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On the Onsager–Wilson Theory of Wien Effect on Strong Binary Electrolytes in a High External Electric Field

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Abstract

In this review paper, we present and critically re-examine the formal expressions for the electrophoretic effect and the ionic field appearing in the unpublished Yale University PhD dissertation of W. S. Wilson which form the basis of the Onsager–Wilson theory of the Wien effect in the binary strong electrolyte solutions. It is pointed out that some of the integrals that make up the flow velocity formula obtained in the thesis and he evaluated at the position of the center ion in the ionic atmosphere (i.e., the coordinate origin) diverge. Therefore they cannot be evaluated by means of contour integrals in the manner performed in his thesis for the reason pointed out in the text of this paper. In this paper, the results for the integrals in question are presented, which are alternatively and exactly evaluated. The details will be described in the follow-up paper presented elsewhere together with the improved formula for the Wien effect on conductivity.
I. Introduction

Non-Ohmic phenomena in charged media, such as plasmas, semiconductors, ionic solutions, subjected to high external electromagnetic fields are much observed in recent years. They not only have numerous practical applications in science and engineering, but also pose much challenge theoretically. Especially, in small systems confined in space, which consequently are subject to a very large field gradient, nonlinear phenomena are usually unavoidable and their theoretical treatment has been of considerable interest as a large body of literature on the subject matter attests to the interest, relevance, and activity in the fields. The usual linear theory would not suffice for an adequate theoretical treatment, and one would require some sort of nonlinear theory of irreversible processes, whether a kinetic theory (statistical mechanics approach) or macroscopic irreversible thermodynamics approach is taken. The present author has developed a nonlinear theory of irreversible processes both in the kinetic theory (molecular theory) approach or the phenomenological irreversible thermodynamics approach when the medium (liquids or gases) is electrically neutral. Naturally, extension of the theories mentioned of neutral media has been one of the aims of recent research of the present author.

In electro-physical chemistry, non-Ohmic behavior of conductivity was observed since 1920s. It is known as the Wien effect in electrolyte solutions. The theories of electrical conductivity in electrolyte solutions have been developed by Lars Onsager and his collaborators over a period stretching over twenty some years beginning from the late 1920s. Onsager’s theories elucidate the important effects underlying the conduction phenomena in charged media which we may make use of for many conduction phenomena observed in the fields and matters mentioned of current interest. Despite their significance and implications there has been very few follow-up studies of his theories by other
authors in which the theories could have been critically reviewed and analyzed for further development at the basic level. Although, superficially, they seem dated from the current standpoint it appears there still are many features and techniques in them from which we could much benefit for the current new things we daily encounter in the fields mentioned earlier. On the strength of this line of reasoning and motivated by the possibility of utility of his theories for new related problems, the present author has been studying his theories as closely as possible at the basic level. We would like to report that even an improvement of one of the results on the Wien effect in binary electrolytes can be achieved that would affect the experimental interpretations in the past of the conductivity in electrolyte solutions carried out on the basis of the Wien effect on electrolytes.

In the path breaking paper of ionic conductivity in strong electrolyte solutions subject to an external electric field, Lars Onsager in 1927 derived a linear conductance formula for strong electrolyte solutions. To derive the formula he took into consideration the electrophoretic effect and the ionic field relaxation effect, which were estimated by means of physical arguments—on the basis of the Stokes law and a relaxation time argument. The formula derived established the limiting laws of ionic conduction, which ever since has appeared in textbooks of physical chemistry and, particularly, physical chemistry of electrolyte solutions. This early linear theory was followed up by W. S. Wilson in his 1936 Yale PhD thesis under Onsager’s supervision in which he obtained the formula for ionic conductance in binary strong electrolytes in high external electric fields—the Wien effect, which was experimentally discovered by M. Wien in 1920s. His thesis has not been published in a journal, but a summary and the tables for the functions representing the electrophoresis effect and the ionic field relaxation time effect have appeared in the well-known monumental reference book on physical chemistry of electrolyte solutions by Harned and Owen. The
reason for not publishing Wilson’s results, according to Harned and Owen, was the partial Fourier transform method used in Wilson’s thesis should be replaced by a full Fourier transform method to be developed later. However, it took two decades for such a method to appear in 1957. In the intervening period, the aforementioned tables prepared by Wilson have been used in connection with the Wien effect in the literature.

When compared with experiment, the Wien effect formula obtained, however, does not fully account for the observed conductance data on strong electrolytes. Therefore, the theory should be improved, but an improvement cannot be achieved unless we know the theory in its intimate detail. Because of the aforementioned deficiency, the ionic conductance formula for the Wien effect has been seminal and played an important role in the development of the idea of the ionic association theory put forward by A. Patterson and his collaborators, who have made use of Bjerrum’s ionic association theory which, coupled with the weak electrolyte theory of Onsager has enabled them to account for the observed conductance data. Thus the idea of degree of ionic association took a place in physical chemistry lore.

Having formulated a nonlinear transport theory—generalized hydrodynamic theory—of non-electrolytes (neutral liquids and gases) by means of kinetic theory and its phenomenological version, the present author in the recent years has been investigating application of the aforementioned generalized hydrodynamic theory to electrolytic conduction under high external electric fields often encountered in various small systems of recent interests in various fields. The natural course to take therefore has been to learn the Onsager line of theories before deciding to apply them to phenomena in mind. Unsatisfied by the brief summary of the theory of Wien effect given by Wilson in the monograph of Harned and Owen, the present author decided to have a close look at Wilson’s
thesis.

In his thesis, by solving the governing equations for the distribution functions and Poisson equations which were earlier established by Onsager and Fuoss\textsuperscript{[11]}, Wilson obtains the solutions for the distribution functions and ionic potentials. Therewith he then obtains a formal expression for the ionic field. He also solves the Navier–Stokes equation for velocity by a (partial) Fourier transform method and obtains a formal expression for the velocity field. These formal expressions (solutions) are made up of complicated integrals [in fact, $\cos(\alpha x)$ and $\sin(\alpha x)$ transforms, where $x$ is the axial coordinate and $\alpha$ the transform variable] involving zeroth-order Bessel functions of second kind $K_0(\lambda \rho)$ with non-simple argument where $\rho$ is the radial distance from the central ion in the cylindrical coordinate system employed and $\lambda$ is an irrational function of $\alpha$, the field strength, and the Debye length characterizing the ion atmosphere of the electrolyte solution of interest. Since the physical quantities of interest are those of the central ion located at the origin of the coordinates (the center of ionic atmosphere), he elects to take $x = 0$ and $\rho = 0$ within the integrals before evaluating them. Then he resorts to contour integration methods and manages to evaluate the integrals in closed analytic forms. The results give rise to the well-known formula for the Wien effect, which was later found to give qualitatively correct results compared with experiments, but not quantitatively in the high field regime.

The aforementioned step of taking special values of the variables, $x = 0$ and $\rho = 0$, is found to give rise to a difficulty because a couple of the resulting integrals preclude the contour integral method that involves a contour at infinite radius in the complex plane. In fact, when closely examined, they diverge as the argument ($\alpha$) tends to infinity on the positive real axis. Therefore, it is not permissible to take $\rho = 0$, which allows to take the Bessel function $K_0(\lambda \rho)$ at $\rho = \ldots$
0 before evaluating the integral. This means, mathematically, that the integrals are not uniformly convergent with respect to $\rho$ because of the characteristics of $K_0(\lambda \rho)$ at $\rho = 0$ in the integrals. In the follow-up of this tutorial review article, the integrals appearing in the formal expressions for the velocity field and ionic field in Wilson’s thesis are evaluated alternatively and exactly. The integrals can be reduced to definite integrals of another zeroth-order Bessel function of second kind, $I_0(\lambda \rho)$, along the imaginary axis, which may be evaluated term by term in terms of quadratures of algebraic functions. They are rather easily amenable to numerical integration. The main purpose of this tutorial article is to introduce to the reader the solution procedures leading to Wilson’s results from the governing equations for the distribution functions and the Navier–Stokes equation with the local force field constructed from the solutions of the governing equations. They are not simple at all, yet not readily available in the main stream scientific literature easily accessible at present. (Wilson’s thesis is only available on interlibrary loan from Yale University.) Besides, Wilson’s dissertation contains a number of important typographical errors often requiring checking the whole solution processes to correct them. In view of the importance and significance of the Wien effect in nonlinear physico-chemical processes in electrolytes it is hoped to provide the reader with the details of the Onsager–Wilson theory of electrolytes. This author believes that their theory should provide significant insights and methodologies for the modern investigations in electrical conductivities and transport properties of electrically charged fluids and condensed matter physics.

This article is organized as follows. In Sec. II, in view of the fact that Wilson’s thesis was not published and its details are not available to the general audience in the mainstream scientific literature it seems appropriate to provide the essential materials beyond what is presented in the monograph of Harned
and Owen. As a matter of fact, it contains valuable lessons and insights for us to theoretically and mathematically treat physical phenomena in electrolytes and plasmas subjected to external electric fields. Thus, for notational purposes we will first present the governing equations and the formal solutions of the governing equations. Then the formal solution is obtained for the Navier-Stokes equation by using the local force field formula supplied by the aforementioned solutions for the governing equations. The velocity field and ionic field obtained are formal, being given in terms of one-dimensional Fourier transforms of zeroth-order Bessel functions mentioned earlier. We then will discuss the procedure used by Wilson to evaluate them, for which he uses the method of contour integration and residues. Instead of his contour integral methods we will use our own contours different from his. They are more easily comprehensible in our opinion. We will indicate an alternative method of evaluation of the integrals, but only the results are presented, the details of which will be dealt with in the regular article by the present author elsewhere. This method gives rise to finite integrals of the zeroth-order Bessel functions of second kind, $I_0(z)$, along the imaginary axis in the $\alpha$ plane, which in fact can be expressed as quadratures of algebraic functions—polynomials. In Sec. IV, Wilson’s results obtained for the velocity field and the ionic field are then used for the formula for ionic conductance of binary strong electrolytes. Sec. V is for the concluding remarks.

II. The Governing Equations and Solutions

To treat transport phenomena in electrolyte solutions Onsager and Fuoss proposed a Fokker–Planck type equation for ion pair correlation functions—probability distribution functions. The distribution functions are introduced in the following manner.

