Microscopic derivation of the Hubbard–Onsager–Zwanzig expression of limiting ionic conductivity

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(Received 28 April 1998; accepted 2 June 1998)

An outstanding problem in the theory of ionic conductivity is a derivation of the well-known Hubbard–Onsager–Zwanzig expression for the dielectric friction on an ion from first principles. In fact, microscopic theories have repeatedly failed to reproduce the Hubbard–Onsager–Zwanzig expression under any limiting conditions. We show in this article that the existing molecular theories and the continuum model treatments calculate two entirely different contributions to the friction on the ion. While the former calculates the contribution from the solvent density mode alone, the latter includes only the contribution from the current mode. Thus the existing molecular theories can never be reduced to the Hubbard–Onsager (H–O) theory. In addition, we show that the existing molecular theories become inconsistent for larger ions where the H–O theory is accurate. The reverse is true for smaller ions. An expression is derived here which is valid at both the limits and for all ion sizes and its consequences discussed. © 1998 American Institute of Physics.

I. INTRODUCTION

The ionic conductivity of a dilute electrolyte solution is usually described by the following well-known Debye–Huckel–Onsager expression

$$\Lambda(\epsilon) = \Lambda_0 - (A + B \Lambda_0) \sqrt{\epsilon},$$  \hspace{1cm} (1)

where $\Lambda_0$ is the limiting ionic conductivity which is obtained by extrapolating the concentration $\epsilon$ to zero, $A$ and $B$ are the two constants determined by the properties of the system.

The limiting ionic conductivity ($\Lambda_0$) is, therefore, determined solely by the ion–solvent interactions. In other words, $\Lambda_0$ is determined by the friction, $\xi$, exerted by the solvent molecules on the ion. The total friction is usually divided into two additive parts. The first is the usual friction due to the viscosity of the medium and is assumed to be given by Stokes law. The second part is assumed to be given by the interaction of the electric field of the ion with solvent polarization and is termed as the dielectric friction ($\xi_{DP}$), a name coined by Born many years ago. However, a theoretical calculation of this dielectric friction has turned out to be a very difficult task. There are several simple expressions that exist in the literature which have been derived through the formulation and analysis of so-called electro-hydrodynamic equations. Two well-known expressions are due to Zwanzig and Hubbard and Onsager. The expression due to Zwanzig is given, for the slip boundary condition, by

$$\xi_{DP,\text{slip}} = \frac{3}{16} \frac{q^2}{R_{\text{ion}}^2} \frac{1 - \epsilon_\infty}{\epsilon_0} \frac{\tau_D}{2 \epsilon_0 + 1},$$  \hspace{1cm} (2)

where $\epsilon_0$ and $\epsilon_\infty$ are the zero and the infinite frequency dielectric constants, respectively, $\tau_D$ is the Debye relaxation time constant of the dipolar solvent, $R_{\text{ion}}$ and $q$ are the radius and the charge of the ion. Zwanzig also obtained the value of the friction for the stick boundary condition where only the prefactor of Eq. (2) increased from 3/16 to 3/8.

In the Hubbard–Onsager (H–O) theory, there are two somewhat different expressions which have been used. The first is a perturbative expression which is of the same form as Zwanzig’s expression, except the prefactors are different and smaller. In the H–O theory, the prefactors are 17/280 and 1/15 for the slip and the stick boundary conditions, respectively. These perturbative expressions, with small prefactors, fail to predict a saturation in the value of the dielectric friction when the ion size becomes smaller than the size of the solvent molecules—a feature termed to be inconsistent with the hydrodynamic calculation. A more thorough analysis of the Hubbard–Onsager equation does yield a saturation effect in the dielectric friction of small ions; however, the underlying physical mechanism involved a rather subtle interplay between electrical and hydrodynamic forces. Subsequently, a more physical expression in terms of viscoelectric effect was derived by Hubbard and Wolynes in terms of a position (from the ion) dependent or local viscosity. This expression gives the desired saturation effect and also a much better agreement with the experimental results for large ions. The basic expression still resembles that of Zwanzig. The problem with small ions, however, remains unsolved. The predicted ion size dependence remains physically unrealistic for small ions.

