Ionic Self-Diffusion in Concentrated Aqueous Electrolyte Solutions

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A self-consistent microscopic theory is developed to understand the anomalously weak concentration dependence of ionic self-diffusion coefficient D_{ion} in electrolyte solutions. The self-consistent equations are solved by using the mean spherical approximation expressions of the static pair correlation functions for unequal sizes. The results are in excellent agreement both with the known experimental results for many binary electrolytes and also with the *new* Brownian dynamics simulation results. The calculated velocity time correlation functions also show quantitative agreement with simulations. The theory also explains the reason for observing different D_{ion} in recent NMR and neutron scattering experiments.

Even after many decades of study, there is still no satisfactory theory of self-diffusion of ions in electrolyte solutions, except perhaps at very low concentrations. In this limit, Onsager [1], in 1945, described a simple theory of self-diffusion coefficients which was essentially an extension of Debye-Huckel ion atmosphere model. The theory includes the relaxation effect well-known in the conductivity theory. Onsager's general equation for ion self-diffusion coefficient is given by the following well-known expression:

$$D_{\text{ion}} = D_{\text{ion}}^0[1 - Z_i^2 L_B(\kappa - \kappa_{\text{di}})/3] \qquad (1)$$

with

$$\kappa_{\text{di}} = 4\pi L_B \sum_j c_j Z_j^2 \frac{D_j^0}{D_i^0 + D_j^0}, \qquad (2)$$

where L_B is the Bjerrum length and κ is the Debye inverse length. Z_i, D_i^0, and c_i are, respectively, the charge, the infinitely diluted solution self-diffusion coefficient, and the concentration of species i. Onsager's limiting law has been tested experimentally and found to be valid below concentrations of about 0.01 M [2].

It is well-known that Onsager's treatment was phenomenological—the use of Debye-Huckel theory itself was a serious limitation. Onsager's treatment has been extended by using more realistic ion-ion pair correlation functions, but the existing theories all fail to provide a satisfactory description of the concentration dependence of self-diffusion coefficient [3]. There is also no quantitative theory of ionic velocity time correlation function (IVCF). A quantitative understanding of ionic self-diffusion coefficients and of IVCF in electrolyte solution [4,5] is a fundamental problem which has wide ranging applications to problems of many disciplines of natural and biological sciences [6–9].

There are now compelling reasons for developing a microscopic theory of self-diffusion of concentrated electrolyte solutions. First, accurate pair correlation functions

for *unequal* ion sizes have become available recently [10]. Second, "smart" Monte Carlo technique has been combined with Brownian dynamics simulations to give accurate values not only of self-diffusion but also of the velocity correlation functions [11]. Last, the well-known mode coupling theory (MCT) [12,13] has been extended recently to treat electrical conductivity [14,15].

In this Letter we develop such a theory to calculate the effects of the ion atmosphere relaxation at finite frequency by using the mode coupling theory. The theory provides nearly quantitative agreement with all the known experimental and simulated results. The agreement with simulated velocity correlation function is also excellent. We believe that this is the first quantitative microscopic theory of self-diffusion of ions in concentrated solutions.

We next describe the theoretical formalism. There are several nontrivial aspects of this problem. First, we need to translate the ion-ion interaction (the classical ion atmosphere) term to a time correlation function formalism. Second, we need to describe the interplay between the single particle and the collective dynamics. Third, we need to develop a self-consistent theory for collective dynamics. The last two are dealt with by formulating a MCT theory. We start with an electrolyte solution consisting of positive and negative ions immersed in a continuum solvent of dielectric constant ϵ. The ions interact through a spherically symmetric short-range potential and a long-range Coulombic interaction potential which is scaled by the value of the dielectric constant. The pair potential of interaction between two ions of charge q_α and q_β is given by

$$u_{\alpha,\beta}(r) = u_{\alpha\beta}^{\text{SR}}(r) + \frac{q_\alpha q_\beta}{\epsilon r}, \qquad (3)$$

where r is the distance between the two ions and $u_{\alpha\beta}^{\text{SR}}(r)$ is a spherically symmetric short-range interaction potential. This so-called primitive model is well known in the studies of structure and dynamics of electrolyte solutions [16]. Throughout this paper, we label the positive ions as species

1 and the negative ions as species 2. We denote the position ($\mathbf{r}$) and time (t) dependent number density of species α as $\rho_\alpha(\mathbf{r}, t)$ and its Fourier transform $\rho_\alpha(\mathbf{k}, t)$ is defined by

$$\rho_\alpha(\mathbf{k}, t) = \int_{-\infty}^{\infty} d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} \rho_\alpha(\mathbf{r}, t). \tag{4}$$

