - y^2 + \sqrt{1 + 2\xi^2y^2} \right)}{1 + 2\xi^2y^2} I_0(\varpi_1 r). \] (A21)

The procedure of evaluating integrals $K^s_1$ with the contour in Fig. 13 is entirely parallel to the one presented above for $K^c_1$. The result for the integral $K^s_1$ is
\[ K^s_1 = \frac{\pi(1 + 2\xi^2)}{8\xi^4} \cos (xt) K_0(\varpi r) \]
\[ - \frac{\pi}{2} \int_0^{2(1+\xi^2)} dy \frac{e^{-xy} \left( 1 - y^2 + \sqrt{1 + 2\xi^2y^2} \right)}{1 + 2\xi^2y^2} \] \[ \times \left[ 1 - \frac{\sqrt{2\xi y}}{\left( 1 + \sqrt{1 + 2\xi^2y^2} \right)} \right] I_0(\varpi_1 r). \] (A22)

This integral also is subject to condition (A20) and in the exterior region the Fourier transform integral must be evaluated numerically. Therefore, collecting results for $K^c_1$ and $K^s_1$, we obtain
\[ \frac{1}{2}K^c_1 + \frac{\xi}{\sqrt{2}}K^s_1 = -\frac{\pi(1 + 2\xi^2)}{8\sqrt{2}\xi^3} \left[ \sin \left( \frac{x}{\sqrt{2\xi}} \right) - \cos (xt) K_0(\varpi r) \right] K_0(\varpi r) \]
\[ - \frac{\pi}{4} \int_0^{2(1+\xi^2)} dy \frac{e^{-xy} \left( 1 - y^2 + \sqrt{1 + 2\xi^2y^2} \right)}{1 + 2\xi^2y^2} \times \]
\[ \left[ 1 - \frac{\sqrt{2\xi y}}{\left( 1 + \sqrt{1 + 2\xi^2y^2} \right)} \right] I_0(\varpi_1 r). \] (A23)

The first line involving sine and cosine functions in this result will be seen canceled by similar terms in the results for integrals $K^c_2$, $K^s_2$, $K^c_3$, and $K^s_3$.

b. $K^c_2$ and $K^s_2$

Evaluation of these integrals proceeds similarly to that of $K^c_1$ and $K^s_1$ with the contour given in Fig. 12 except that since the integrand does not have a branch cut on the imaginary axis, there
is no integral along the imaginary axis. There are only contributions from the residues at the singularities. They give rise to the following results:

\[ K_c^2 = -\frac{\sqrt{2} \pi (1 + 2\xi^2)}{8\xi^3} \sin \left( \frac{x}{\sqrt{2\xi}} \right) K_0(\omega r), \]  
\[ K_s^2 = \frac{\pi (1 + 2\xi^2)}{8\xi^4} \cos \left( \frac{x}{\sqrt{2\xi}} \right) K_0(\omega r). \]  

Therefore we obtain

\[ \frac{1}{2} K_c^2 + \frac{\xi}{\sqrt{2}} K_s^2 = -\frac{\pi (1 + 2\xi^2)}{8\sqrt{2}\xi^3} \left[ \sin \left( \frac{x}{\sqrt{2\xi}} \right) - \cos \left( \frac{x}{\sqrt{2\xi}} \right) \right] K_0(\omega r). \]  

\( A26 \)

c. \( K_3^c \) and \( K_3^s \)

In the present cases, the integrands involve a branch cut along the imaginary axis from \( z = -i \) to \( +i \). Therefore the appropriate contour to use is \( C_3 \) depicted in Fig. 13. Evaluation of integrals \( K_3^c \) and \( K_3^s \) is entirely parallel to those of integrals \( K_1^c \) and \( K_1^s \). The results of their evaluation are as follows:

\[ K_3^c = -\frac{\sqrt{2} \pi}{16\xi^5} (1 + 2\xi^2) K_0(\omega r) \sin \left( \frac{x}{\sqrt{2\xi}} \right) + \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy} y^2 (1 - y^2)}{1 + 2\xi^2 y^2} I_0(\omega_3 r), \]  
\[ K_3^s = \frac{\pi}{8\xi^4} (1 + 2\xi^2) K_0(\omega r) \cos \left( \frac{x}{\sqrt{2\xi}} \right) - \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy} y (1 - y^2)}{1 + 2\xi^2 y^2} I_0(\omega_3 r). \]  