Let the two volume elements $dV_1$ and $dV_2$ be at $r_2$ and $r_1$, respectively, at
time (duration) \( t \). Let the fraction of time \( t_j \) of \( t \) be the time duration in which particle \( j \) is found in \( dV_1 \). The probability (density) \( n_j \) of finding \( j \) in \( dV_1 \) during that time duration is then, by the ergodic hypothesis:

\[
\frac{t_j}{t} = n_j dV_1,
\]

whereas the probability \( n_i \) of finding \( i \) in \( dV_2 \) during that time duration is

\[
\frac{t_i}{t} = n_i dV_2.
\]

Now let \( t_{ji} \) be the time duration of \( t_j \) (i.e., the fraction of \( t_j \)) in which an ion \( i \) is found in \( dV_2 \), given an ion \( j \) in \( dV_1 \). The conditional probability \( n_{ji} \) of finding an \( i \) ion in \( dV_2 \) is then

\[
\frac{t_{ji}}{t_j} = n_{ji} dV_2.
\]

Similarly, in the reversed case,

\[
\frac{t_{ij}}{t_i} = n_{ij} dV_1.
\]

Since

\[
\frac{t_{ji}}{t} = \frac{t_{ij}}{t},
\]

it follows

\[
n_j n_{ji} dV_1 dV_2 = n_i n_{ij} dV_1 dV_2. \tag{1}
\]

We may write

\[
f_{ji} (r_1, r_{21}) \equiv n_j n_{ji} = n_i n_{ij} \equiv f_{ij} (r_2, r_{12}). \tag{2}
\]

Here \( r_1 \) and \( r_2 \) are position vectors of ion \( j \) and ion \( i \), respectively, in a suitable coordinate system and

\[
r \equiv r_{21} = r_2 - r_1 = -r_{12}. \tag{3}
\]

The \( f_{ji} (r_1, r_{21}) \) is the probability of finding ion \( i \) at \( r_2 \) in \( dV_2 \) at distance \( r_{21} \) from ion \( j \) at \( r_1 \) in \( dV_1 \), and inversely for \( f_{ij} (r_2, r_{12}) \). These are pair distribution functions of the particle pair \((i, j)\).
The charge density $\rho_j$ at a position $r$ from ion $j$ is then given by

$$\rho_j = \sum_i n_{ji} e_i = \sum_i \frac{f_{ji}}{n_j} e_i,$$

(4)

where $e_i$ is the charge on ion $i$. The potential due to the $j$ ion and its atmosphere is denoted $\psi_j (r_1, r_{21})$, which obeys the Poisson equation

$$-\nabla \cdot \nabla \psi_j (r_1, r_{21}) = -\frac{4\pi}{D} \sum_i \frac{f_{ji} (r_1, r_{21})}{n_j} e_i,$$

(5)

where $D$ is the dielectric constant.

Let the velocity of ion $i$ in the neighborhood of ion $j$ be $v_{ji} = v_{ji} (r_1, r_{21})$ and inversely $v_{ij} = v_{ij} (r_2, r_{12})$. With the relative coordinate $r$ introduced, the position coordinates $r_1$ and $r_2$ can be suppressed and we may write $v_{ji} (r_1, r_{21}) = v_{ji} (r)$ and $v_{ij} (r_2, r_{12}) = v_{ij} (-r)$.

In the Brownian motion model it is assumed that

$$v_{ji} (r) = v (r) + \omega_i (K_{ji} - k_B T \ln f_{ji}),$$

(6)

$$v_{ij} (-r) = v (r) + \omega_j (K_{ij} - k_B T \ln f_{ij}),$$

(7)

where $v (r)$ is the barycentric velocity, the total force $K_{ji}$ is given in terms of the external force $F$, and fluctuating forces of Brownian motion

$$K_{ji} = k_i + \text{fluctuating forces},$$

and $\omega_i$ is the mobility of ion $i$ that produces velocity $\omega_i k_i$ when $k_i$ acts on ion $i$. In the relative coordinates adopted, the probability $f_{ji} (r_1, r_{21})$—pair distribution function—is assumed to obey the equation of continuity

$$-\frac{\partial f_{ji} (r_1, r_{21})}{\partial t} = \nabla_1 \cdot [f_{ji} v_{ji} (r_1, r_{21}) + f_{ij} v_{ij} (r_2, r_{12})].$$

(8)

With the Brownian motion model (6) and (7) a steady state Fokker–Planck type equation is obtained from Eq. (8) for $f_{ji}$:

$$-\nabla \cdot [f_{ji} v_{ji} (r) - f_{ij} v_{ij} (-r)] = \nabla_1 \cdot \omega_j (f_{ij} K_{ij} - k_B T \nabla_1 f_{ij})

+ \nabla_2 \cdot \omega_i (f_{ji} K_{ji} - k_B T \nabla_2 f_{ji}).$$

(9)
Equations (5) and (9) are the basic steady-state governing equations for the distribution functions $f_{ji}$ and potentials $\psi_j$ in the Onsager–Fuoss theory of electrolytic transport processes in external electric fields. They are coupled as will be clear presently. Further assumptions/approximations are made to Eq. (9).

Since the fluctuating forces making up the total force $K_{ji}$ mainly originate from ionic interactions within the ionic atmosphere and between ionic atmospheres of ions $i$ and $j$, they must be getting contributions from ionic potentials $\psi_i$ and $\psi_j$. Neglecting the ionic forces of $O\left(e^2\right)$ or higher, the total forces in the Onsager–Fuoss theory $K_{ji}$ are looked for in the form

$$K_{ji} = k_i - e_i \nabla_i \psi'_i (0) - e_i \nabla_i \psi_j (r_1, r_{21}),$$

where the prime denotes the nonequilibrium correction to $\psi_i$ beyond the Debye–Hückel equilibrium potential $\psi^0_j$ obeying the Poisson–Boltzmann equation

$$\nabla \cdot \nabla \psi^0_j = \frac{4 \pi}{k_BT} \sum_{i=1}^{s} n_i e_i^2 \psi^0_j = \kappa^2 \psi^0_j.$$  

Here the Debye parameter (inverse Debye length) $\kappa$ is defined by

$$\kappa = \sqrt{\frac{4 \pi}{k_BT} \sum_{i=1}^{s} n_i e_i^2}.$$  

Thus we now see that Eqs. (5) and (9) are coupled. We look for the solutions in the forms

$$\psi_j (r_1, r_{21}) = \psi^0_j (r) + \psi'_j (r_1, r_{21}),$$

$$n_{ji} (r_1, r_{21}) = n_{ji}^0 (r) + n'_{ji} (r_1, r_{21}).$$  

On substitution of Eq. (10), (12), and (14), the steady-state governing equations
for \( f_{ji} \) are now given by the equation

\[
\nabla \cdot \left[ (v_{ji}(r) - v_{ij}(-r)) f_{ji} \right] = \omega_i k_i \cdot \nabla f_{ji}(r) - \omega_j k_j \cdot \nabla f_{ji}(r) \\
- \nabla \cdot \omega_i n_j n_i \left[ e_i \nabla \psi_j(r) + \frac{k_B T n_j n_i}{n_j n_i} \nabla f_{ji}(r) \right] \\
- \nabla \cdot \omega_j n_j n_i \left[ e_j \nabla \psi_i(-r) + \frac{k_B T n_j n_i}{n_j n_i} \nabla f_{ji}(r) \right] \\
\quad (i, j = 1, 2, \cdots, s).
\]

(15)

Note that \( \nabla \cdot k_i = 0 \) is made use of in this equation since in the experiments of interest the external forces \( k_i \) are maintained constant in space. For this equation we have also made use of the fact that

\[
f_{ji} - n_i n_j = O(e_i e_j) = O(e^2),
\]

(16)

\[
f_{ji}(r) = f_{ij}(-r),
\]

(17)

and neglected the terms containing \( \nabla \psi_i'(0) \) and \( \nabla \psi_j'(0) \) owing to the fact that they are \( O(e^2) \). This final form of the governing equation for \( f_{ji} \) are coupled to the Poisson equation

\[
\nabla^2 \psi_i(r) = -\frac{4\pi}{D} \sum_{i=1}^{s} f_{ji}(r) e_i.
\]

(18)

Wilson solved this set for binary electrolyte solutions on which the external electric field \( X \) acting in the direction of positive \( x \) axis:

\[
k_1 = e_1 X, \quad k_2 = e_2 X.
\]

(19)

Written out for a binary electrolyte—in fact, a uni-uni electrolyte, Eq. (15) and
Poisson equations becomes a set of six coupled equations:

\[ n^2 e \left\{ \nabla^2 \left[ \psi_1 (r) + \psi_1 (-r) \right] \right\} + 2k_B T f_{11} (r) = 0, \quad (20) \]

\[ -n^2 e \left\{ \nabla^2 \left[ \psi_2 (r) + \psi_2 (-r) \right] \right\} + 2k_B T f_{22} (r) = 0, \quad (21) \]

\[ X e (\omega_1 + \omega_2) \nabla_x f_{12} (r) - n^2 e \left\{ \omega_1 \nabla^2 \psi_2 (-r) - \omega_2 \nabla^2 \psi_1 (-r) \right\} + k_B T (\omega_1 + \omega_2) \nabla^2 f_{12} (r) = 0, \quad (22) \]

\[ -X e (\omega_2 + \omega_1) \nabla_x f_{21} (r) - n^2 e \left\{ \omega_1 \nabla^2 \psi_2 (-r) - \omega_2 \nabla^2 \psi_1 (r) \right\} + k_B T (\omega_1 + \omega_2) \nabla^2 f_{21} (r) = 0, \quad (23) \]

\[ \nabla^2 \psi_1 (r) = -\frac{4\pi e}{Dn} \left[ f_{11} (r) - f_{12} (r) \right], \quad (24) \]

\[ \nabla^2 \psi_2 (r) = -\frac{4\pi e}{Dn} \left[ f_{21} (r) - f_{22} (r) \right]. \quad (25) \]

Here \( \nabla_x = \partial / \partial x \). Note that for a binary electrolyte

\[ n_1 e_1 + n_2 e_2 = 0 \quad (26) \]

by electroneutrality and \( n_1 = n_2 \). These coupled equations are solved subject to the boundary conditions. At this point, it will be useful to remind ourselves that these governing equations, when solved, would provide us with the electrical perturbations to the pair distribution functions and the potentials. In Onsager’s theory there is no provision for calculation of the equilibrium part of the pair distribution functions in the absence of the external field. The equilibrium distribution functions should be calculated and supplied separately, if necessary. For them we may make use of the modern theory of equilibrium charged fluids.\[22\]

### III. Boundary Conditions

Eqs. (20)–(25) are subject to the following boundary conditions.
A. Flow

The number of ions $F_{ji} (\Omega)$ leaving the interior of a region $S$ is

$$-rac{\partial F_{ji}}{\partial t} = \int_S f_{ji} (r) \{ e_n \cdot [v_{ji} (r) - v_{ij} (-r)] \} dS$$

$$= \int_\Omega \nabla \cdot f_{ji} (r) [v_{ji} (r) - v_{ij} (-r)] d\Omega = 0, \quad (27)$$

where $e_n$ is the unit vector normal to the surface $S$. It is equal to zero by the law of mass conservation. Since volume $\Omega$ can be as small as possible, the limit of $\Omega \to 0$ may be taken:

$$\lim_{\Omega \to 0} \int_S f_{ji} (r) e_n \cdot [v_{ji} (r) - v_{ij} (-r)] dS = 0. \quad (28)$$

This means that the flow field $f_{ji} (r) [v_{ji} (r) - v_{ij} (-r)]$ must be sourceless. That is, $f_{ji} (r)$ must satisfy this condition. According to Eq. (15) this flow condition implies

$$f_{ji} (r) [v_{ji} (r) - v_{ij} (-r)] = \omega_i [k_i f_{ji} (r)] - \omega_j [k_j f_{ij} (-r)]$$

$$- [\omega_i e_i n_i n_j \nabla \psi_j (r) + \omega_j e_j n_i n_j \nabla \psi_i (-r)]$$

$$- k_B T (\omega_i + \omega_j) \nabla f_{ji} (r). \quad (29)$$

This condition will be made use of later.