Recently, a microscopic approach has been developed which proceeds on an entirely different line. Here the dielectric friction is determined by using the force–force correlation function. The final expression is given by a sum of three terms.
\[ \xi_{\text{mol}} = \xi_{\text{bin}} + \xi_{pp} + \xi_{\text{mic,DF}}, \]

where \( \xi_{\text{bin}} \) is the friction due to the binary interaction between the solute and the solvent molecules, the second term, \( \xi_{pp} \) is the contribution to the friction due to the collective solvent number density fluctuation. Detailed expressions for these two terms have recently been presented. It is the third term, \( \xi_{\text{mic,DF}} \), which is of interest in the present study. This term gives the friction due to coupling of the ion with the orientational polarization of the dipolar solvent.\(^6\text{–}^9\) The magnitude of the dielectric friction for small ions appears to be of the right magnitude. A significant aspect of the microscopic theory is that both ultrafast solvation and the self-motion of the ion play important roles in accelerating the relaxation of the frictional force on the ion and thereby in reducing the magnitude of the dielectric friction.\(^9\)

In view of the relative success of the microscopic theory, one asks the following question that has been repeatedly raised in the past. Is it possible to reduce the microscopic expression of the dielectric friction to that of Hubbard–Onsager–Zwanzig? The answer seems to be negative. This is to be contrasted with the case of the rotational dielectric friction where the molecular expression neatly goes over to the continuum model expression under the proper conditions.\(^10\) The failure of the molecular expression to reproduce the correct continuum model expression has remained an enigma in this field.

We show in this article that the existing microscopic theory can never be reduced to the continuum model simply because the two theories calculate two entirely different contributions to the friction. While the continuum model focuses on the contribution arising from the polarization current term, the molecular theories calculate the contribution from the density term. The final expression for the total friction is given by

\[ \frac{1}{\xi} = \frac{1}{\xi_{\text{bin}} + \xi_{pp} + \xi_{\text{mic,DF}}} + \frac{1}{\xi_{\text{hyd}} + \xi_{\text{hyd,DF}}}, \]

where \( \xi_{\text{hyd}} \) and \( \xi_{\text{hyd,DF}} \) are the hydrodynamic friction (without the polar contribution) and the hydrodynamic (polarization current) dielectric friction. A derivation of this term is provided in Sec. III. Note here that the relative contributions of these terms are determined by several factors, the most important being the ion–solvent size ratio. For large ions, the second term in Eq. (4) dominates and one expects to recover the Hubbard–Onsager–Zwanzig expression. For small ions (like Li\(^+\) and Na\(^+\)), on the other hand, the first term dominates and the microscopic expression provides the correct description.

However, there is a serious corollary associated with the above result. In the microscopic theory, the contribution of \( \xi_{\text{bin}} + \xi_{pp} \) is equated with \( 4 \pi \eta_0 R_{\text{ion}} \), where \( \eta_0 \) is the solvent viscosity and \( R_{\text{ion}} \) is the radius of the ion. This is clearly inconsistent, even though for some intermediate size ions (like Cs\(^+\) in water), the two terms are numerically close. This inconsistency becomes glaring for small ions, like Li\(^+\). We shall come back to this point in Sec. IV.

Equation (4) provides the marriage between the two disjoint approaches to limiting ionic conductivity. It clearly shows that the friction on a large ion is dominated by hydrodynamic forces while microscopic solvent fluctuation effects dominate the friction for small ions.

The organization of the rest of the paper is as follows. Section II deals with the strategy of obtaining continuum results from a microscopic theory. Section III contains the derivation of Eq. (4). Finally Sec. IV concludes with a brief discussion of the results.

II. STRATEGY FOR DERIVING CONTINUUM RESULTS FROM MOLECULAR THEORIES

The success of a molecular theory is often judged by its ability to reproduce the correct phenomenological theory. In the present context this implies that the microscopic approach adapted here should be able to reproduce the continuum model results. We shall give two examples here to stress this point. In the case of the dielectric friction on a rotating dipole the microscopic expression could be success-fully reduced\(^10\) to the continuum model expression of Nee–Zwanzig–Hubbard–Wolynes.\(^11\) Another example of such a reduction is provided by molecular hydrodynamics.

The mode-coupling theory expression for the translational friction correctly goes over to the Stokes’ hydrodynamic relation (with the slip boundary condition) when the size of the tagged particle is much larger than that of the solvent molecules.\(^12\text{–}^13\) In all the above cases, the following strategy has been used.

(i) The response of the liquid is Markovian with only one relaxation time. For the case of the rotational dielectric friction, this is the Debyé relaxation time of the dielectric function while in the case of the translational friction, it is the viscous relaxation time of the transverse momentum current autocorrelation function.

