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Derivation from the Liouville Equation of the Fuoss-Onsager Theory of Ionic Conductivity

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Recent advances in the theory of Brownian motion are used to derive the Fuoss-Onsager theory of the conductivity of ionic solutions from the Liouville equation for N solvent particles and two heavy Brownian particles. The Fuoss-Onsager theory is shown to be sufficiently accurate to give the correct value of the conductivity through order $c \ln c$ in the concentration c ; however, it is seen that the Fuoss-Onsager theory does not take into account some terms which affect the conductivity to first order in the concentration.

INTRODUCTION

The Fuoss-Onsager theory¹⁻⁸ of ionic solutions rests on a number of *ad hoc* assumptions which must be carefully checked on the basis of the microscopic theory of fluids. The Fuoss-Onsager theory utilizes the "primitive" model of the ionic solution, in which the ions are considered as charged hard spheres moving in a structureless, incompressible fluid characterized only by its dielectric constant ϵ and its viscosity η . The theory results in an expression for the equivalent conductivity Λ of the form

$$\Lambda = \Lambda_0 + \Lambda_1(c)^{1/2} + \Lambda_2 c \ln c + \Lambda_2 c + \dots, \quad (1)$$

where c is the ionic concentration. The concentration dependent terms of lower than first order in c are due to the long-range nature of the Coulomb potential among the ions; short-range effects do not influence the coefficients Λ_1 and Λ_2 .

In the context of the primitive model, the Fuoss-Onsager theory rests on the fundamental assumption that in the presence of a weak homogeneous external field, the drift velocity $V_{i,j}(\mathbf{r}_1; \mathbf{r}_2)$ of an ion of species i located at \mathbf{r}_1 in the vicinity of an ion of species j located at \mathbf{r}_2 is given by

$$V_{i,j} = V_{i,j}^s + D_i(\mathbf{F}_{i,j}/kT - \nabla_i \ln n_{ij}), \quad (2)$$

where $V_{i,j}^s$ is the velocity of the solvent at \mathbf{r}_1 , $\mathbf{F}_{i,j}$ is the average force on ion i in the presence of ion j , ∇_i is the gradient with respect to \mathbf{r}_1 , and $n_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ is the pair distribution function for ions i and j . The diffusion constant D_i for ions of species i is assumed

to be given by the Einstein relation $D_i = kT\omega_i$, where ω_i is the mobility of ion i in the solvent. The assumption (2) is *not* in general valid; the Einstein relation does not apply to the case in which ion i interacts with ion j , either directly or through the interaction of both ions with the solvent. In this case the diffusion constant should properly be replaced by the diffusion tensor, which depends on the vector $\mathbf{r}_1 - \mathbf{r}_2$ as well as on the characteristics of ions i and j . However, as we will see below, the *ad hoc* addition of the solvent velocity to the diffusion term in Eq. (2) results in correct values for the coefficients Λ_0 , Λ_1 , and Λ_2 in Eq. (1).

THE PAIR CONTINUITY EQUATION

Using projection operator techniques, Mazo⁹ has derived from the Liouville equation for N fluid particles and two Brownian particles a kinetic equation of the Fokker-Planck type:

$$\begin{aligned} (\partial f_2 / \partial t) + \sum_{j=1,2} (\mathbf{p}_j / m_j \cdot \nabla_j + \mathbf{F}_j \cdot \partial / \partial \mathbf{p}_j) f_2 \\ = kT \sum_{i,j=1,2} (\partial / \partial \mathbf{p}_i) \cdot \boldsymbol{\xi}_{ij} \cdot [(\partial / \partial \mathbf{p}_j) + (\mathbf{p}_j / m_j kT)] f_2. \end{aligned} \quad (3)$$

Here $f_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t)$ is the pair distribution function for the positions and momenta of the two Brownian particles, \mathbf{F}_j is the force on Brownian particle j averaged over the phases of the fluid particles, and the $\boldsymbol{\xi}_{ij}$ are the friction tensors for the Brownian particles moving in the fluid. Equation (3) is valid for times sufficiently large so that f_2 is independent of the arbitrary initial phases of the fluid particles, and applies to Brownian

particles whose mass is very large compared with the mass of the fluid particles.

Using a method of the Chapman-Enskog type, Aguirre and Murphy¹⁰ have obtained from Eq. (3) a diffusion equation for the space distribution function $n_2(\mathbf{r}_1, \mathbf{r}_2; t)$ of the Brownian particles:

$$\partial n_2 / \partial t = \sum_{i,j=1,2} \nabla_i \cdot \mathbf{D}_{ij} \cdot [\nabla_j - (\mathbf{F}_j / kT)] n_2 \quad (4)$$

with

$$\mathbf{D}_{11} = kT(\xi_{11} - \xi_{12} \cdot \xi_{22}^{-1} \cdot \xi_{21})^{-1},$$

$$\mathbf{D}_{12} = kT(\xi_{21} - \xi_{22} \cdot \xi_{12}^{-1} \cdot \xi_{11})^{-1},$$

$$\mathbf{D}_{21} = kT(\xi_{12} - \xi_{11} \cdot \xi_{21}^{-1} \cdot \xi_{22})^{-1},$$

$$\mathbf{D}_{22} = kT(\xi_{22} - \xi_{21} \cdot \xi_{11}^{-1} \cdot \xi_{12})^{-1}.$$