B. Ionic Fields

The space charge within $\Omega$ is

$$\int_\Omega d\Omega \rho_j (r) = -\frac{D}{4\pi} \int_\Omega d\Omega \nabla \cdot \nabla \psi_j (r) \quad (30)$$

As $\Omega \to 0$, the volume of the ion $j$ at the origin, the left-hand side of this equation is equal to $e_j$ if the charge is located at the origin of the coordinates, or equal to zero if the charge is not in $\Omega$. Thus we may write it as

$$\rho_j (r) = e_j \delta (r). \quad (31)$$
Therefore
\[
\nabla \cdot \nabla \psi_j (\mathbf{r}) = -\frac{4\pi e_j}{D} \delta (\mathbf{r})
\]
(32)
or
\[
\lim_{\Omega \to 0} \int_{S} dS \cdot \nabla \psi_j (\mathbf{r}) = -\frac{4\pi e_j}{D} \delta
\]
(33)
where
\[
\delta = 1 \quad \text{if } e_j \text{ is at } \mathbf{r} = 0
\]
\[
= 0 \quad \text{otherwise.}
\]
Since near \( \mathbf{r} = 0 \), the screening effect is equal to zero and hence the potential is equal to
\[
\psi_j = \frac{e_j}{Dr}
\]
(34)
and in the large distances
\[
\lim_{r \to \infty} \psi_j = 0.
\]
(35)
Hence the boundary conditions on \( \psi_j \) are deduced to be
\[
\psi_j - \frac{e_j}{Dr} < \infty \text{ as } |\mathbf{r}| \to 0,
\]
(36)
\[
\psi_j (\infty) = 0.
\]
(37)
If the charge is of finite size \( \sigma_j \), then this should be modified to
\[
\psi_j - \frac{e_j}{Dr} < \infty \text{ as } |\mathbf{r}| > \sigma_j,
\]
(38)
\[
\psi_j (\infty) = 0.
\]
(39)
The Onsager–Wilson theory does not take the case of finite ion sizes into consideration as should have been.
C. Symmetry Conditions for Potentials and Distribution Functions

1. Potentials

Since the distribution functions are even

\[ f_{ii}(r) = f_{ii}(-r), \quad f_{jj}(r) = f_{jj}(-r), \quad (40) \]

\[ f_{ji}(r) = f_{ij}(-r), \quad (41) \]

it is possible to deduce the symmetry conditions for the potentials. From the Poisson equations we find

\[ \nabla^2 \psi_j(r) = -\frac{4\pi e_j}{Dn} [f_{jj}(r) - f_{ji}(r)], \quad (42) \]

\[ \nabla^2 \psi_i(-r) = -\frac{4\pi e_i}{Dn} [f_{ii}(-r) - f_{ij}(-r)]. \quad (43) \]

Adding the two equations yields

\[ \nabla^2 [\psi_j(r) + \psi_i(-r)] = -\frac{4\pi e}{Dn} [z_jf_{jj}(r) + z_if_{ii}(r)]. \quad (44) \]

From this follows

\[ \nabla^2 [\psi_j(-r) + \psi_i(r)] = -\frac{4\pi e}{Dn} [z_jf_{jj}(r) + z_if_{ii}(r)]. \quad (45) \]

Here \( e_i = ez_i \) and \( e_j = ez_j \). Subtracting it from the previous equation, we obtain

\[ \nabla^2 [\psi_j(r) - \psi_j(-r) + \psi_i(-r) - \psi_i(r)] = 0. \quad (46) \]

By the boundary conditions on the potentials

\[ \psi_j(r) - \psi_j(-r) < \infty. \quad (47) \]

That is, it is finite. Therefore \( \psi_j(r) - \psi_j(-r) + \psi_i(-r) - \psi_i(r) \) is also finite.

According to the theory of harmonic analysis, any finite function satisfying the Laplace equation is a constant. Therefore, we may set

\[ \psi_j(r) - \psi_j(-r) + \psi_i(-r) - \psi_i(r) = 0 \]
or

\[
\psi_j (r) - \psi_j (-r) = \psi_i (r) - \psi_i (-r) .
\]  

(48)

That is, the odd parts of the potentials are equal independently of \( i \) and \( j \). This means we may set

\[
\psi_j (r) - \psi_j (-r) = \psi_i (r) - \psi_i (-r) = 2Y (r) ,
\]  

(49)

where \( Y (r) \) is the odd part of the potential.

The symmetry conditions for the even part of the potential is obtained as follows. From Eq. (15) taken to \( O (e^2) \)

\[- \nabla \cdot \omega_i [ez_i n^2 \nabla \psi_i (r) + k_B T \nabla f_{ii} (r)] = 0. \]

On integrating it over \( \Omega \) and observing the boundary conditions discussed earlier, we find

\[
0 = \nabla \left[ -\omega_i e z_i n^2 [\psi_i (r) + \psi_i (-r)] - 2k_B T f_{ii} (r) \right]
\]  

(50)

which means

\[-\omega_i e z_i n^2 [\psi_i (r) + \psi_i (-r)] - 2\omega_i k_B T f_{ii} (r) = c, \]

but \( \psi_i (\infty) = 0 \) and \( f_{ii} (\infty) = n^2 \). Therefore \( c = n^2 \) and we find

\[
f_{ii} (r) = f_{ii} (-r) = n^2 - \frac{z_i e n^2}{2k_B T} [\psi_i (r) + \psi_i (-r)]
\]  

(51)

and similarly

\[
f_{jj} (r) = f_{jj} (-r) = n^2 - \frac{z_j e n^2}{2k_B T} [\psi_j (r) + \psi_j (-r)] .
\]  

(52)
Upon use of the Poisson equations (44) and (45), it follows
\[
\nabla^2 \left[ \psi_j(r) + \psi_j(-r) + \psi_i(r) + \psi_i(-r) \right] = -8\pi e \frac{Dn}{\varepsilon} \left\{ z_j n^2 - \frac{z_j^2 e n^2}{2k_B T} \left[ \psi_j(r) + \psi_j(-r) \right] \right\} - 8\pi e \frac{Dn}{\varepsilon} \left\{ z_i n^2 - \frac{z_i^2 e n^2}{2k_B T} \left[ \psi_i(r) + \psi_i(-r) \right] \right\} = \frac{8\pi e^2 |z_i z_j| n}{D k_B T} \left[ \psi_j(r) + \psi_j(-r) + \psi_i(r) + \psi_i(-r) \right],
\]
which yields
\[
\left( \nabla \cdot \nabla - \frac{\kappa^2}{2} \right) \left[ \psi_j(r) + \psi_j(-r) + \psi_i(r) + \psi_i(-r) \right] = 0. \tag{54}
\]
Note that \( z = |z_i| = |z_j| \). By the boundary conditions
\[
[\psi_j(r) + \psi_j(-r) + \psi_i(r) + \psi_i(-r)] = \text{finite}
\]
or
\[
\psi_j(r) + \psi_j(-r) + \psi_i(r) + \psi_i(-r) = 0. \tag{55}
\]
Therefore there exists a function \( \Gamma(r) \) independently of \( i \) and \( j \) such that
\[
\psi_j(r) + \psi_j(-r) = -[\psi_i(r) + \psi_i(-r)] = 2\Gamma(r). \tag{56}
\]
Here \( \Gamma(r) \) is the even part of the potential. Thus we have now identified the even and odd part of the potential. Therefore we finally obtain
\[
\psi_j(r) = -\psi_i(-r) = \Gamma(r) + Y(r), \tag{57}
\]
\[
\psi_j(-r) = -\psi_i(r) = \Gamma(r) - Y(r). \tag{58}
\]
These are symmetry conditions for ionic potentials.
2. Diagonal Distribution Functions

With conditions (57) and (58) we deduce the diagonal parts of the distribution function matrix

\[ f_{ii}(r) = f_{ii}(-r) = n^2 + \frac{z_i e n^2}{2k_B T} [\psi_i(r) + \psi_i(-r)] = n^2 + \frac{z_i e n^2}{k_B T} \Gamma(r), \]  
\[ f_{jj}(r) = f_{jj}(-r) = n^2 - \frac{z_j e n^2}{2k_B T} [\psi_j(r) + \psi_j(-r)] = n^2 - \frac{z_j e n^2}{k_B T} \Gamma(r). \]  

3. Cross Distribution Functions

It is expected from Eq. (29) that cross distribution functions also consist of even and odd parts. We will write them as

\[ f_{ij}(\mp r) = f_{ji}(\pm r) = n^2 + G(r)\pm U(r). \]  

Before proceeding further we would like to note that in Harned and Owen\[14\] \( n^2 \) is inserted in the even part whereas in Wilson’s thesis the factor \( n^2 \) is absent. If \( f_{ij} \sim n^2 \) as \( r \to \infty \), then the boundary value of \( G(r) \) would be \( G(r) \to n^2 \). If \( f_{ij} \) is a perturbation to the equilibrium distribution function as it is here, there is no need for addition of \( n^2 \). We have put \( n^2 \) in Eq. (61) assuming it is for the entire distribution function.

D. Differential Equations for Even and Odd Parts

Inserting Eq. (61) into Eq. (29), separating the symmetric and antisymmetric parts, and making use of the Poisson equations, we finally obtain four
coupled second-order differential equations for $G$, $U$, $\Gamma$, and $Y$:

\[
\left(\nabla^2 - \frac{1}{2} \kappa^2\right) G(r) - \frac{1}{2} \eta' n^2 \kappa^2 \Gamma(r) = -\mu' \frac{\partial U(r)}{\partial x}, \tag{62}
\]

\[
\left(\nabla^2 - \frac{1}{2} \kappa^2\right) U(r) = -\mu' \frac{\partial G(r)}{\partial x}, \tag{63}
\]

\[
\nabla^2 \Gamma(r) - \frac{\kappa^2}{2} \Gamma(r) = \frac{\kappa^2}{2 n^2 \eta'} G(r), \tag{64}
\]

\[
\nabla^2 Y(r) = \frac{\kappa^2}{2 n^2 \eta'} U(r), \tag{65}
\]

where

\[
\mu' = \frac{z e X}{k_B T}, \tag{66}
\]

\[
\eta' = \frac{z e}{k_B T} \tag{67}
\]

with

\[
z = |z_i| = |z_j|
\]

for binary electrolytes. Solutions of the equations given above would yield the potentials and distribution functions with which to calculate average quantities for the binary electrolyte.