Therefore we find

\[ -2\xi^2 K_3^c - \sqrt{2} \xi K_3^s = \frac{\pi}{4\sqrt{2}\xi^3} (1 + 2\xi^2) K_0(\omega r) \left[ \sin \left( \frac{x}{\sqrt{2\xi}} \right) - \cos \left( \frac{x}{\sqrt{2\xi}} \right) \right] \]
\[ - \frac{\pi}{2} \int_0^1 dy \frac{e^{-xy} \sqrt{2\xi y} (1 - y^2) (\sqrt{2\xi y} - 1)}{1 + 2\xi^2 y^2} I_0(\omega_3 r). \]  

The integrals in Eqs. \( A27 \) and \( A28 \) are subject to the condition deduced from the Jordan lemma, namely, \( x > r \).

d. Summary for the Reduced Axial Velocity

Collecting the results presented earlier, we obtain the reduced axial velocity

\[ \hat{v}_x (x, r, \xi) = -\frac{\pi}{2\sqrt{2}\xi} (\hat{v}_x)_{me} (x, r, \xi) \]
\[ - \frac{\pi}{4} \left[ \mathcal{C}_1 (x, r, \xi) - \mathcal{G}_1 (x, r, \xi) \right] - \frac{\pi}{2} \left[ \mathcal{C}_2 (x, r, \xi) - \mathcal{G}_2 (x, r, \xi) \right], \]  

\( A30 \)
where various symbols are defined by

\[
(\hat{v}_x)_{\text{me}} = \frac{x}{(x^2 + r^2)^{3/2}} + \sqrt{2}\xi \left[ \frac{1}{(x^2 + r^2)^{1/2}} - \frac{r^2}{2(x^2 + r^2)^{3/2}} - \frac{2x^2 - r^2}{(x^2 + r^2)^{3/2}} \right], \tag{A31}
\]

\[
C_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{(1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} e^{-xy} I_0(\omega_1 r), \tag{A32}
\]

\[
C_2(x, r; \xi) = \int_0^{1} dy \frac{2\xi^2 y^2 (1 - y^2)}{1 + 2\xi^2 y^2} e^{-xy} I_0(\omega_3 r), \tag{A33}
\]

\[
S_1(x, r; \xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{\sqrt{2}\xi y (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})}{(1 + 2\xi^2 y^2) \left(1 + \sqrt{1 + 2\xi^2 y^2}\right)} e^{-xy} I_0(\omega_1 r), \tag{A34}
\]

\[
S_2(x, r; \xi) = \int_0^{1} dy \frac{\sqrt{2}\xi y (1 - y^2)}{1 + 2\xi^2 y^2} e^{-xy} I_0(\omega_3 r). \tag{A35}
\]

As noted earlier, the terms made up of trigonometric functions in Eqs. \(A23\), \(A26\), and \(A29\) indeed cancel each other out. This velocity formula \(A30\) is the axial velocity profile of the countercurrent of the ion and its ion atmosphere in the coordinate system fixed at the center ion of the ion atmosphere, both of which are pulled by the external electric field. The first four terms making up \((\hat{v}_x)_{\text{me}}(x, r, \xi)\) represent the “deterministic” part of the velocity \(\hat{v}_x\), and the integrals \(C_1, C_2, S_1, \text{and } S_2\) involving the Bessel functions \(I_0(\omega_1 r)\) and \(I_0(\omega_3 r)\) stem from the Brownian motion part of the mean local force—namely, the dressed-up part of the local body force arising from the interaction of the center ion, its ion atmosphere, and their interaction with the external electric field, which distorts the ion atmosphere to an asymmetric form. This velocity formula obtained in Eq. \(A30\) is in a convenient form to analyze Wilson’s result, further examine the cause of divergence, and find a way to avoid the divergence difficulty in the evaluation of the electrophoretic coefficient. This aspect is discussed in the main text.

