Solvation dynamics in ionic fluids: An extended Debye–Hückel dielectric continuum model

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(Received 23 April 2009; accepted 6 July 2009; published online 23 July 2009)

Motivated by our recent proposition on the possibility of using dielectric continuum models to interpret experimental measurements of solvation dynamics in room temperature ionic liquids [J. Phys. Chem. A 110, 8623 (2006)], some detailed simulation studies are performed to test the validity of our proposition. From these simulation studies, it seems to be justified that an extended Debye–Hückel continuum model can be used to understand the solvation dynamics of ionic fluids. The theoretical underpinning of such an extended Debye–Hückel model is presented from the general dispersion relation in electrodynamics. The connection with the static extension from the dressed ion theory of electrolyte solutions is also discussed. Such a connection between the Debye–Hückel theory and the dispersion relation may be exploited to enhance our understanding of the electric double layer problem not only for the static case but also for dynamic situations.

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I. INTRODUCTION

Room temperature ionic liquids (RTILs) are becoming an increasingly rich area of study because of their utility as environmentally friendly solvents and because of a host of practical applications.1–4 Their growing utility has stimulated studies to understand the fundamentals of their behaviors. One of such fundamental properties of ionic fluids is the dielectric response, which plays a significant role in the reactions involving charge rearrangements.

Early studies of solvation dynamics by ionic fluids were provided by Huppert and co-workers using molten salts,5,6 and by Chapman and Maroncelli using nonaqueous solutions of dissolved ions.7 More recently, solvation dynamics by RTILs has been studied using fluorescence techniques by Karmakar and Samanta8–10 and by Maroncelli and co-workers.11,12 Several groups13–16 used the optical Kerr effect to study the dielectric response of ionic liquids. Dielectric spectroscopy is also used to gain insights into the dielectric response of ionic fluids.17,18 Karmakar and Samanta argued that the solvation dynamics is biphasic, with a short component corresponding to diffusional motion of the anion and a long component corresponding to the collective motion of the anion and the cation. Arzhantsev et al.12 and Shim19,20 however, stressed the nonexponential, dispersive, heterogeneous nature of the solvation dynamics.

Several simulations have been performed to understand solvation dynamics and dielectric response of RTILs. The initial rapid solvation events have been the object of some computer simulations. Shim et al.19,20 placing a dipolar excitation on a model diatomic solute in a RTIL, observed a fast initial relaxation and suggested that it arises from translational motions of the anions. Znamenskiy and Kobrak performed molecular dynamics simulations of the dye betaine-30 and coumarin 153 (C153) in various RTILs,21–23 and they argued that collective motions are the dominating factors in the solvation dynamics even though the relative importance of the translational and rovibrational components of the ionic species may vary. Margulis and co-workers also did extensive studies on the heterogeneity of the solvation dynamics in RTILs at high viscosity.24–26 Recently, Schroeder et al. calculated the whole dielectric function of a room temperature ionic liquid.27

A fundamental problem in the study of ionic liquids is assessing the relative importance of translational motion of ions,11,12,20,22 which can roughly be identified with ac conductivity, and the dielectric relaxation of dipoles. Recently, we proposed an alternative view of the origin of dynamic solvation by ionic fluids,28,29 namely, that it arises from the dielectric relaxation of dipoles resulting from ion pairs due to local neutrality and permanent dipoles carried by the ions besides the contribution of the translation motions of ionic species. As a clear separation of the ac conductivity and the dielectric function is not possible except at zero frequency (the static case), we will view the total dielectric function arising from the conductivity contribution, which is roughly related to the translational motion of ions, and the rest of dielectric function, which is due to the polarization relaxation. For the polarization relaxation, the major contribution is from the ion pairs, ion clusters, and the dipole moments carried by the cations and anions. The size of these dipole moments can be estimated by taking the geometric center of the ions as the origin. For electrolyte solutions and molten salts, this point of view has been used fruitfully to interpret the experimental dielectric spectra.30

However, the question of whether dielectric continuum models can accurately describe solvation dynamics in ionic liquids had been contested by others.12,31 There are two major issues related to this debate. The first one is the completeness of the dielectric function used as the input to the continuum model and the second is how to account for the
Debye screening of the ionic fluids. In order to address these issues, computer simulations are performed to calculate the whole dielectric function of some model ionic fluids. At the same time, solvation correlation functions are also computed from simulations using the same force field of the model ionic fluids with a model solute (C153 in this work). Then the solvation correlation function based on an extended Debye–Hückel dielectric continuum model is calculated from the simulated dielectric function and the solute model used in the simulation. A direct comparison of the solvation correlation functions from these two routes is made, and based on the obtained good agreements, we concluded that the dielectric continuum model used in our work can be used to interpret solvation dynamics results in ionic fluids.