IV. Formal Solutions

Owing to the fact that the external field is applied in the positive $x$ direction the system is axially symmetric. Therefore we will adopt the cylindrical coordinate system with the $x$ direction as the axis of the cylinder. The coordinates are denoted $(x, \rho, \theta)$, where $\theta$ is the azimuthal angle and $\rho$ is the radial coordinate. In this coordinates the Laplacian is given by

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2}. \tag{68}
\]

Because of the axial symmetry, the solutions are independent of angle $\theta$. The angular derivative in $\nabla^2$ therefore can be ignored. The functions $G$, $U$, $\Gamma$, and
Y then depend on \( x \) and \( \rho \) only. We define one-dimensional Fourier transforms of these functions as follows:

\[
\begin{align*}
\left( \begin{array}{c}
G(x, \rho, 0) \\
\Gamma(x, \rho, 0)
\end{array} \right) &= \frac{2}{\pi} \int_0^\infty d\alpha \cos(\alpha x) \left( \begin{array}{c}
g(\alpha, \rho) \\
\gamma(\alpha, \rho)
\end{array} \right), \\
\left( \begin{array}{c}
U(x, \rho, 0) \\
Y(x, \rho, 0)
\end{array} \right) &= \frac{2}{\pi} \int_0^\infty d\alpha \sin(\alpha x) \left( \begin{array}{c}
u(\alpha, \rho) \\
y(\alpha, \rho)
\end{array} \right),
\end{align*}
\]

(69) (70)

where \( \alpha \) is the Fourier transform variable. It should be noted that odd functions \((U,Y)\) are sine transforms whereas the even functions are cosine transforms.

Taking Fourier transforms of Eqs. (62)–(65) according to Eqs. (69) and (70), we obtain differential equations for \( g(\alpha \rho) \), \( \gamma(\alpha \rho) \), \( u(\alpha \rho) \), and \( y(\alpha \rho) \):

\[
\begin{align*}
\frac{1}{\rho} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \alpha^2 - \frac{\kappa^2}{2} g(\alpha, \rho) &= \mu' \alpha g(\alpha, \rho), \\
\left( \frac{1}{\rho} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \alpha^2 - \frac{\kappa^2}{2} \right) g(\alpha, \rho) - \frac{1}{2} \eta' n^2 \kappa^2 \gamma(\alpha, \rho) &= -\mu' \alpha u(\alpha, \rho), \\
\left( \frac{1}{\rho} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \alpha^2 - \frac{\kappa^2}{2} \right) \gamma(\alpha, \rho) &= \frac{\kappa^2}{2n^2 \eta'} g(\alpha, \rho), \\
\frac{1}{\rho} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \alpha^2 \right) y(\alpha, \rho) &= \frac{\kappa^2}{2n^2 \eta'} u(\alpha, \rho).
\end{align*}
\]

(71) (72) (73) (74)

The boundary conditions on potentials are deduced from the boundary conditions already established:

\[
\begin{align*}
\lim_{\rho \to 0} \rho \frac{\partial \gamma(\alpha, \rho)}{\partial \rho} &= -\frac{e}{D}, \\
\lim_{\rho \to 0} \rho \frac{\partial y(\alpha, \rho)}{\partial \rho} &= 0.
\end{align*}
\]

(75) (76)

This set of equations can be solved more concisely if an equivalent eigenvalue problem is solved for the set. However, to remain as close as possible to the original approach, we follow his approach.

Eliminating \( u(\alpha, \rho) \) and \( \gamma(\alpha, \rho) \) between Eqs. (71), (72), and (73) we obtain a fourth-order differential equation

\[
\left( \frac{1}{\rho} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - c^2 \right)^2 g(\alpha \rho) = \left( \frac{1}{4} \kappa^4 - \mu^2 \alpha^2 \right) g(\alpha, \rho),
\]

(77)

\[
c^2 = \alpha^2 + \frac{1}{2} \kappa^2.
\]

(78)
The solution of the homogeneous differential equation of Eq. (77)
\[ \frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} \phi - c^2 \phi = 0, \]  
which is finite at \( \rho = \infty \), is found to be the zeroth-order Bessel function\( K_0 \) of second kind \( K_0 (c\rho) \):
\[ \phi (\rho) = \phi_0 K_0 (c\rho). \]  
Therefore the solution of Eq. (77), \( g(\alpha, \rho) \), must be a linear combination of zeroth-order Bessel functions of second kind. The coefficients are determined as follows: Set
\[ g(\alpha, \rho) = \omega (\alpha) K_0 (\lambda \rho), \]  
where \( \omega (\alpha) \) and \( \lambda \) are determined such that \( \omega (\alpha) K_0 (\lambda \rho) \) is a solution of Eq. (77). On substituting Eq. (81) into Eqs. (77) we find
\[ (\lambda^2 - c^2)^2 = \left( \frac{1}{4} \kappa^4 - \mu^2 \alpha^2 \right) \]  
and the solution for \( \lambda^2 \) is
\[ \lambda_1^2 = c^2 + \frac{1}{2} \kappa^2 R = \alpha^2 + \frac{1}{2} \kappa^2 + \frac{1}{2} \kappa^2 R, \]  
\[ \lambda_2^2 = c^2 - \frac{1}{2} \kappa^2 R = \alpha^2 + \frac{1}{2} \kappa^2 - \frac{1}{2} \kappa^2 R, \]  
where
\[ R = \sqrt{1 - \frac{4\mu^2 \alpha^2}{\kappa^4}}. \]  
The existence of two values of \( \lambda \) implies that the solution for \( g(\alpha, \rho) \) is the linear combination
\[ g(\alpha, \rho) = \omega_1 (\alpha) K_0 (\lambda_1 \rho) + \omega_2 (\alpha) K_0 (\lambda_2 \rho). \]  
Similarly, the functions \( u(\alpha, \rho), \gamma(\alpha, \rho), \) and \( y(\alpha, \rho) \) can be determined as the
linear combinations

\begin{align*}
\gamma (\alpha, \rho) &= \chi_1 (\alpha) K_0 (\lambda_1 \rho) + \chi_2 (\alpha) K_0 (\lambda_2 \rho) + \chi_3 (\alpha) K_0 (\lambda_3 \rho), \\
u (\alpha, \rho) &= \psi_1 (\alpha) K_0 (\lambda_1 \rho) + \psi_2 (\alpha) K_0 (\lambda_2 \rho) + \psi_3 (\alpha) K_0 (\lambda_3 \rho), \\
y (\alpha, \rho) &= \xi_1 (\alpha) K_0 (\lambda_1 \rho) + \xi_2 (\alpha) K_0 (\lambda_2 \rho) + \xi_3 (\alpha) K_0 (\lambda_3 \rho) \\
&\quad+ \xi_4 (\alpha) K_0 (\lambda_4 \rho),
\end{align*}

where

\begin{align*}
\lambda_3^2 &= \alpha^2 + \frac{1}{2}\kappa^2, \\
\lambda_4 &= \alpha.
\end{align*}

The coefficients \(\omega_1 (\alpha), \chi_1 (\alpha), \psi_1 (\alpha), \xi_1 (\alpha),\) etc. are determined on substitution of Eqs. \((85)–(88)\) into Eqs. \((71)–(74)\). Since \(K_0 (\lambda_1 \rho), K_0 (\lambda_2 \rho),\) \(K_0 (\lambda_3 \rho),\) and \(K_0 (\lambda_4 \rho)\) are independent, the aforementioned substitution yields the set of equations for the coefficients:

\begin{align*}
\frac{1}{2}\kappa^2 R \psi_1 (\alpha) - \mu'\alpha \omega_1 (\alpha) &= 0, \\
\frac{1}{2}\kappa^2 R \psi_2 (\alpha) + \mu'\alpha \omega_2 (\alpha) &= 0, \\
\left( \lambda_1^2 - \alpha^2 - \frac{\kappa^2}{2} \right) \omega_1 (\alpha) + \frac{1}{2}\eta n^2 \kappa^2 \chi_1 (\alpha) + \mu'\alpha \psi_1 (\alpha) &= 0, \\
\left( \lambda_2^2 - \alpha^2 - \frac{\kappa^2}{2} \right) \omega_2 (\alpha) + \frac{1}{2}\eta n^2 \kappa^2 \chi_2 (\alpha) + \mu'\alpha \psi_2 (\alpha) &= 0, \\
\frac{1}{2}\eta n^2 \kappa^2 \chi_3 (\alpha) - \mu'\alpha \psi_3 (\alpha) &= 0, \\
\left[ \left( \lambda_1^2 - \alpha^2 - \frac{\kappa^2}{2} \right) \chi_1 (\alpha) - \frac{\kappa^2}{2\eta n^2 \eta'} \omega_1 (\alpha) \right] &= 0, \\
\left[ \left( \lambda_2^2 - \alpha^2 - \frac{\kappa^2}{2} \right) \chi_2 (\alpha) - \frac{\kappa^2}{2\eta n^2 \eta'} \omega_2 (\alpha) \right] &= 0, \\
\left( \lambda_1^2 - \alpha^2 \right) \xi_1 (\alpha) - \frac{\kappa^2}{2\eta n^2 \eta'} \psi_1 (\alpha) &= 0, \\
\left( \lambda_2^2 - \alpha^2 \right) \xi_2 (\alpha) - \frac{\kappa^2}{2\eta n^2 \eta'} \psi_2 (\alpha) &= 0, \\
\left( \lambda_3^2 - \alpha^2 \right) \xi_3 (\alpha) - \frac{\kappa^2}{2\eta n^2 \eta'} \psi_3 (\alpha) &= 0.
\end{align*}
From the boundary conditions follow the equations

\[ \sum_{l=1}^{3} \chi_l(\alpha) = \frac{e}{D}, \quad (101) \]

while since the flow is sourceless and the field is divergenceless it follows

\[ \lim_{\rho \to 0} \frac{\rho}{\rho} \left[ n^2 \eta' \frac{\partial \gamma(\alpha, \rho)}{\partial \rho} \frac{\partial g(\alpha, \rho)}{\partial \rho} \right] = 0, \]

\[ \lim_{\rho \to 0} \frac{\partial u(\alpha, \rho)}{\partial \rho} = 0, \]

which provide additional equations

\[ -n^2 \eta' (\chi_1 + \chi_2 + \chi_3) + \omega_1 + \omega_2 = 0, \quad (103) \]

\[ \psi_1 + \psi_2 + \psi_3 = 0. \quad (104) \]

Therefore on combining Eqs. (101)–(104) we obtain

\[ \chi_1(\alpha) = \frac{e (1 + R)}{2DR^2}, \quad (107) \]

\[ \chi_2(\alpha) = \frac{e (1 - R)}{2DR^2}, \quad (108) \]

\[ \chi_3(\alpha) = (1 - R^2) \frac{e}{DR^2}, \quad (109) \]