2. Distribution Functions and Potentials

The same methods of contour integration can be employed for the distribution functions \(f_{ji}(r)\) representing the nonequilibrium ionic liquid structure (pair distribution function) and the mean
ionic potential $\psi_j(r)$. They are summarized below:

$$f_{ij} = f_{ji}(\pm r)$$

$$= n^2 + \frac{2\kappa n^2 e^2}{\pi D k_B T} \left\{ -\frac{\pi}{2\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-yx} \left( 1 + \frac{1}{\sqrt{1+2\xi^2 y^2}} \right) I_0(\omega_1 r) \right. $$

$$+ \left. \frac{\pi\xi}{2\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-xy}(1 + \sqrt{1+2\xi^2 y^2})}{(1+2\xi^2 y^2)} I_0(\omega_1 r) \right\} (A36)$$

and

$$\psi_j(\pm r) = -\psi_i(\mp r)$$

$$= \frac{\kappa e}{\sqrt{2\pi D}} \left\{ \frac{\pi}{2} \int_0^{\sqrt{2(1+\xi^2)}} dy e^{-xy} \left( 1 + \sqrt{1+2\xi^2 y^2} \right) I_0(\omega_1 r) \right. $$

$$- 2\pi \xi^2 \int_0^1 dy \frac{e^{-xy}y^2}{1+2\xi^2 y^2} I_0(\omega_3 r) \right\}$$

$$\left. + \frac{\pi\xi}{\sqrt{2}} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{ye^{-xy}}{1+2\xi^2 y^2} I_0(\omega_2 r) \right\}$$

$$- \sqrt{2\pi} \int_0^1 dy \frac{ye^{-xy}}{1+2\xi^2 y^2} I_0(\omega_3 r) \} \right\} (A37)$$

in the region of $(x, r)$ in the upper plane where Jordan's lemma is satisfied. These results can be easily obtained by using the contour integration method described earlier in this Appendix. We notice that the nonequilibrium pair distribution functions and potentials do not contain mechanical contributions, but only the Brownian motion contributions. The reason is that $f_{ji}(r)$ and $\psi_j(r)$ are solutions of the OF equations and Poisson equations for the nonequilibrium part described by the Brownian motion model.

[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge U.P., London, 1970), third edition.
[2] E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).
[3] C. S. Ting, ed., *Physics of Hot Electron Transport in Semiconductors* (World Scientific, Singapore, 1992).
[4] B. R. Nag, *Electron Transport in Compound Semiconductors* (Springer, Berlin, 1980).
[5] P. T. Landsberg, *Basic Properties of Semiconductors*, Vol. 1 (North-Holland, Amsterdam, 1992).
[6] M. Wien, Ann. Physik. 85, 795 (1928); Phys. Z. 29, 751(1928); Ann. Physik. 5, 1, 400 (1929); Phys. Z. 32, 545 (1931); J. Malsch and M. Wien, Ann. Physik. [4] 83, 305 (1927).
[7] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold, New York, 1958).

[8] R. M. Fuoss and F. Accascina, *Electrolytic Conductance* (Interscience, New York, 1959).

[9] J. W. Daily and M. M. Micci, J. Chem. Phys. **131**, 094501 (2009).

[10] O. M. Shabanov, R. T. Kachaev, S. A. Dzhamalova, and A. A. Iskakova, Russian J. Electrochem. **46**, 1390 (2010); O. M. Shabanov, S. M. Gadhizh, A. A. Iskakova, R. T. Kachaev, A. O. Magomedova, and S. I. Suleimanov, ibid. **47**, 221 (2011).

[11] Y. Wang, C. Li, W. Wang, J. Jiang, D. Zhou, R. Xu, and S. P. Friedman, Soil Sci. Soc. Am. J. **73**, 569 (2008).

[12] E. W. Castner and J. F. Wishart, J. Chem. Phys. **132**, 120901 (2010).

[13] R. D. Rogers and K. R. Seddon, eds., *Ionic Liquids IIA, Fundamentals, Progress, Challenges, and Opportunities. Properties and Structure*, ACS Symposium Series Vol. 901; R. D. Rogers and K. R. Seddon, eds., *Ionic Liquids IIB, Fundamentals, Progress, Challenges and Opportunities. Transformations and Progress*. ACS Symposium Series Vol. 902 (American Chemical Society, Washington DC, 2005).