(ii) The pair correlation function between the solute and the solvent molecules is replaced by the asymptotic limiting result. For example, for the rotational dielectric friction, it is the dipole–dipole direct correlation function, \( c_{d\leftrightarrow d}(k) \) which is replaced by its asymptotic form. In the Gaskell–Miller\(^12\) reduction of the mode coupling expression to the slip hydrodynamic result, it was the form factor which takes the form of a step function. Subsequently, the same derivation has been carried out in a more microscopic manner where the relevant vertex functions are replaced by simple forms.\(^13\)

(iii) One neglects the self-motion of the solute molecules.

However, this strategy fails completely when one tries to derive the continuum model expressions for the translational friction from the microscopic theory of Wolynes.\(^5\text{,}^7\) As noted by Wolynes himself, the main problem is that the relevant correlation functions vary too strongly for any continuum limit to exist.\(^7\) Earlier, I presented a derivation of Zwanzig’s result by following the strategy outlined above.\(^8\) However, in order to obtain a limiting result, it was necessary to replace the wave vector dependent screening term \( [1 - 1/\varepsilon_\ell(k)] \) by a Lorentzian term of the following form\(^8\)

\[ 1 - \frac{1}{\varepsilon_\ell(k)} = \left( 1 - \frac{1}{\varepsilon_0} \right) \left[ 1 + (k\lambda)^2 \right]^{-1}, \]
where \( \lambda \) is a fitting parameter. Under these approximations one recovers an expression for dielectric friction of the following form: 

\[
\xi_{DF} = \frac{d^2}{3\lambda^3} \left( 1 - \frac{1}{\epsilon_0} \right) \tau_L. \tag{6}
\]

where \( \tau_L \) is the longitudinal relaxation time obtained from the solvent dielectric relaxation parameters as follows: 

\[ \tau_L = (\epsilon_s/\epsilon_0) \tau_D. \]

This expression is close to that of Zwanzig’s.

Note, however, that the above reduction is flawed because \([1 - \epsilon_L(k)^{-1}]\) is an increasing function of \( k \) at small wave numbers! We have presented the above analysis to emphasize the conceptual and analytical difficulty one faces in reducing the microscopic expression to the continuum limit.

III. THE MICROSCOPIC DERIVATION

There are several ways to derive Eq. (4). The simplest one is to appeal to fluctuating hydrodynamics,\(^{14}\) which provide the following equations for the time dependence of the tagged particle number density \( n_s(r,t) \) and the current term \( J(r,t) \)

\[
\frac{\partial n_s}{\partial t} = -\nabla J(r,t), \tag{7}
\]

\[
J(r,t) = -D_{\text{mic}} \nabla n_s(r,t) + J_R(r,t), \tag{8}
\]

where \( D_{\text{mic}} \) is the microscopic diffusion term determined by the short range interactions between the ion and the solvent molecules. The term \( J_R \) is the source of thermal fluctuations which will be neglected here.

Equations (7)–(8) have a nice physical meaning. The position of the tagged particle can change either by interactions with its immediate neighbors, which will cause Brownian motion of the particle, or by the coupling of the particle to the natural currents of the liquid. These two stochastic processes occur at different length scales. While the former is determined primarily by the structural relaxation, and hence by the molecular dynamics, the latter is determined by the usual Navier–Stokes hydrodynamics and hence by the viscosity of the medium. Equation (8) leads to the following decomposition of the self-diffusion coefficient:

\[
D = D_{\text{mic}} + D_{\text{hyd}}. \tag{9}
\]

Note that essentially the same expression has been derived by several workers before.\(^{15,16}\)

It still remains to determine \( D_{\text{mic}} \) and \( D_{\text{hyd}} \) which are the real nontrivial problems. In order to determine them, we turn to the mode-coupling theory which, by itself, also leads to the form given by Eq. (4). The starting point of our derivation is the following expression for the time dependent friction:

\[
\xi(t) = \frac{\beta}{mV} \int d1d2d1'd2' \left[ \hat{q} \cdot \nabla_{\mathbf{r}_1} v(\mathbf{r}_1 - \mathbf{r}_2, \Omega_2) \right] \times G'(12;1'2'|t) \left[ \hat{q} \cdot \nabla_{\mathbf{r}_1} v(\mathbf{r}_1' - \mathbf{r}_2', \Omega_2') \right], \tag{10}
\]

where \( v(\mathbf{r}_1 - \mathbf{r}_2, \Omega_2) \) is the interaction potential between the ion and a dipolar solvent molecule. \( d1 = d\mathbf{r}_1 d\mathbf{p}_1 \) and \( d2 = d\mathbf{r}_2 d\mathbf{p}_2 d\Omega_2 \) where \( \mathbf{r}, \mathbf{p}, \Omega \) denote the position, momentum, and the orientation of either a tagged solute (with subscript 1) or of a dipolar solvent molecule (with subscript 2). \( G'(12;1'2'|t) \) is the resolvent operator which describes the correlated time evolution of the positions and moments of both the tagged particle and the surrounding solvent molecules. That is, as the ion moves from \((\mathbf{r}_1, \mathbf{p}_1)\) at time \( t \) to \((\mathbf{r}_1', \mathbf{p}_1')\) at \( t' \), the solvent molecule at \((\mathbf{r}_2, \mathbf{p}_2, \Omega_2)\) moves to \((\mathbf{r}_2', \mathbf{p}_2, \Omega_2')\). Thus, the Green’s function describes the time evolution of the two particle (coupled solute–solvent) system.