There are 13 equations for 12 variables. These equations are first reduced to equations for \( \chi_i \) only. Then all other variables are determined from \( \chi_i \). We obtain
which give rise to the solutions

\[
\omega_1(\alpha) = n^2 \eta e \left(\frac{1 + R}{2DR}\right), \quad \omega_2(\alpha) = -n^2 \eta e \left(\frac{1 - R}{2DR}\right),
\]

\[
\psi_1(\alpha) = n^2 \eta \sqrt{1 - R^2} e \left(\frac{1 + R}{DR^2}\right), \quad \psi_2(\alpha) = n^2 \eta \sqrt{1 - R^2} e \left(\frac{1 - R}{DR^2}\right),
\]

\[
\psi_3(\alpha) = -n^2 \eta \frac{2\alpha \mu'}{\kappa^2} e \left(\frac{1}{DR^2}\right) = -n^2 \eta \sqrt{1 - R^2} e \left(\frac{1}{DR^2}\right),
\]

\[
\xi_1(\alpha) = \sqrt{1 - R^2} e \left(\frac{1}{2DR^2}\right), \quad \xi_2(\alpha) = \sqrt{1 - R^2} e \left(\frac{1}{2DR^2}\right),
\]

\[
\xi_3(\alpha) = -\sqrt{1 - R^2} e \left(\frac{1}{DR^2}\right), \quad \xi_4 = 0.
\]

Finally, the solutions for \(g(\alpha, \rho),\) etc. are obtained:

\[
g(\alpha, \rho) = \frac{n^2 \eta}{D} \left[ \frac{(1 + R)}{2R} K_0(\lambda_1 \rho) - \frac{(1 - R)}{2R} K_0(\lambda_2 \rho) \right], \quad (119)
\]

\[
u(\alpha, \rho) = \frac{n^2 \eta \mu'}{D \kappa^2} \left[ \frac{\alpha (1 + R)}{R^2} K_0(\lambda_1 \rho) + \frac{\alpha (1 - R)}{R^2} K_0(\lambda_2 \rho) - \frac{2\alpha}{R^2} K_0(\lambda_3 \rho) \right], \quad (120)
\]

\[
\gamma(\alpha, \rho) = \frac{e}{D} \left[ \frac{(1 + R)}{2R^2} K_0(\lambda_1 \rho) + \frac{(1 - R)}{2R^2} K_0(\lambda_2 \rho) - \frac{1}{R^2} K_0(\lambda_3 \rho) \right], \quad (121)
\]

\[
y(\alpha, \rho) = \frac{e \mu'}{D \kappa^2} \left[ \frac{\alpha}{R^2} K_0(\lambda_1 \rho) + \frac{\alpha}{R^2} K_0(\lambda_2 \rho) - \frac{2\alpha}{R^2} K_0(\lambda_3 \rho) \right], \quad (122)
\]

with which the Fourier transforms of the final solutions for the distribution functions and potentials can be constructed in the manner of Eqs. (69) and (70). For this purpose it is convenient to define the following abbreviations for
the integrals:

\[ G_1 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{(1 + R)}{2R} \cos (\alpha x) K_0 (\lambda_1 \rho), \quad (123) \]

\[ G_2 (\rho) = -\frac{2}{\pi} \int_0^\infty d\alpha \frac{(1 - R)}{2R} \cos (\alpha x) K_0 (\lambda_2 \rho), \quad (124) \]

\[ U_1 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{\alpha (1 + R)}{R^2} \sin (\alpha x) K_0 (\lambda_1 \rho), \quad (125) \]

\[ U_2 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{\alpha (1 - R)}{R^2} \sin (\alpha x) K_0 (\lambda_2 \rho), \quad (126) \]

\[ U_3 (\rho) = -\frac{2}{\pi} \int_0^\infty d\alpha \frac{2\alpha}{R^2} \sin (\alpha x) K_0 (\lambda_3 \rho), \quad (127) \]

\[ \Gamma_1 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{(1 + R)}{2R^2} \cos (\alpha x) K_0 (\lambda_1 \rho), \quad (128) \]

\[ \Gamma_2 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{(1 - R)}{2R^2} \cos (\alpha x) K_0 (\lambda_2 \rho), \quad (129) \]

\[ \Gamma_3 (\rho) = -\frac{2}{\pi} \int_0^\infty d\alpha \frac{1 - R^2}{R^2} \cos (\alpha x) K_0 (\lambda_3 \rho), \quad (130) \]

\[ Y_1 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{\alpha}{R^2} \sin (\alpha x) K_0 (\lambda_1 \rho), \quad (131) \]

\[ Y_2 (\rho) = \frac{2}{\pi} \int_0^\infty d\alpha \frac{\alpha}{R^2} \sin (\alpha x) K_0 (\lambda_2 \rho), \quad (132) \]

\[ Y_3 (\rho) = -\frac{2}{\pi} \int_0^\infty d\alpha \frac{2\alpha}{R^2} \sin (\alpha x) K_0 (\lambda_3 \rho). \quad (133) \]

The formal solutions for the distribution functions and potentials are given by the forms:

\[ f_{ii} (x) = n^2 + \frac{2Ze^2n^2}{Dk_BT} [\Gamma_1 (\rho) + \Gamma_2 (\rho) + \Gamma_3 (\rho)], \quad (134) \]

\[ f_{jj} (x) = n^2 - \frac{2Ze^2n^2}{Dk_BT} [\Gamma_1 (\rho) + \Gamma_2 (\rho) + \Gamma_3 (\rho)], \quad (135) \]

\[ f_{ij} (\pm x) = f_{ji} (\pm x) = \frac{n^2e\eta}{D} [G_1 (\rho) + G_2 (\rho)] \pm \frac{n^2e\eta\mu'}{Dk_T^2} [U_1 (\rho) + U_2 (\rho) + U_3 (\rho)], \quad (136) \]
and

\[ \psi_j (r) = -\psi_i (-r) \]
\[ = \frac{e}{D} \left[ \Gamma_1 (\rho) + \Gamma_2 (\rho) + \Gamma_3 (\rho) \right] + \frac{e\mu'}{D\kappa^2} \left[ Y_1 (\rho) + Y_2 (\rho) + Y_3 (\rho) \right], \quad (137) \]

\[ \psi_j (-r) = -\psi_i (r) \]
\[ = \frac{e}{D} \left[ \Gamma_1 (\rho) + \Gamma_2 (\rho) + \Gamma_3 (\rho) \right] - \frac{e\mu'}{D\kappa^2} \left[ Y_1 (\rho) + Y_2 (\rho) + Y_3 (\rho) \right]. \quad (138) \]

These formal solutions given in terms of quadratures of the zeroth-order Bessel functions of second kind can be used to calculate various local mean quantities associated with transport in binary electrolyte solutions. Since the Bessel functions are not a trivial function to compute the quadratures with, it is useful to review briefly their mathematical properties we can make use of to evaluate the quadratures in question.

The Bessel function \( K_\nu (z) \) obeys the differential equation\(^{23,24}\)

\[ \left[ \frac{1}{z} \frac{d}{dz} z \frac{d}{dz} - \left( 1 + \frac{\nu^2}{z^2} \right) \right] K_\nu (z) = 0. \quad (139) \]

It is a regular function in complex \( z \) plane cut from \( z = 0 \) to \( z = -\infty \). One of its integral representation is given by

\[ K_\nu (z) = \int_0^\infty dt e^{-z \cosh t} \cosh (\nu t) \left( |\arg z| < \frac{\pi}{2} \right). \quad (140) \]

We will make use of this integral representation. We also note one of the recurrence relations

\[ K'_\nu (z) = -K_{\nu+1} (z) + \frac{\nu}{z} K_\nu (z). \quad (141) \]

Here the prime denotes differentiation with respect to \( z \). This recurrence relation implies

\[ K'_0 (z) = -K_1 (z). \quad (142) \]

In particular, \( K_0 (z) \) may be represented by the ascending series

\[ K_0 (z) = - \left[ \ln \left( \frac{z}{2} \right) + \gamma \right] I_0 (z) + \sum_{i=1}^\infty \left( 1 + \frac{1}{2} + \cdots + \frac{1}{i} \right) \frac{(\frac{z}{2})^{2n}}{(i!)^2}, \quad (143) \]
where $I_0(z)$ is the other independent solution of Eq. (139), which is given by the ascending series

$$I_0(z) = \sum_{i=0}^{\infty} \frac{(z^2)^{2n}}{(i!)^2}. \quad (144)$$

This function is an entire function if the cut $z$ plane. The asymptotic behaviors of $K_0(z)$ and $I_0(z)$ are follows: as $|z| \to \infty$

$$K_0(z) = \sqrt{\frac{\pi}{2z}} e^{-z} \left[ 1 + O(z^{-1}) \right], \quad (145)$$

$$I_0(z) = \sqrt{\frac{1}{2\pi z}} e^z \left[ 1 + O(z^{-1}) \right] \quad (146)$$

for $|\arg z| < \frac{\pi}{2}$. It is useful to note that the presence of $\ln \left( \frac{z}{2} \right)$ in $K_0(z)$ clearly indicates that $K_0(z)$ is not only discontinuous across the branch cut, but also diverges logarithmically as $z \to 0$. If $K_0(z)$ is analytically continued across the cut, we obtain, for example,

$$K_0(e^{i\pi}z) = K_0(z) - \pi i I_0(z). \quad (147)$$

This relation is easily seen to be true from Eq. (143).

Wilson makes use of only Eqs. (142) and (143) to evaluate integrals for the velocity and ionic field, which involve the Bessel functions. This analytically continued form as well as the properties presented above can be made use of for exact evaluation of the quadratures presented in Eqs. (123)–(133), as will be shown elsewhere[19].

V. Electrophoresis

Onsager in his 1927 paper[9] proposed that there exist two effects in electrolytic conduction, one the electrophoretic effect and the other the relaxation time effect. In Ref.[9] the electrophoretic effect was treated by making use of the Stokes law[25] and the relaxation time effect by estimating relaxation time by a heuristic argument[14] first used by J. C. Maxwell. In the Onsager–Wilson theory
the electrophoresis effect is calculated by solving the Navier–Stokes equations\textsuperscript{25} and the time of relaxation effect by calculating the ionic field using the solutions presented in the previous section. In this section, we discuss the electrophoresis effect.