Equation (4) is valid for times sufficiently large so that the distribution function $f_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t)$ depends on time only through the time dependence of the space distribution function $n_2(\mathbf{r}_1, \mathbf{r}_2; t)$, and for the case in which the fractional spatial gradients of f_2 and of the average potential felt by the Brownian particles are small over a distance of the order of a Brownian particle-fluid particle mean free path. In particular, Eq. (4) is *not* valid when the two Brownian particles are so close together that their interparticle potential cannot be assumed uniform over a distance of the order of the Brownian-fluid mean free path. For the case of particles moving slowly in an incompressible viscous fluid, Aguirre and Murphy found explicit expressions for the diffusion tensors \mathbf{D}_{ij} to first order in the ratio of the characteristic hydrodynamic radius of the particles to the interparticle distance r_{12} :

$$\mathbf{D}_{ii} = (kT\omega_i)\mathbf{I} = D_i\mathbf{I}; \quad \mathbf{D}_{12} = \mathbf{D}_{21} = kT\mathbf{T}. \quad (5)$$

Here \mathbf{I} is the unit tensor, and the Lorentz tensor \mathbf{T} is given by

$$\mathbf{T} = (8\pi\eta r_{12})^{-1}[\mathbf{I} + (\mathbf{r}_{12}\mathbf{r}_{12}/r_{12}^2)],$$

where η is the viscosity of the solvent.

Inserting Eq. (5) in Eq. (4), we obtain in the steady state

$$\begin{aligned} \nabla_1 \cdot [D_1(\nabla_1 - \mathbf{F}_1/kT)n_2 + \mathbf{T} \cdot (kT\nabla_2 - \mathbf{F}_2)n_2] \\ + \nabla_2 \cdot [D_2(\nabla_2 - \mathbf{F}_2/kT)n_2 + \mathbf{T} \cdot (kT\nabla_1 - \mathbf{F}_1)n_2] = 0. \end{aligned} \quad (6)$$

In the Fuoss-Onsager theory, the pair continuity equation is given by

$$\nabla_1 \cdot (\mathbf{V}_{i,j}n_2) + \nabla_2 \cdot (\mathbf{V}_{j,i}n_2) = 0,$$

where $\mathbf{V}_{i,j}$ is given by Eq. (2). With the appropriate change of notation, this is identical with Eq. (6), provided that we make the identification

$$\mathbf{V}_{i,j} = \mathbf{T} \cdot (kT\nabla_j \ln n_2 - \mathbf{F}_j). \quad (7)$$

Equation (5) is valid to first order in $1/r_{12}$; to this order, and also to lowest order in the concentration and the external field, Eq. (7) gives for the radial

component of $\mathbf{V}_{i,j}$ ⁸

$$(\mathbf{V}_{i,j})_r = e_i X \cos\theta / 4\pi\eta r_{12},$$

where e_i is the charge on an ion of species i , X is the magnitude of the external field, and θ is the angle between \mathbf{r}_{12} and the direction of the external field. This result is identical to that found by Fuoss.⁸

In the Fuoss-Onsager theory the external field is considered to be sufficiently weak so that the pair distribution function may be set equal to the known equilibrium pair distribution function plus a small perturbation proportional to the strength of the external field, and explicit expressions are used for the forces $\mathbf{F}_{i,j}$ in terms of the pair distribution function. The pair continuity equation can then be solved for the perturbed pair distribution function, and the resulting pair distribution function can be used to calculate the conductivity. When this is done, it is seen that $\mathbf{V}_{i,j}$ ⁸ does not affect the value of the conductivity coefficient Λ_1 in Eq. (1), and that only the leading term in $1/r_{12}$ affects the coefficient Λ_2 . Thus we see that the statistical-mechanical theory of N solvent particles and two heavy Brownian particles reproduces the Fuoss-Onsager results for those terms in the pair distribution function which affect the conductivity through order $c \ln c$ in the concentration, without assuming the validity of the Einstein relation for interacting Brownian particles or treating the "velocity of the solvent" in a separate manner on phenomenological *ad hoc* grounds. The exact treatment, however, does not reproduce the Fuoss-Onsager results for those terms in the pair distribution function which affect only Λ_2 and higher order terms in the conductivity; this will be discussed in more detail further on.

THE CONDUCTIVITY EQUATION

The equivalent conductivity Λ of an ionic solution is given by

$$\Lambda = (F/X) \sum_i |e_i| V_{i,z} / e_i, \quad (8)$$

where F is Faraday's constant and $V_{i,z}$ the average velocity in the field direction of an ion of species i . The average velocity \mathbf{V}_i of an ion of species i is given by

$$\mathbf{V}_i = \int d\mathbf{r}_2 \sum_j n_{ij} \mathbf{V}_{i,j} / n_i, \quad (9)$$

where $n_i(\mathbf{r}_1) \equiv \int d\mathbf{r}_2 \sum_j n_{ij}(\mathbf{r}_1, \mathbf{r}_2)$.