As we are interested in calculating the frequency dependent friction on a moving ion, we consider a single tagged ion of charge q_s. The velocity of the tagged ion is $v_s(t)$ at time t. Its time evolution can be described by the following generalized Langevin equation:

$$\frac{\partial}{\partial t} v_s(t) = -\int_0^{\infty} dt' \, \zeta_s(c, t - t') v_s(t') + f_s(c, t), \tag{5}$$

where $\zeta_s(c, t)$ is the total friction acting on the single tagged ion and $f_s(c, t)$ is the random force. The frequency dependent friction $\zeta_s(c, \omega)$ is defined as the Fourier-Laplace transform of $\zeta_s(c, t)$,

$$\zeta_s(c, \omega) = \int_0^{\infty} dt \, e^{i\omega t} \zeta_s(c, t). \tag{6}$$

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

$$D_{\text{ion}}(\omega) = \frac{k_B T}{m} [-i\omega + \zeta_s(c, \omega)]^{-1}, \tag{7}$$

where m is the mass of the tagged ion.

The friction on the ion is now divided into two parts:

$$\zeta_s(c, t) = \zeta_{\text{SR}} + \delta\zeta(c, t), \tag{8}$$

where ζ_{SR} is the friction from the short-range interactions and $\delta\zeta(c, t)$ is the electrolyte friction which we calculate by mode coupling theory. According to the latter, the electrolyte friction acting on the tagged ion can, on rather general terms, be decomposed into two parts [12,13]. The first part is due to the microscopic interaction of the tagged ion with the surrounding (Debye-Huckel) ion atmosphere, and the second part originates from the hydrodynamic coupling of the velocity of the tagged ion with the charge current mode of the surrounding ions [14]. It has been shown by the mode coupling theory that a small neutral solute's diffusion in nonpolar liquid is dominated by the microscopic term only, that is, by the terms which arise from collisional contributions and density fluctuations [12,13]. The situation for electrolyte friction turns out to be no different, but for an entirely different reason, as discussed below.

The microscopic friction is most easily analyzed by using the Kirkwood's formula for friction which expresses it in terms of an integration over the force-force time correlation function [16].

$$\delta\zeta_{s,mic}(c, t) = \frac{1}{3k_B T} \int d\mathbf{r} \, \langle F(\mathbf{r}, t) F(\mathbf{r}, 0) \rangle, \tag{9}$$

where $F(\mathbf{r}, t)$ is the time dependent force exerted on the tagged ion due to its interaction with all other ions in the solution. An expression for $F(\mathbf{r}, t)$ can be obtained from time dependent density functional theory, and the micro-

scopic friction can be formally expressed as an integral over the wave-vector space in the following form:

$$\delta\zeta_{s,mic}(c, t) = \frac{k_B T}{3(2\pi)^3} \sum_{\alpha,\beta} \int d\mathbf{k} \, k^2 c_{s\alpha}(k) \sqrt{\rho_\alpha \rho_\beta}$$
$$\times G_{\alpha\beta}(k, t) c_{s\beta}(k) F_s(k, t), \tag{10}$$

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

$$G_{\alpha\beta}(k, t) = (N_\alpha N_\beta)^{-1/2} \langle \rho_\alpha(\mathbf{k}, t) \rho_\beta(-\mathbf{k}, 0) \rangle, \tag{11}$$

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

$$G_{\alpha\beta}(k, \omega) = [-i\omega + D_\alpha(\omega)k^2]^{-1} S_{\alpha\beta}(k)$$
$$+ \frac{D_\alpha(\omega)k^2}{-i\omega + D_\alpha(\omega)k^2} \sum_{\gamma=1}^{2} \sqrt{\rho_\alpha \rho_\gamma}$$
$$\times c_{\alpha\gamma}(k) G_{\gamma\beta}(k, \omega), \tag{12}$$

where the frequency dependent diffusion coefficient $D_\alpha(\omega)$ is related to friction by Eq. (7). $S_{\alpha\beta}(k) = G_{\alpha\beta}(k, t = 0)$ where $S_{\alpha\beta}(k)$ is the partial static structure factor between species α and β. $S_{\alpha\beta}(k)$ is related to the Fourier transform of the pair correlation function $h_{\alpha\beta}(k)$ by the following relation:

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + \sqrt{\rho_\alpha \rho_\beta} \, h_{\alpha\beta}(k). \tag{13}$$

The four coupled equations ($\alpha, \beta = 1, 2$) as given by Eq. (12) can be solved analytically to obtain the frequency dependence of the ionic Van Hove functions. Note that the Laplace transform of the self-dynamic structure factor of the tagged ion is related to the frequency dependent diffusion by the following relation:

$$F_s(k, \omega) = \frac{1}{-i\omega + D_{\text{ion}}(\omega)k^2}. \tag{14}$$

Thus, the MCT equations need to be solved self-consistently [17]. We still require the solutions of the static structure factors and the direct correlation functions for the calculation of the microscopic electrolyte friction. The direct correlation functions are related to the static structure factors by the Ornstein-Zernike equations. The solutions of the pair correlation functions required for the calculation of the quantities $S_{\alpha\beta}(k)$ and $c_{s\alpha}(k)$ have been obtained from the solution of the mean spherical approximation (MSA) [18] by the formula

$$h_{\alpha\beta}(k) = -\frac{4\pi}{k} \mathcal{I}_m \tilde{G}_{ij}(ik), \tag{15}$$
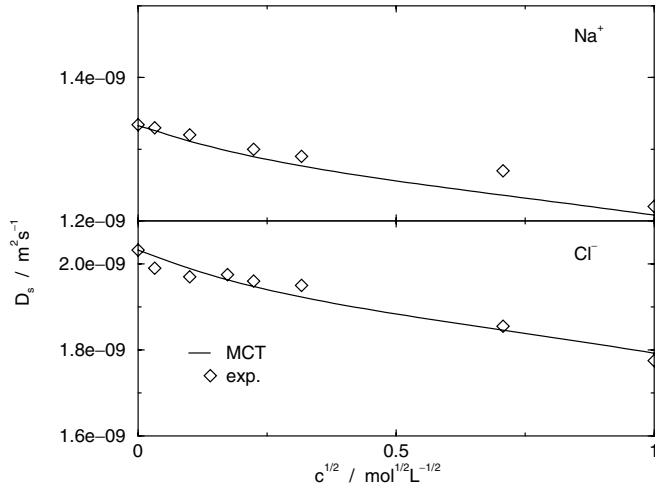
FIG. 1. Self-diffusion coefficient of Na^+ (upper) and Cl^- (below) in NaCl solution. Comparison between self-consistent MCT (solid line) and experiments (diamonds).
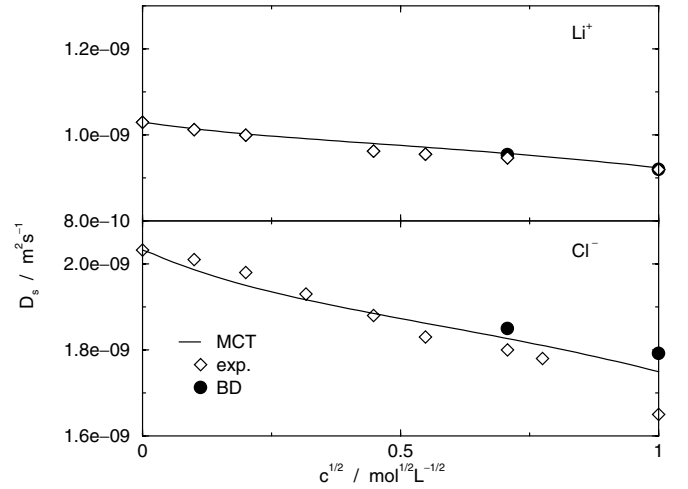

FIG. 2. Self-diffusion coefficient of Li^+ (upper) and Cl^- (below) in NaCl solution. Comparison between self-consistent MCT (solid line), Brownian dynamics (circles), and experiments (diamonds).

where $\tilde{G}_{ij}$ is the Laplace transform used in the Baxter-Wertheim factorization method for charged systems [19]. We considered the whole analytical solution of the MSA with different sizes so that the Stillinger-Lovett sum rule is exactly verified.

We particularly studied three dissociated electrolytes KCl, LiCl, NaCl up to 1 M. The experimental data have been taken from the critical analysis given in [2]. The MSA, which is a primitive model approximation, needs to know the diameters σ_i of the ions. The latter have been taken from [20] $\sigma_{K^+} = 2.95$ Å, $\sigma_{Li^+} = 4.35$ Å, $\sigma_{Na^+} = 3.05$ Å, and $\sigma_{Cl^-} = \sigma_{Pauling} = 3.62$ Å. These parameters are able to reproduce equilibrium (osmotic pressure) and transport properties (conductivity and mutual diffusion) accurately from Smoluchowski-MSA theory of electrolytes. Thus, our MCT of self-diffusion does not involve any adjustable parameter.