The Navier–Stokes equations\textsuperscript{25} necessary for the calculation of the effect may be cast into the forms

\begin{equation}
\eta_0 \nabla \times \nabla \times \mathbf{v} = -\nabla p + \mathbf{F},
\end{equation}

\begin{equation}
\nabla \cdot \mathbf{v} = 0,
\end{equation}

where \( \mathbf{F} \) is the local external force, \( p \) is the pressure, and \( \eta_0 \) is the shear viscosity of the fluid. In solving these equations Wilson makes the following assumption: the forces exerted by the field due to an ion and the ion atmosphere upon the charges in the ion atmosphere may be neglected, because they are proportional to the square of the charges of the central ion. This means the external forces include forces linearly proportional to the external force \( X \) and the ionic potentials. Therefore

\[ \mathbf{F} = \rho \mathbf{X} \]

and since the charge density \( j \) is described by the Poisson equation

\begin{equation}
F_x = -\frac{DX}{4\pi} \nabla^2 \psi_j (\mathbf{r})
\end{equation}

and the Navier–Stokes equation may be put in the form

\begin{equation}
\eta_0 \nabla \times \nabla \times \mathbf{v} = -\nabla p + \mathbf{F}
\end{equation}

for a binary electrolyte.

To solve Eq. \textsuperscript{151} we look for a vector \( \mathbf{a} \) satisfying

\begin{equation}
\eta_0 \nabla^2 (\nabla^2 \mathbf{a}) = \mathbf{F},
\end{equation}

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where $\mathbf{F}$ is the vector form of Eq. (150). Eliminating $\mathbf{F}$ between Eq. (148) and Eq. (152), we obtain

$$
\eta_0 \nabla \times \nabla \times \mathbf{v} + \nabla p - \eta_0 \nabla^2 (\nabla^2 \mathbf{a}) = 0.
$$

Noting the identity in vector algebra

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

it is possible to express Eq. (153) as

$$
\eta_0 \nabla \times \nabla (\mathbf{v} + \nabla^2 \mathbf{a}) + \nabla \left[ p - \eta_0 \nabla^2 (\nabla \cdot \mathbf{a}) \right] = 0,
$$

but

$$
\nabla \times \nabla \times (\nabla^2 \mathbf{a}) = \nabla \times \nabla \times [\nabla^2 \mathbf{a} - \nabla \mathbf{a}] = -\nabla \times \nabla \times \nabla \nabla \times \mathbf{a},
$$

because

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

Inserting Eq. (155) into Eq. (154), we obtain

$$
\eta_0 \nabla \times \nabla \times (\mathbf{v} - \nabla \times \mathbf{a}) + \nabla \left[ p - \eta_0 \nabla^2 (\nabla \cdot \mathbf{a}) \right] = 0.
$$

Since two terms in Eq. (154) are independent, it is found

$$
\mathbf{v} = \nabla \times \nabla \times \mathbf{a},
$$

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

In Eq. (157) for $\mathbf{v}$, the sign error in Wilson’s thesis is corrected, and $\eta_0$ is also added in Eq. (158). In any case, the solution of Eq. (152) provides the velocity field and the local pressure arising from the local potentials. It, however, should be noted that the solution of the equation

$$
\nabla \left[ p - \eta_0 \nabla^2 (\nabla \cdot \mathbf{a}) \right] = 0
$$
is more generally
\[ p - \eta_0 \nabla^2 (\nabla \cdot \mathbf{a}) = p_0, \]
where \( p_0 \) must be uniform in space in the hydrodynamic scale for the Navier–Stokes equation, so that
\[ \nabla p_0 = 0. \]

Therefore, \( p_0 \) may be regarded as a uniform equilibrium pressure in the absence of the external field. Thus, to be correct, \( p_0 \) is added to Eq. (158). The \( p_0 \) is missing in Wilson’s expression (158) for \( p \). Here \( p_0 \) is the equilibrium pressure of the solution that may be given, for example, by the virial form of pressure:
\[ p_0 = n k_B T - \frac{2 \pi}{3} \sum_{i<j} n_i n_j \int_0^\infty dr r^3 \frac{d u_{ij}}{dr} g_{ij}^0 (r), \]
where \( u_{ij} \) is the intermolecular potential of pair \((i, j)\) and \( g_{ij}^0 (r) \) is the equilibrium pair correlation function. The index \( i \) runs over the species in the fluid, including ions. Determination of \( g_{ij}^0 (r) \) should be made by following the modern theory of equilibrium Coulomb (ionic) fluids.

It is now necessary to find the vector \( \mathbf{a} \) by solving Eq. (152). Since the local force \( F_x \) is a linear combination of the solutions for potentials, it may be written in the form
\[ F_x (x, \rho) = \eta_0 \sum_{i=1}^3 C_i K_0 (\lambda_i \rho) + \eta_0 \sum_{i=1}^3 S_i K_0 (\lambda_i \rho), \]
where \( C_i, S_i, K_0 \) are constants.
where $C_i$ and $S_i$ are integral operators defined in $\alpha$ space as below:

$$
C_1 = -\frac{eX}{2\pi^2\eta_0} \int_0^\infty d\alpha \cos(\alpha x) \frac{(1 + R)(\lambda_i^2 - \alpha^2)}{2R^2},
$$

$$
C_2 = -\frac{eX}{2\pi^2\eta_0} \int_0^\infty d\alpha \cos(\alpha x) \frac{(1 - R)(\lambda_i^2 - \alpha^2)}{2R^2},
$$

$$
C_3 = \frac{eX}{2\pi^2\eta_0} \int_0^\infty d\alpha \cos(\alpha x) \frac{(1 - R^2)(\lambda_i^2 - \alpha^2)}{R^2},
$$

$$
S_1 = -\frac{eX\mu'}{2\pi^2\eta_0\kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \frac{\alpha(\lambda_i^2 - \alpha^2)}{R^2},
$$

$$
S_2 = -\frac{eX\mu'}{2\pi^2\eta_0\kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \frac{\alpha(\lambda_i^2 - \alpha^2)}{R^2},
$$

$$
S_3 = \frac{eX\mu'}{2\pi^2\eta_0\kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \frac{2\alpha(\lambda_i^2 - \alpha^2)}{R^2}.
$$

With $F_x$ so expressed, the equation for the $x$ component of vector $a$, Eq. (152), reads

$$
\nabla^2 (\nabla^2 a_x) = \sum_{i=1}^3 C_i K_0(\lambda_i \rho) + \sum_{i=1}^3 S_i K_0(\lambda_i \rho).
$$

This is solved by

$$
\nabla^2 a_x = \sum_{i=1}^3 (C_i + S_i) \frac{K_0(\lambda_i \rho)}{\lambda_i^2 - \alpha^2} + A^*,
$$

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

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

It must be also a linear combination of $K_0(\lambda_i \rho)$, but since it must satisfy the boundary conditions we choose it in the form

$$
A^* = -\sum_{i=1}^3 (C_i + S_i) \frac{K_0(\alpha \rho)}{\lambda_i^2 - \alpha^2}.
$$

Therefore we have

$$
\nabla^2 a_x = \sum_{i=1}^3 (C_i + S_i) \frac{[K_0(\lambda_i \rho) - K_0(\alpha \rho)]}{\lambda_i^2 - \alpha^2}.
$$

It should be remarked that this solution is opposite in sign to Wilson's. The solution of this equation must be also a linear combination of the Bessel functions $K_0(\lambda_i \rho)$ and $K_0(\alpha \rho)$. Wilson does not make the solution process for this
equation explicit. Here we make it transparent. The solution is sought in the form

\[ a_x = \sum_{i=1}^{3} (C_i + S_i) \frac{1}{\lambda_i^2 - \alpha^2} \{ b_1 [K_0(\lambda_i\rho) - K_0(\alpha\rho)] + b_2 [K_0(\beta_i\rho) - K_0(\alpha\rho)] \}, \]

(168)

where \( \beta \) is a parameter to be determined such that the right hand side is a solution of Eq. (167). On inserting this into Eq. (167) we find

\[
\left[ b_1 \left( \lambda_i^2 - \alpha^2 \right) - 1 \right] K_0(\lambda_i\rho) + b_2 \left( \beta_i^2 - \alpha^2 \right) K_0(\beta_i\rho) + K_0(\alpha\rho) = 0.
\]

Now, \( b_1 \) and \( b_2 \) are chosen such that

\[ b_1 = \frac{1}{\lambda_i^2 - \alpha^2} \]  
(169)

and

\[
\lim_{\beta_i \to \alpha} b_2 \left( \beta_i^2 - \alpha^2 \right) K_0(\beta_i\rho) + K_0(\alpha\rho) = 0,
\]

that is,

\[
\lim_{\beta_i \to \alpha} b_2 \left( \beta_i^2 - \alpha^2 \right) K_0(\beta_i\rho) = -K_0(\alpha\rho).
\]

(170)

Then we find

\[ b_2 = -\frac{1}{\beta_i^2 - \alpha^2}. \]  
(171)

Now, since

\[
\lim_{\beta_i \to \alpha} \frac{1}{\beta_i^2 - \alpha^2} \left[ K_0(\beta_i\rho) - K_0(\alpha\rho) \right] = \frac{1}{2\alpha} \lim_{\beta_i \to \alpha} \frac{[K_0(\beta_i\rho) - K_0(\alpha\rho)]}{(\beta_i^2 + \alpha^2)}
\]

\[ = \frac{\rho}{2\alpha} K_0'(\alpha\rho) \]

\[ = -\frac{\rho}{2\alpha} K_1(\alpha\rho) \]

(172)

in which we have used recurrence relation (142) for the last equality and the prime denotes the derivative with respect to the argument \( \alpha\rho \), we finally obtain the solution of Eq. (167) in the form

\[ a_x = \sum_{i=1}^{3} (C_i + S_i) \left\{ \frac{K_0(\lambda_i\rho) - K_0(\alpha\rho)}{(\lambda_i^2 - \alpha^2)^2} + \frac{\rho K_1(\alpha\rho)}{2\alpha (\lambda_i^2 - \alpha^2)} \right\}. \]

(173)
With this result for $a_x$ it is possible to calculate the velocity by using the expressions

$$\text{div } a = \sum_{i=1}^{3} \left\{ -C_i + S_i \right\} \left\{ \frac{\alpha}{(\lambda_i^2 - \alpha^2)^2} \left[ K_0(\lambda_i \rho) - K_0(\alpha \rho) \right] + \frac{\rho}{2(\lambda_i^2 - \alpha^2)} K_1(\alpha \rho) \right\},$$  \hspace{1cm} (174)

$$\nabla_x \text{div } a = -\sum_{i=1}^{3} \left\{ C_i + S_i \right\} \left\{ \frac{\alpha^2}{(\lambda_i^2 - \alpha^2)^2} \left[ K_0(\lambda_i \rho) - K_0(\alpha \rho) \right] + \frac{\alpha \rho}{2(\lambda_i^2 - \alpha^2)} K_1(\alpha \rho) \right\}. \hspace{1cm} (175)$$