To first order in $1/r_{12}$, the pair continuity equation together with Eqs. (4) and (5) give in our notation

$$n_{ij} \mathbf{V}_{i,j} = \omega_i (\mathbf{F}_{i,j} - kT\nabla_i) n_{ij} + \mathbf{T} \cdot (\mathbf{F}_{j,i} - kT\nabla_j) n_{ij}.$$

Equation (9) then becomes

$$\begin{aligned} \mathbf{V}_i = (\omega_i / n_i) \int d\mathbf{r}_2 \sum_j \mathbf{F}_{i,j} n_{ij} - kT(\omega_i / n_i) \nabla_i \int d\mathbf{r}_2 \sum_j n_{ij} \\ + (1/n_i) \int d\mathbf{r}_2 \mathbf{T} \cdot \sum_j (\mathbf{F}_{j,i} - kT\nabla_j) n_{ij}. \end{aligned}$$

Since in this case the over-all density of each species is uniform, $\nabla n_i = 0$ and we have

$$\mathbf{V}_i = \omega_i \mathbf{F}_i + (1/n_i) \int d\mathbf{r}_2 \mathbf{T} \cdot \sum_j (\mathbf{F}_{j,i} - kT \nabla_j) n_{ij},$$

where \mathbf{F}_i is the average force on an ion of species i . For the component of \mathbf{V}_i in the field direction we find

$$V_{i,z} = \omega_i F_{i,z} + \int d\mathbf{r}_2 (8\pi\eta n_i r_{12})^{-1} (\hat{\mathbf{i}} + \hat{\mathbf{r}} \cos\theta) \cdot \sum_j (\mathbf{F}_{j,i} - kT \nabla_j) n_{ij}, \quad (10)$$

where $\hat{\mathbf{i}}$ and $\hat{\mathbf{r}}$ are unit vectors in the field direction and the \mathbf{r}_{12} direction, respectively. n_{ij} and thence $F_{i,z}$ and $\mathbf{F}_{j,i}$ are calculated from the pair continuity equation and inserted in Eq. (10), and $V_{i,z}$ is then inserted in Eq. (8) to give the conductivity. Equation (10) is identical to the result of Fuoss and Onsager; the term $\omega_i F_{i,z}$ contains the terms they refer to as the "relaxation" and "osmotic" terms, while the second term in Eq. (10) is referred to by Fuoss and Onsager as the "electrophoresis" term. However, Fuoss and Onsager add on the electrophoresis term on phenomenological *ad hoc* grounds, whereas in the present approach it appears directly from the Liouville equation for two heavy Brownian particles and N solvent particles, and is treated in the same way as all other terms. The integrand in Eq. (10) is accurate to first order in $1/r_{12}$; evaluation of the integral shows that this is the only term that contributes to the coefficients Λ_1 and Λ_2 in Eq. (1); however, terms of higher order in $1/r_{12}$ which do not appear in Eq. (10) or in the Fuoss-Onsager theory will contribute to Λ_2 .

LIMITATIONS OF THE FUOSS-ONSAGER THEORY

Starting from the Liouville equation for two Brownian particles and N solvent particles, we have rederived those terms in the Fuoss-Onsager theory of ionic conductivity which affect the coefficients Λ_1 and Λ_2 in Eq. (1). In principle, evaluation of all terms which contribute to Λ_2 would require that Eq. (5) be replaced by a hydrodynamic expression valid to all orders in $1/r_{12}$. However, there is a more fundamental problem in the evaluation of Λ_2 . Equation (4) is not valid if particle two is so close to particle one that the interparticle distance is of the same order as a Brownian particle-solvent particle mean free path; in fact, in this case Eq. (3) for $f_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t)$ cannot be reduced to *any* equation for $n_2(\mathbf{r}_1, \mathbf{r}_2; t)$ alone. Thus there is an unknown correction to the pair distribution

function when particle two is within a small, fixed volume containing particle one; the size of this volume is independent of concentration. As the *a priori* probability that particle two lies within this volume is proportional to the concentration, the contribution of this correction to the conductivity will be of first order in the concentration. The coefficients Λ_1 and Λ_2 thus remain unaffected by this difficulty; indeed, they are not affected by any changes in the system that are "short range" in this sense, such as changes in the assumed hard-core diameter of the ions or in the hydrodynamic boundary conditions at the surface of an ion. However, it should be noted that the derivation of the Fuoss-Onsager theory for Λ_1 and Λ_2 is dependent upon the assumption that the mass of the ions is large compared to the mass of the solvent molecules.

CONCLUSION

The Fuoss-Onsager theory utilizes the scalar one-particle diffusion relation rather than the tensorial two-particle diffusion relation to express the time rate of change of the two-particle distribution function. We have shown that this is compensated for by the *ad hoc* addition of terms representing the "velocity of the solvent," the resulting theory giving the same results as the exact theory through order $c \ln c$ in the concentration. Higher order terms in the concentration, however, are not given exactly by the Fuoss-Onsager theory.

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