In Eq. (10) \( \hat{q} \) is a unit vector in the laboratory fixed frame \( \beta = (k_B T)^{-1} \). The subsequent steps follow the treatment of Sjogren and Sjolander\(^{17}\) closely. One first separates the binary interaction term. For this derivation we include only the isotropic part of the short range interaction in the binary term. The frictional contribution of this binary term is also nontrivial for continuous potentials but one knows how to deal with it. The rest of the Green’s function is then expanded into the hydrodynamic modes which are the conserved variables. For solutes, they are the density and the momenta as the energy fluctuations are neglected. For the solvent molecules, the number density includes the orientational terms as well.

As stated before, we are neglecting the angular momentum relaxation of the solvent molecules. Therefore, the analysis required here is essentially the same as presented in Ref. 17. The final expression of the friction can be written as

\[
\xi(z) = \xi_{\text{mic}}(z) - \frac{\xi_{\text{mic}}(z)}{\xi_{\text{curr}}(z)} \xi(z), \tag{11}
\]

\( \xi_{\text{mic}}(z) \) is the microscopic friction given by

\[
\xi_{\text{mic}}(z) = \xi_{\text{bin}} + \xi_{\rho\rho}(z) + \xi_{PP}(z). \tag{12}
\]

\( \xi_{\rho\rho}(z) \) is the contribution from the isotropic density fluctuation which would be present even in a nondipolar liquid while \( \xi_{PP}(z) \) is the contribution from the polarization fluctuation. We can now identify \( \xi_{PP} \) with the dielectric friction of the molecular theories, that is, with \( \xi_{\text{DF}} \) of Eq. (3). \( \xi_{\text{curr}}(z) \) is the natural hydrodynamic term containing a contribution from the current flows. Equation (11) can be solved to obtain

\[
\frac{1}{\xi(z)} = \frac{1}{\xi_{\text{mic}}(z)} + \frac{1}{\xi_{\text{curr}}(z)} \tag{13}
\]

This is essentially the same as Eq. (4), so our derivation is over. But we still need to show that all the terms are available and that the current term goes over to the Hubbard–Onsager–Zwanzig form. This is detailed below.

The expression for the two density terms can be obtained directly from the density functional theory, which leads to the following expression of the force density on a tagged ion: \(^{7–9}\)

\[
\mathbf{F}(r,t) = k_B T n_{\text{ion}}(r,t) \nabla \int d\mathbf{r}' d\Omega' c_{id}(\mathbf{r}, \mathbf{r}', \Omega') \delta \rho(\mathbf{r}', \Omega', t). \tag{14}
\]

The frictional contribution can be obtained by using Kirkwood’s formula. This leads to the following expressions for \( R_{\rho\rho} \) and \( R_{PP} \) terms.\(^{9,13,17}\)
\[ R_{pp}(t) = \frac{\rho k_B T}{m(2\pi)^3} \int dk' \left( \dot{k}, \dot{k}' \right)^2 (k')^2 F^3(k', t) \times [\varepsilon^\text{id}(k')]^2 F(k', t), \]
\[ R_{tp}(t) = \frac{2k_B T \rho}{3(2\pi)^2} \int dk k^2 S^\text{ion}(k, t) \left[ \varepsilon^\text{id}(k) \right]^2 S^\text{solvent}(k, t), \]
where \( \varepsilon^\text{id}(k) \) and \( \varepsilon^\text{id}(k) \) are the isotropic and the longitudinal components of the ion–dipole direct correlation functions, respectively. \( S^\text{solvent}(k, t) \) is the orientational dynamic structure factor of the pure solvent. In defining these correlation functions, the wave number \( k \) is taken parallel to the \( z \) axis. \( \rho_0 \) is the average number density of the solvent. \( F_i(k, t) \) denotes the self dynamic structure factor of the ion.