[14] B. C. Eu, “Brownian movement theory of nonequilibrium statistical mechanics, transport, and hydrodynamics of strong asymmetric electrolyte solutions in an electric field” (to be submitted).

[15] B. C. Eu and H. Xu, “Wien effect on ionic conductance of asymmetric strong electrolytes in an electric field. (to be submitted).

[16] L. Onsager, Phys. Z. **27**, 388 (1926); **28**, 277 (1927).

[17] P. Debye and E. Hückel, Physik. Z. **24**, 305 (1923).

[18] G. G. Stokes, *Mathematical and Physical Papers* (Cambridge U.P., London, 1880), Vol. 1, pp 36-43.

[19] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon. Oxford, 1958).

[20] G. K. Batchelor, *Fluid Dynamics* (Cambridge U.P., London, 1967).

[21] R. B. Bird, W. E. Stewart, E. N. Lightfoot, *Transport Phenomena* (Wiley, New York, 1960), p. 132.

[22] L. Onsager and R. M. Fuoss, J. Phys. Chem. **36**, 2698 (1932).

[23] M. von Smoluchowski, Physik. Z. **17**, 557, 585 (1916).

[24] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975), second ed.

[25] W. S. Wilson, *The Theory of the Wien Effect for a Binary Electrolyte*, PhD Thesis, Yale University, June, 1936.

[26] J. G. Kirkwood, J. Chem. Phys. (1946).

[27] B. C. Eu, J. Chem. Phys. **87**, 1238 (1985).

[28] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992).

[29] B. C. Eu, *Nonequilibrium Statistical Mechanics* (Kluwer, Dordrecht, 1998).

[30] E. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge U. P., London, 1952).

[31] B. C. Eu, H. Xu, and K. Rah, the following paper entitled “Wien effect on ionic conductance of binary strong electrolyte solutions in a high external electric field”.

[32] G. N. Watson, *Theory of Bessel Functions* (Cambridge U. P., London, 1966).
[33] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, DC, 1966).

[34] N. I. Muskhelishvili, *Singular Integral Equations* (P. Noordhoff, Groningen, 1953).

[35] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).

[36] R. Haase, *Thermodynamics of Irreversible Processes* (Dover, New York, 1969), Chapter 4 and, in particular, Sec. 4-16.

[37] B. C. Eu, (to be submitted).

[38] S. Ichimaru, *Basic Principles of Plasma Physics* (Benjamin/Cummings, reading, MA, 1973); E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).

[39] N. Benabdallah, A. Arnold, P. Degond, I. M. Gamba, R. T. Glassey, C. D. Levermore, C. Ringhofer, eds., *Transport in Transition Regimes* (Springer, Heidelberg, 2004).

[40] D. K. Ferry and S. M. Goodnick, *Transport in Nanostructure* (Cambridge U. P., London, 1997); G. Em Karniadakis and A. Beskok, *Micro Flows* (Springer, Heidelberg, 2002).

[41] Y. Tanaka, ed., *Ion Exchange Membranes: Fundamentals and Applications* (Elsevier, Amsterdam, 2007).
Figure Captions

Fig. 1 The cylindrical coordinate system employed. The $x$ axis is parallel to the external electric field.

Fig. 2 Nonequilibrium part of the distribution function $\Delta f_{ij}(+r)$ is plotted in $(x, r)$ plane at $\xi = 1$. Here $\Delta f_{ij}(+r) = \left[ f_{ij}(+r) - n^2 \right] / (\sqrt{2}\kappa z e^2/\pi Dk_B T)$. $\Delta f_{ij}(+r)$ is computed with the contour integration methods within the range defined by Ineq. (148) and, outside this range, by means of the method of principal values for singular integrals.