A. Axial Velocity

Inserting the formula for $a_x$ into Eq. (157) and Eq. (158) and making use of Eqs. (174) and (175) we readily obtain the velocity field. The axial velocity is finally obtained as below:

$$v_x(x, \rho, 0) = \frac{eX}{2\pi^2 \eta_0} \int_0^\infty d\alpha \cos(\alpha x) \times$$

$$\left\{ \frac{(1 + R)}{2R^2(\lambda_1^2 - \alpha^2)} \left[ K_0(\lambda_1 \rho) - K_0(\alpha \rho) \right] + \frac{(1 - R)}{2R^2(\lambda_2^2 - \alpha^2)} \left[ K_0(\lambda_2 \rho) - K_0(\alpha \rho) \right] \right\}$$

$$- \frac{eX \mu'}{2\pi^2 \eta_0 \kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \left\{ \frac{\alpha \lambda_1^2}{R^2(\lambda_1^2 - \alpha^2)} \left[ K_0(\lambda_1 \rho) - K_0(\alpha \rho) \right] \right\}$$

$$+ \frac{\alpha \lambda_2^2}{R^2(\lambda_2^2 - \alpha^2)} \left[ K_0(\lambda_2 \rho) - K_0(\alpha \rho) \right]$$

$$- \frac{2\alpha \lambda_3^2}{R^2(\lambda_3^2 - \alpha^2)} \left[ K_0(\lambda_3 \rho) - K_0(\alpha \rho) \right]. \hspace{1cm} (176)$$
in which the integral operators $C_i$ and $S_i$ defined in Eqs. (161) and (162) are made explicit. Further simplifying it, we obtain

$$v_x(x, \rho, 0) = eX \frac{\cos(\alpha x)}{2\pi^2 \eta_0} \int_0^\infty d\alpha \left\{ \frac{1}{\kappa^2 R^2} \left[ \lambda_1^2 K_0(\lambda_1 \rho) + \lambda_2^2 K_0(\lambda_2 \rho) - 2\lambda_3^2 (1 - R^2) K_0(\lambda_3 \rho) \right] - \frac{2\lambda_3^2}{\kappa^2} K_0(\alpha \rho) + \frac{\alpha^2}{2} K_1(\alpha \rho) \right\}$$

$$- eX \frac{\mu'}{2\pi^2 \eta_0 \kappa^2} \int_0^\infty d\alpha \sin(\alpha x) \frac{2\alpha}{\kappa^2 R^2} \left[ \lambda_1^2 K_0(\lambda_1 \rho) + \lambda_2^2 K_0(\lambda_2 \rho) - 2\lambda_3^2 K_0(\lambda_3 \rho) \right].$$

(177)

Since the quantity of interest for electrophoresis is the axial velocity at the center ion (the coordinate origin) Wilson at this point consider the special case of $v_x(x, \rho, 0)$ at $x = 0$ and $\rho = 0$ before fully evaluating the integrals in Eq. (176). That is, if $x = 0$ and $\rho = 0$ are taken, the axial velocity component at the center ion is given by

$$v_x(0, 0, 0) = eX \frac{\cos(\alpha x)}{2\pi^2 \eta_0} \int_0^\infty d\alpha \left\{ - \frac{\lambda_1^2 (1 + R)}{2R^2 (\lambda_1^2 - \alpha^2)} \ln \left( \frac{\lambda_1}{\alpha} \right) - \frac{\lambda_2^2 (1 - R)}{2R^2 (\lambda_2^2 - \alpha^2)} \ln \left( \frac{\lambda_2}{\alpha} \right) + \frac{\lambda_3^2 (1 - R^2)}{R^2 (\lambda_3^2 - \alpha^2)} \ln \left( \frac{\lambda_3}{\alpha} \right) - \frac{1}{2} \right\}. \quad (178)$$

He then evaluates these integrals by using the method of contour in complex $\alpha$ plane. For the purpose it should be noted that

$$\frac{\lambda_1^2 (1 + R)}{2R^2 (\lambda_1^2 - \alpha^2)} = \frac{\kappa^2}{2} \frac{1 + t^2 + \sqrt{1 - 2x^2 t^2}}{1 - 2x^2 t^2},$$

$$\frac{\lambda_2^2 (1 - R)}{2R^2 (\lambda_2^2 - \alpha^2)} = \frac{\kappa^2}{2} \frac{1 + t^2 - \sqrt{1 - 2x^2 t^2}}{1 - 2x^2 t^2},$$

$$\frac{\lambda_3^2 (1 - R^2)}{R^2 (\lambda_3^2 - \alpha^2)} = x^2 \frac{2t^2 (1 + t^2)}{1 - 2x^2 t^2},$$

where

$$x = \frac{\mu'}{\kappa}, \quad t = \frac{\sqrt{2} \alpha}{\kappa}.$$ 

These expressions mean that there are simple poles at $t = \pm 1/(\sqrt{2}x)$ in the
integrands. The arguments of the logarithmic functions have branch points

\[ t = \pm i \sqrt{2(1 + x^2)} \quad \text{for } \lambda_1 \]

\[ t = 0, -\infty \quad \text{for } \lambda_2 \]

\[ t = \pm i \quad \text{for } \lambda_3. \]

Furthermore, the integrands of the first three integrals vanish to zero as \( |t| \to \infty \).

Therefore the first three integrals can be evaluated by applying the method of contour integration. Wilson asserts that the integral of \(-\frac{1}{2}\) for the last term can be replaced by a contour integral \(C\) used for the other integrals and the contour integral vanishes because the integrand is constant and hence

\[ \int_C \frac{dz}{z^2} = 0. \]

Thus the last integral does not contribute to the electrophoretic effect. On this ground, he obtains from Eq. \(178\) the formula for the electrophoretic effect as represented by the formula

\[ v_x(0, 0, 0) = -\frac{Xe\kappa}{6\sqrt{2\pi\eta_0}} f(x) \quad \text{(179)} \]

where

\[
\begin{align*}
f(x) &= 1 + \frac{3}{4\sqrt{2\pi x}} \left\{ 2x^2 \sinh^{-1} x + \sqrt{2}x - x\sqrt{1 + x^2} \\ &\quad - (1 + 2x^2) \tan^{-1} \left( \sqrt{2}x \right) + (1 + 2x^2) \tan^{-1} \frac{x}{\sqrt{1 + x^2}} \right\}. \quad \text{(180)}
\end{align*}
\]

In effect, this result is correct, provided the last integral does not contribute to the electrophoretic effect or negligible. However, as it stands, Eq. \(178\) definitely contains a divergent integral.

In fact, in the case of \( x = 0 \) the integral in Eq. \(176\)

\[ -\int_0^\infty d\alpha \frac{\alpha \rho}{2} K_1(\alpha \rho) \]

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can be exactly evaluated for all values of $\rho > 0$. By using $K_0'(z) = -K_1(z)$ and the integral representation for $K_0(\alpha \rho)$ it is easy to show that
\[
\int_0^\infty d\alpha \alpha K_1(\alpha \rho) = \frac{\pi}{2 \rho^2},
\] (181)
which indicates the integral is singular at $\rho = 0$. Therefore $\rho = 0$ should not be taken within the integral. In fact, if the ions are assumed to be hard spheres as is usually assumed in the treatment of electrolytes—in fact, this is what is done in the Debye–Hückel theory underlying the Onsager theory of conductivity—it may be appropriate to take the mean hard sphere radius, say, $\sigma$ for the minimum value of $\rho$; $\rho = \sigma$ or even $\rho = \kappa^{-1}$, the radius of the ion atmosphere. Then the axial velocity emerges finite for $\sigma \leq \rho < \infty$. But then, it is necessary to evaluate, for example, the integrals for $v_x(0, \sigma, 0)$ with the form
\[
v_x(0, \sigma, 0) = \frac{eX}{2\pi^2\eta_0} \int_0^\infty d\alpha \left\{ \frac{(1 + R) \lambda_1^2}{2R^2 (\lambda_1^2 - \alpha^2)} [K_0(\lambda_1 \sigma) - K_0(\alpha \sigma)] + \frac{(1 - R) \lambda_2^2}{2R^2 (\lambda_2^2 - \alpha^2)} [K_0(\lambda_2 \sigma) - K_0(\alpha \sigma)] - \frac{(1 - R^2) \lambda_3^2}{R^2 (\lambda_3^2 - \alpha^2)} [K_0(\lambda_3 \sigma) - K_0(\alpha \sigma)] \right\} - \frac{3eX}{8\pi\eta_0 \sigma}. \tag{182}
\]
The integrals in this expression, however, cannot be evaluated by the method used by Wilson. It would be straightforward to evaluate the integrals numerically on computer. There then would be an extra contribution to the electrophoretic effect arising from the last term on the right in Eq. (182), and as a matter of fact, the terms associated with $K_0(\alpha \sigma)$ in Eq. (182) all together also contribute
\[-\frac{eX \kappa}{8\pi\eta_0 (\kappa \rho)^3},\]
to the velocity. It also diverges as $\rho \to 0$. If these are evaluated at $\rho = \sigma$ or $\rho = \kappa^{-1}$, they are not negligible at all and hence would modify Wilson’s electrophoretic effect significantly.
It is therefore possible to conclude that Wilson’s result for the electrophoretic effect represents only the nondivergent part with the divergent contribution arbitrarily discarded. This divergence difficulty might have been the underlying reason for not publishing the one-dimensional Fourier transform approach taken in Wilson’s treatment in favor of a full three-dimensional Fourier transform approach that had to wait twenty years until the Onsager-Kim theory \cite{12}; see page 146, section 8, Chapter 4 of Ref.\cite{13}.