We next calculate the current term. This can again be obtained from the elegant treatment of this term by Gaskell and Miller. The current contribution to the friction can be obtained by projecting the velocity field of the ion on the binary term \( \rho_0 j_k^\text{ion} \), where \( \rho_0 \) is the ion density and \( j_k \) is the current of the liquid. The subsequent steps are well documented—we simply present the final expressions
\[ R_{\text{curr}}(t) = \frac{\beta}{3 \rho(2\pi)^3} \int dk F^3(k) \frac{\mathbf{j}(k)}{k^2} \eta(k, t), \]
where \( \mathbf{j} \) is a form factor which takes into account the finite size of the solvent.

The following steps are now employed in the evaluation of the current term in the hydrodynamic limit:

(i) The current–time correlation function is given by the following simple expression:
\[ C_i(k, t) = C_i(k, t = 0) \exp(-\eta k^2 t), \]
where \( \eta \) is the viscosity of the medium.

(ii) The viscosity of the medium is a sum of two terms. The first term is the usual shear viscosity, \( \eta_0 \), of the pure liquid. The second term is the enhancement of the viscosity due to the presence of the ion. This is a viscoelectric effect. The enhancement of the fluid viscosity is given by the following well-known expression:
\[ \eta = \eta_0 \left[ 1 + \left( \frac{\tau_D}{16\pi \eta_0} \right) (\varepsilon_0 - \varepsilon_s)^2 E^2 \right], \]
where \( E \) is the screened electric field of the ion. The enhanced solvent viscosity in the vicinity of the ion is the picture originally used by Fuoss. This, one has to deal with a position dependent or local viscosity given by
\[ \eta(r) = \eta_0 \left[ 1 + \frac{\tau_D (\varepsilon_0 - \varepsilon_s) q^2}{16 \pi \eta_0 \varepsilon_0^2 q^4} \right]. \]
(iii) Replace the position dependent viscosity \( \eta(r) \) by \( \eta(r = R_\text{ion}) \), that is, by the value at the surface. This approximation can be improved but calls for numerical work which again is not necessary here.

(iv) As mentioned before, neglect the ionic self-motion term, that is, set \( F_i(k, t) \) equal to unity.

We next follow the treatment of Gaskell and Miller to obtain the hydrodynamic approximation of the current term. The following expressions are obtained for the two hydrodynamic boundary conditions
\[ \zeta_\text{curr} = 4\pi \eta R_\text{ion} + \frac{1}{4} q^2 (1 - \varepsilon_0 / \varepsilon_s) \tau_D \eta_0, \]
for the slip boundary condition and
\[ \zeta_\text{curr} = 6\pi \eta R_\text{ion} + \frac{3}{8} q^2 (1 - \varepsilon_0 / \varepsilon_s) \tau_D \eta_0, \]
for the stick boundary condition. Note that a continuum analysis of dielectric friction on an ion which deals with a local viscosity leads essentially to the same equations, as was shown earlier by Stiles and Hubbard.

One can now easily identify the dielectric friction due to the current term. The expressions are identical with the forms obtained by Hubbard and Onsager but with a prefactor which is somewhat larger.

It is possible to carry out a full evaluation of the current term, but at the expense of extensive numerical work because even after making the continuum model-like approximations, we need to solve for the current time correlation function in terms of the position dependent viscosity. When this is done, the value of the friction is expected to decrease and become closer to that of Hubbard and Onsager.

IV. CONCLUSION

In this article we have presented a microscopic derivation of the dielectric friction on a moving ion in a dipolar liquid. The final expression [Eq. (4)] provides a “marriage” between the two different theories of the dielectric friction. Equation (4) is more accurate than either of the two approaches, but calls for the use of proper evaluation of the respective contributions.

What are the consequences of Eq. (4)? First, it provides the much needed description of the crossover from the structural relaxation dominated regime for small ions to the hydrodynamic dominated regime for large ions. In this crossover, all the five terms of Eq. (4) play an important role. This was not appreciated before. Second, the scenario is really interesting for ions with size slightly larger than that of the solvent. For example, the friction on the lower members of quaternary alkyl ammonium ions in water and acetonitrile may involve contribution from both \( \zeta_\text{mic} \) and \( \zeta_\text{hyd} \) terms. One should also consider the implication of Eq. (4) for the time (or frequency) dependence of dielectric friction.

ACKNOWLEDGMENTS

The author thanks Dr. Joe Hubbard for an interesting discussion where he suggested that the author should look for a marriage between the two theoretical approaches. The author is also grateful to Professor Peter Wolynes for several discussions. He is particularly thankful to Ranjit Biswas who has collaborated with him on much of the work on ionic mobility. This work was supported in part by grants from CSIR and DST, India.