Because of the long time tail of the relaxation term, whose characteristic time is the Debye relaxation time, close to 1 ns in our case, classical molecular dynamics is not able to calculate self-diffusion coefficients properly. Thus we used Brownian dynamics (BD) at the Smoluchowski level of approximation [11] to obtain such long time correlation functions. Indeed, this method is able to calculate exactly the Kirkwood integral (9). The efficiency of the simulation has been improved by evaluating the probability of each displacement with a smart Monte Carlo criterion in order to increase the time step.

The self-diffusion coefficients are shown in Figs. 1 and 2. It is clear that the theoretical predictions are in excellent agreement with both the experimental results and the Brownian dynamics simulations even at high concentrations.

The time dependence of the phenomenon can be given by the IVCF $Z(t)$. If the electrolyte friction $\delta\zeta(c,t)$ is less than the short-range friction ζ_{SR}, and if the Debye relaxation time $[\tau_D^{-1} = \frac{e^2}{\epsilon k_B T}(D_1 Z_1^2 C_1 + D_2 Z_2^2 C_2)]$ of the ionic atmosphere is greater than the short-range time $\tau_{SR} = m/\zeta_{SR}$, which is indeed the case in our electrolyte solutions, then we have the following simple expression:

$$Z(t) = \frac{k_B T}{m} \exp(-\zeta_{SR} t/m) - \frac{k_B T}{\zeta_{SR}^2} \delta\zeta(c,t). \quad (16)$$

Note that for 1 M solutions, τ_{SR} is typically 1 ps while τ_D is only 1 ns. Thus, the above approximate equation should be satisfactory. Two examples of IVCF (relaxation part) are given in Fig. 3. The more the concentration, the faster is the long time decay. We believe this provides the microscopic explanation of the weak concentration dependence
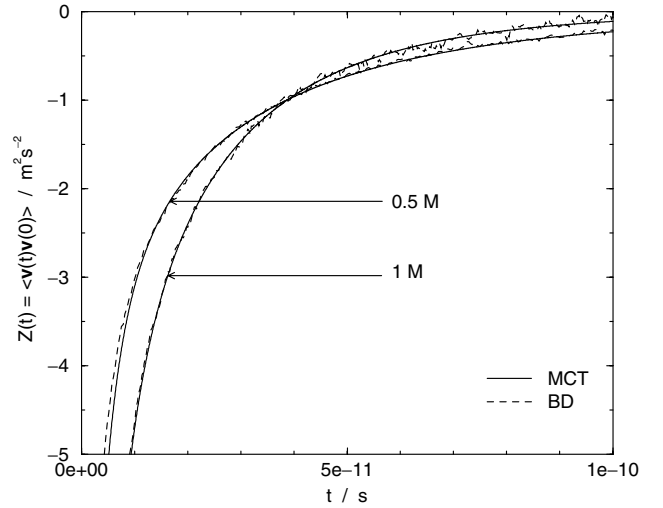

FIG. 3. Velocity correlation function of Cl^- for $c = 0.5$ M and $c = 1$ M KCl solutions. Comparison between MCT (solid line) and Brownian dynamics (dashed line).
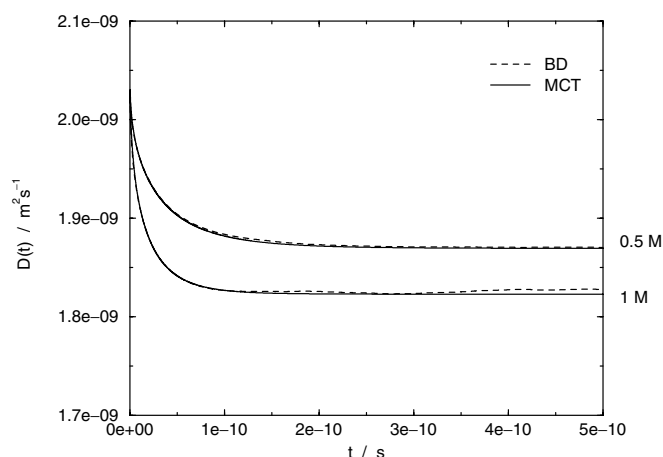
FIG. 4. Time dependent self-diffusion coefficient of Cl^- for $c = 0.5$ M and $c = 1$ M KCl solutions. Comparison between MCT (solid line) and Brownian dynamics (dashed line).

of the self-diffusion coefficients of the ions. The agreement with the BD simulations is again excellent.