VI. Ionic Field

To calculate diffusion of ions it is necessary to know the ionic field of ion \( j \) located at \( x = 0 \)—the center of ion atmosphere. More precisely, we need the contribution to the ionic field arising from the ion atmosphere. It is given by

\[
\Delta X (r) = -\nabla \psi_j (r). \tag{183}
\]

Since \( \psi_j (r) \) is already known it is trivial to compute. Inserting the formula for \( \psi_j (r) \) obtained earlier we find it in the form

\[
\begin{align*}
\Delta X (r) &= -\frac{2e}{\pi D} \nabla \int_0^\infty d\alpha \cos (\alpha x) \left[ \frac{(1 + R)}{2R^2} K_0 (\lambda_1 \rho) + \frac{(1 - R)}{2R^2} K_0 (\lambda_2 \rho) \\
&\quad - \frac{1 - R^2}{R^2} K_0 (\lambda_3 \rho) \right] \\
&\quad \mp \frac{2e\mu'}{\pi DR^2} \int_0^\infty d\alpha \sin (\alpha x) \left[ \frac{\alpha}{R^2} K_0 (\lambda_1 \rho) + \frac{\alpha}{R^2} K_0 (\lambda_2 \rho) \\
&\quad - \frac{2\alpha}{R^2} K_0 (\lambda_3 \rho) \right] \tag{184}
\end{align*}
\]
and hence

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

\[ \mp e_x e \frac{\mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \cos (\alpha x) \left[ \frac{\alpha}{R^2} K_0(\lambda_1 \rho) + \frac{\alpha}{R^2} K_0(\lambda_2 \rho) - \frac{2\alpha}{R^2} K_0(\lambda_3 \rho) \right] \]

\[ - e_\rho e \frac{\mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \alpha \cos (\alpha x) \left[ \frac{(1 + R) \lambda_1}{2R^2} K_1(\lambda_1 \rho) - \frac{(1 - R^2) \lambda_3}{R^2} K_1(\lambda_3 \rho) \right] \]

\[ \mp e_\rho e \frac{\mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \sin (\alpha x) \left[ - \frac{\alpha \lambda_1}{R^2} K_1(\lambda_1 \rho) - \frac{\alpha \lambda_2}{R^2} K_1(\lambda_2 \rho) + \frac{2\alpha \lambda_3}{R^2} K_1(\lambda_3 \rho) \right] \] (185)

Therefore if we set \( x = 0 \) then

\[ \Delta X(0, \rho, 0) = e_x \Delta X_x(0, \rho, 0) \]

\[ = \mp e_x e \frac{\mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \frac{\alpha^2}{R^2} [K_0(\lambda_1 \rho) + K_0(\lambda_2 \rho) - 2K_0(\lambda_3 \rho)] \] (186)

Wilson calculates the force on ion \( j \) in the axial direction by further setting \( \rho = 0 \) in this equation, which then is given by the expression

\[ \Delta X(0, 0, 0) = \pm e_x \frac{e \mu'}{\pi D \kappa^2} \int_0^\infty d\alpha \frac{\alpha^2}{R^2} \ln \left( \frac{\lambda_1^2 \lambda_2^2}{\lambda_3^2} \right) \] (187)

He then evaluates it by integration by parts in the form

\[ \Delta X(0, 0, \theta) = \mp e \frac{\mu' \kappa}{2D} g(x), \] (188)

\[ g(x) = - \frac{1}{2x^2} \left[ -x \sqrt{1 + x^2} + \tan^{-1} \left( \frac{x}{\sqrt{1 + x^2}} \right) + \sqrt{2} x - \tan^{-1} \left( \sqrt{2} x \right) \right] \] (189)

The original formula in Wilson’s thesis is different from this, but this is the formula in the summary of his work given in the monograph\(^{[13]}\) of Harned and Owen. We may verify it by a different integration method as follows. The
integral in Eq. (187) may be written as

\[ I_L \equiv \int_0^\infty d\alpha \frac{\alpha^2}{R^2} \ln \left( \frac{\lambda_1^2 \lambda_2^3}{\lambda_3^3} \right) \]

\[ = \left( \frac{\kappa}{\sqrt{2}} \right)^3 \frac{1}{2\xi^2} \int_0^\infty dt \frac{t^2}{a^2 - t^2} \left[ \ln \lambda_1^2 + \ln \lambda_2^2 - 2 \ln \lambda_3^2 \right]. \]

Using the properties of \( \lambda_i \) given earlier for the axial velocity [see Eqs. (82)–(84) and Eqs. (89)] by applying the method of contour integrations\(^{19}\) similar to those for axial velocity integrals, we obtain

\[ I_L = \frac{\kappa^3}{4\sqrt{2}\xi^2} \left[ - \int_0^{\sqrt{2}(1+\xi)} dt \frac{t^2}{a^2 - t^2} (-\pi i) + 2 \int_0^i dt \frac{t^2}{a^2 - t^2} (-\pi i) \right] \quad (t = \text{complex}) \]

\[ = \frac{\pi \kappa^3}{4\sqrt{2}\xi^2} \left[ \int_0^{\sqrt{2}(1+\xi)} dy \frac{y^2}{a^2 + y^2} - 2 \int_0^{1} dy \frac{y^2}{a^2 + y^2} \right] \]

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

(190)

Here we note that

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

by the addition theorem of tangents. On inserting this integral into Eq. (187), we obtain \( g(\xi) \) as in Eq. (189). The result for \( g(\xi) \) in Eq. (190) agrees with Wilson’s.

This completes the critical review of the calculations of the axial velocity and ionic field and Wilson’s evaluation of \( f(\xi) \) and \( g(\xi) \) on the basis of Onsager’s theory of conductivity. We have pointed out that taking \( \rho = 0 \) within the integrals before they are evaluated can cause a difficulty because of the lack of uniform convergence of some of the integrals. If \( \rho \neq 0 \) then an alternative method of evaluating integrals must be used. An alternative method will be discussed elsewhere\(^{19}\) that yields exact analytical results for the integrals for all values of \( \rho \). This method recovers Wilson’s results as the leading order contributions and the correction terms are at least \( O(\kappa^2 \rho^2) \).
In any case, the axial velocity formula (176) given here does not appear in the existing literature. Our analysis of the axial velocity will start from Eq. (176) in the sequel to this tutorial review article.

VII. Conductance

The total field strength $E$ is given by

$$E = X + \Delta X_j(0),$$  \hspace{1cm} (191)

where $\Delta X_j(0)$ is the field arising from the ion atmosphere interacting with $X$. This term is called the relaxation effect, but in effect it is a local dressed field in the modern terminology. The velocity $v_j$ of ion $j$ in the effective (dressed) field is then given by

$$v_j = e_j\omega_jX \left(1 + \frac{\Delta X_j(0)}{X}\right) + v_x(0,0,0).$$  \hspace{1cm} (192)

Here $v_x(0,0,0)$ is Wilson’s axial velocity. It is useful to remark that the diffusion current (velocity) may be written relative to $v_x(0,0,0)$ as

$$J_j = v_j - v_x(0,0,0).$$  \hspace{1cm} (193)

Then it is seen that the first term on the right of Eq. (193) is the diffusion flux in the absence of a density gradient and that the so-called electrophoresis effect is nothing but the reference velocity suitably chosen in linear irreversible thermodynamic theory, or kinetic theory, of transport processes. In fact, the calculation of $v_x(0,0,0)$ clearly supports this interpretation. Thus inserting the results for $\Delta X_j(0)$ and $v_x(0,0,0)$ we obtain

$$v_j = X \left(e_j\omega_j - \frac{e_j^2\omega_j\mu\kappa}{DX}g(\xi) - \frac{|e_j|\kappa}{6\sqrt{2\pi\eta_0}}f(\xi)\right).$$  \hspace{1cm} (194)

The mobility in electrostatic units is

$$u_j = \frac{|v_j|}{X}$$  \hspace{1cm} (195)
and in practical units

$$u_j = \frac{1}{300} \left( |e_j| \omega_j - \frac{e_j^2 \omega_j \kappa}{DX} g(\xi) - \frac{|e_j| \kappa}{6 \sqrt{2 \pi \eta_0}} f(\xi) \right).$$ \begin{equation} \tag{196} \end{equation}

At infinite dilution $\kappa \rightarrow 0$, and the limiting mobility is given by

$$u_j^0 = \frac{|e_j| \omega_j}{300}$$ \begin{equation} \tag{197} \end{equation}

Since the limiting conductance is

$$\Lambda_j^0 = 964931 u_j^0,$$ \begin{equation} \tag{198} \end{equation}

we have

$$\Lambda_j = \Lambda_j^0 - \frac{e_j^2 \kappa}{Dk_B T} \Lambda_j^0 g(\xi) - \frac{|e_j| \kappa}{6 \times 300 \sqrt{2 \pi \eta_0}} f(\xi).$$ \begin{equation} \tag{199} \end{equation}

With the definition of equivalent conductance

$$\Lambda = \Lambda_+ + \Lambda_- \equiv \Lambda_1 + \Lambda_2,$$

the equivalent conductance for the electrolyte is given by

$$\Lambda(\xi) = \Lambda^0 - \frac{z^2 e^2 \kappa}{Dk_B T} \Lambda^0 g(\xi) - \frac{(|e_1| + |e_2|) \kappa}{6 \times 300 \sqrt{2 \pi \eta_0}} f(\xi).$$ \begin{equation} \tag{200} \end{equation}

In experiment, the relative equivalent conductance

$$\Delta \Lambda(\xi) = \Lambda(\xi) - \Lambda(0)$$ \begin{equation} \tag{201} \end{equation}

is measured and reported. We use the ratio of the relative equivalent conductance

$$\frac{\Delta \Lambda(\xi)}{\Lambda(0)} = \frac{z^2 e^2 \kappa}{Dk_B T} \Lambda^0 g(0) \left[ 1 - \frac{g(\xi)}{g(0)} \right] + \frac{(|e_1| + |e_2|) \kappa}{6 \times 300 \sqrt{2 \pi \eta_0}} f(0) \left[ 1 - \frac{f(\xi)}{f(0)} \right].$$ \begin{equation} \tag{202} \end{equation}

This expression can be used to compute conductance and compare it with experimental data.
VIII. Concluding Remarks

Charged particles in condensed phase in an external electric field are common occurrence in physics, chemistry, and biology. It, especially, is important to comprehend theories of transport properties of such systems and have practical theoretical tools for them from statistical mechanics standpoints. Among the existing theories, the theoretical development initiated a long time ago by Onsager and his collaborators\cite{10,11,12,18} provided useful theoretical models that after complex mathematical treatments have yielded some useful well known analytical results, but his theories have not received critical reviews by other workers that might have stimulated studies for possible further developments in the field and other related fields, which are many currently. His theories should be as relevant today as they were useful when they were developed. Given the power of Onsager’s analytical theories on the subject of electrochemistry, the apparent scarcity of critical follow-up studies of the theories\cite{28,29} is quite curious. The present author sees that there seem to be considerable insights and lessons one can draw from them only if we critically examine the theories and benefit from them for the current topics of interest. Motivated by this thought and their possible utilities of the theories for the currently investigated phenomena in charged condensed matters subjected to external electromagnetic fields, the present author has been studying his theories. In this tutorial review article one of his early work described in Wilson’s PhD thesis has been studied critically and in detail. It is found that it has a difficulty in one respect, but a way out of the difficulty has been found that would improve Wilson’s result for the Wien effect on equivalent conductance. As a preparation for this line of investigation the present author has described a tutorial review of the so-far unpublished theory up to the point where the formal formulas for the axial velocity and ionic field are presented. The details of derivations are given here for
the formulas which are not available in the existing scientific journal literature. The formal formulas mentioned will be treated in full by using an alternative method of evaluation elsewhere\[19\] which should produce exact formulas for the electrophoretic and relaxation time effects for the Wien effect on conductance of binary electrolytes subjected to high external electric field. The results we obtain shows, despite the difficulty in the original evaluation of the integrals by Wilson, his electrophoretic effect appears to be the lowest order contribution, provided that the contributions \(-eX\kappa/8\pi\eta_0 (\kappa\rho) - 3eX\kappa/8\pi\eta_0 (\kappa\rho)^3\) can be set equal to zero or a finite value in some limit. What such a condition or limit would be is not clear at this point unless the velocity expression is fully evaluated in \((x, \rho, \xi)\) space. Only then will Wilson’s result would be properly understood. This aspect will be the subject of the forthcoming work.

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