Fig. 3 Nonequilibrium part of the potential $\Delta \psi_j(+r)$ is plotted in $(x, r)$ plane at $\xi = 1$. Here $\Delta \psi_j(+r) = \psi_j(+r)/(\kappa z e/\sqrt{2}\pi D)$ with $\psi^0_j$ denoting the Debye–Hückel potential. In Eq. (92) $\psi^0_j$ is not explicitly put in since $\psi_j(\pm r)$ is the nonequilibrium part of the potential in the external field. Therefore $\Delta \psi_j(+r)$ should be understood as $\Delta \psi_j(+r) = \left[ \psi_j(+r) - \psi^0_j \right] / (\kappa z e/\sqrt{2}\pi D)$. Within the range of $x$ and $r$ satisfying Ineq. (90) [also see Ineq. (A20)] the contour integration method is used and outside the region the method of principal value integration is used for computation.

Fig. 4 The reduced axial velocity profile $\hat{v}_x(x, r, \xi)$ is plotted in $(x, r)$ plane at $\xi = 1$. Within the range of $x$ and $r$ satisfying Ineq. (148) the contour integration method is used and outside the region the method of principal value integration is used for computation. The axial velocity profile is directional, being positive the positive $x$ direction parallel to the external field before vanishing to zero at large distance whereas being negative in the transversal (radial) direction before vanishing to zero as $r$ increases. Thus the boundary conditions are satisfied in both $x$ and $r$ directions. This figure indicates the mode of behaviors of the counterflow of the medium to the ionic movement when the external field is turned on.

Fig. 5 The electrophoretic factor $f(x, r, \xi)$ is plotted in 3D in a similar color coding to Fig. 4 in the case of $\xi = 1$.

Fig. 6 The projection of surface $f(x, r, \xi)$ onto $(x, r)$ plane. There are two sets of quasi-elliptical level curves; one with the major axis on the $x$ axis and the other on the $r$ axis. The former corresponds to the contours of the negative part of the $f(x, r, \xi)$ surface projected onto $(x, r)$ plane, and the latter to the contours of the positive part projected onto $(x, r)$ plane. The outermost level curve $C_p$ is the locus of $f(x, r, \xi) = 0$. This level curve $C_p$ depicts the moving ion atmosphere distorted by the external electric field from the spherical form assumed by the ion atmosphere at $\xi = 0$. This moving ion atmosphere is seen polarized toward the field direction.

Fig. 7 The distorted ion atmosphere is seen to have the center at $(x_c, 0)$ on the $x$ axis. The field dependence of the center of the ion atmosphere $(x_c, 0)$ describes the trajectory of its motion.
The trajectory is shown in this figure. The curve indicates the mode of migration for the center from the origin of the coordinate system where the center is located when $\xi = 0$, as the field strength is increased. It decreases to a plateau after reaching a maximum as $\xi$ increases.

Fig. 8  Plot of an example for $f(x, r, \xi)$ at $x = r = 0.5$ as a function of $\xi$ and its comparison with Wilson’s electrophoretic coefficient $f(\xi)$. The solid line, the present theory; the dotted line, the OW theory.

Fig. 9  A $3-D$ relaxation time coefficient $g(x, r; \xi)$. A combination of the contour integration results and the method of principal integration is used to construct the surface.

Fig. 10  Plot of and example for $g(x, r, \xi)$ at $x = r = 0.5$ as a function of $\xi$ and its comparison with Wilson’s electrophoretic coefficient $g(\xi)$. The solid line, the present theory; the dotted line, the OW theory.

Fig. 11  Contour $C_1$ for integrals $K_1^c$ and $K_1^s$. This contour also applies to integrals $J_1^c$ and $J_1^s$ and $P_1^c$ and $P_1^s$. The bold line denotes the branch cut.

Fig. 12  Contour $C_3$ for integrals $K_3^c$ and $K_3^s$. This contour also applies to integrals $J_3^c$ and $J_3^s$ and $P_3^c$ and $P_3^s$. The bold line denotes the branch cut.

Fig. 13  Contour $C_2$ for integrals $K_2^c$ and $K_2^s$. This contour also applies to integrals $J_2^c$ and $J_2^s$ and $P_2^c$ and $P_2^s$. The bold line denotes the branch cut on the negative real axis.
FIG. 1:

FIG. 2:
FIG. 6:

FIG. 7:
This figure "Fig_1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_5.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_6.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_7.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_11.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_12.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1
This figure "Fig_13.jpg" is available in "jpg" format from:

http://arxiv.org/ps/1207.1144v1