The time dependent self-diffusion coefficient, $D_{ion}(t)$ (Fig. 4) shows a very interesting shape. For small times (greater than τ_{SR} but less than τ_D), the self-diffusion coefficient is close to the infinitely diluted solution value. The relaxation effect decreases this transport coefficient only for times greater than τ_D. This result can indeed explain the discrepancy between the self-diffusion coefficients measured by time of flight neutron scattering and NMR or tracer methods [21]. The typical time scale of such neutron scattering experiments is typically 20 ps, which is much less than the relaxation time of the ionic atmosphere. Consequently the values obtained do not take into account the whole relaxation effect. They are found to be greater that those measured by long time methods such as NMR.

The present study reveals several interesting points. First, the weak concentration dependence of ionic self-diffusion arises not only from the absence of the charge current contribution, but also from the faster decay of the velocity time correlation functions in the more concentrated solutions. Second, the hydrodynamic interactions are not important for the diffusion of these small ions. Third, because of the great separation of time scale between ion atmosphere relaxation time and the other time scales of the system, different experiments can measure different values of the self-diffusion coefficient, as indeed has happened in the past.

With the success of the present theory for self-diffusion, the important remaining problem of viscosity and the viscoelasticity of concentrated solutions can now be treated within the mode coupling theory approach, where the self-consistent dynamic structure evaluated here shall prove useful.

[1] L. Onsager, Ann. N.Y. Acad. Sci. **46**, 241 (1945).
[2] R. Mills and V. M. M. Lobo, *Self-diffusion in Electrolyte Solutions,* Physical Sciences Data Vol. 36 (Elsevier, New York, 1989).
[3] The Fuoss-Onsager-MSA calculations of Ref. [22] do not agree with the simulations of Ref. [11].
[4] E. C. Zhong and H. L. Friedman, J. Phys. Chem. **92**, 1685 (1988).
[5] A. Chandra, Dongqing Wei, and G. N. Patey, J. Chem. Phys. **99**, 2083 (1993).
[6] M. K. Kropman and H. J. Bakker, Science **291**, 2118 (2001).
[7] A. Chandra, Phys. Rev. Lett. **85**, 768 (2000).
[8] J. M. G. Barthel, H. Krienke, and W. Kunz, *Physical Chemistry of Electrolyte Solutions* (Springer, New York, 1998).
[9] J. B. Hubbard and P. G. Wolynes, in *Chemical Physics of Solvation Part D,* edited by R. R. Dogonadze *et al.* (Elsevier, Amsterdam, 1988).
[10] O. Bernard and L. Blum, J. Chem. Phys. **104**, 4746 (1996).
[11] M. Jardat, O. Bernard, P. Turq, and G. R. Kneller, J. Chem. Phys. **110**, 7993 (1999).
[12] L. Sjögren and A. Sjölander, J. Phys. C **12**, 4369 (1979).
[13] B. Bagchi and S. Bhattacharyya, in *Advances in Chemical Physics,* edited by I. Prigogine and Stuart A. Rice (John Wiley & Sons, New York, 2001), Vol. 116, pp. 67−221.
[14] A. Chandra and B. Bagchi, J. Chem. Phys. **110**, 10 024 (1999).
[15] A. Chandra and B. Bagchi, J. Phys. Chem. B **104**, 9067 (2000).
[16] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, Orlando, 1986).
[17] For infinitely diluted solutions, the self-consistency is automatically satisfied. As a matter of fact, we also performed non-self-consistent calculations in order to test this approximation.
[18] L. Blum, in *Theoretical Chemistry: Advances and Perspectives,* edited by H. Eyring and D. Henderson (Academic Press, New York, 1980), Vol. 5, pp. 1−66.
[19] L. Blum and J. S. Høye, J. Phys. Chem. **81**, 1311 (1977).
[20] J.-F. Dufrêche, O. Bernard, and P. Turq, J. Chem. Phys. **116**, 2085 (2002).
[21] W. Kunz, P. Turq, M.-C. Bellisent-Funel, and P. Calmettes, J. Chem. Phys. **95**, 6902 (1991).
[22] O. Bernard, W. Kunz, P. Turq, and L. Blum, J. Phys. Chem. **96**, 398 (1992).