The gist of our extended Debye–Hückel dielectric continuum model is a dynamical extension of the traditional Debye–Hückel theory and the theoretical foundation of such an extension is discussed from the dispersion relation of electrodynamics widely used in plasma physics. 32 It is shown that the dressed ion theory, 32,33 which is a static extension of the Debye–Hückel theory, is a special case of our general extension of the Debye–Hückel theory.

This paper is organized as follows. In Sec. II, a general formulation of solvation dynamics and our dynamical extension of the Debye–Hückel theory is discussed. In Sec. III, applications of our theory to the solvation dynamics of C153 in NaCl melt and [BMI][PF6] is presented. Some concluding remarks are given in Sec. IV.

II. THEORETICAL DEVELOPMENT

A. A general formulation of solvation dynamics

For the sake of completeness and self-consistency of notation, we briefly outline the general formulation of solvation dynamics used in this paper. Consider a solute molecule embedded in a solvent where the solute has two electronic states; the ground state (g) and the excited state (e). Ignoring interstate coupling, the nuclear Hamiltonian of the system can be written as

\[ H = H_g|g\rangle\langle g| + H_e|e\rangle\langle e|, \]  

(1)

where \( H_g = H_g^{(0)} + H_g + H_{gs} \) and \( H_e = H_e^{(0)} + H_e + H_{es} \). \( H_g^{(0)} \) and \( H_e^{(0)} \) are the gas phase Hamiltonians of the solute molecule in the ground state and the excited state, \( H_g \) is the Hamiltonian of the solvent, and \( H_{gs} \) and \( H_{es} \) are the interactions between the solute and the solvent in the two electronic states.

Imagine that the solvent is initially in equilibrium with the solute in its ground electronic state. After instantaneous excitation from the ground state to the excited state, the surrounding solvent molecules will relax to a new equilibrium consistent with the excited state. This relaxation can be probed by ultrafast spectroscopy experiments. 35–37 For example, the solvation correlation function,

\[ S(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)}, \]  

(2)

is measured in a time-dependent Stokes shift experiment. The peak shift is used to probe the solvation dynamics in three-pulse photon-echo experiments. 35,36 In Eq. (2) the time-dependent fluorescence frequency is given by

\[ \hbar \omega(t) = \hbar \omega_0 + \Delta E(t). \]  

(3)

Here, \( \hbar \omega_0 = H_e^{(0)} - H_g^{(0)} \) is the gas phase frequency shift and \( \Delta E(t) \) is the solvation energy change due to the charge distribution change between the two electronic states. As such, the solvation correlation function can be rewritten in terms of the time variation in the solvation energy,

\[ S(t) = \frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)}. \]  

(4)

To estimate the time-dependent solvation energy change, we assume that the solvent-solute interactions, \( H_{gs} \) and \( H_{es} \), differ only in so far as the charge distributions of the ground and excited states differ. In that case,

\[ \Delta E(t) = -\frac{1}{2} \int d\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \Delta \mathbf{E}(\mathbf{r}, t), \]  

(5)

where \( \Delta \mathbf{E}(\mathbf{r}, t) = \theta(t) \Delta \mathbf{E}(\mathbf{r}) \) with \( \Delta \mathbf{E}(\mathbf{r}) \) denoting the change in electric field due to the instantaneous change in charge distribution of the solute at time zero signified by the Heaviside function \( \theta(t) \). \( \mathbf{P}(\mathbf{r}, t) \) is the subsequent induced polarization of the solvent and the induced current contribution in ionic fluids is included in the time dependence of the polarization. According to the linear response theory, 38

\[ \mathbf{P}(\mathbf{r}, t) = \int_0^t dt' \int d\mathbf{r}' \chi^{(m)}(\mathbf{r}, \mathbf{r}'; t-t') \cdot \Delta \mathbf{E}(\mathbf{r}', t'), \]  

(6)

where \( \chi^{(m)}(\mathbf{r}, \mathbf{r}'; t) \) is the susceptibility tensor of the solution. Thus, to the extent that the linear response description is valid, the solvation energy change can be expressed as

\[ \Delta E(t) = -\frac{1}{2} \int_0^t dt' \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathbf{E}(\mathbf{r}, t) \cdot \chi^{(m)}(\mathbf{r}, \mathbf{r}'; t-t') \cdot \Delta \mathbf{E}(\mathbf{r}', t'). \]  

(7)

Its Laplace transform is

\[ \tilde{\Delta E}(\mathbf{s}) = \int_0^\infty e^{-st} \Delta E(t) \]  

\[ = -\frac{1}{2s} \int d\mathbf{r} \int d\mathbf{r}' \Delta \mathbf{E}(\mathbf{r}) \cdot \tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; s) \cdot \Delta \mathbf{E}(\mathbf{r}'), \]  

(8)

where \( s \) is a complex variable. In doing so, the analytical properties of the response function can be exploited.

The time-dependent solvation energy change \( \Delta E(t) \) can be related to the dielectric susceptibility, \( \tilde{\chi}^{(m)}(\mathbf{r}, \mathbf{r}'; \omega) \), which is the response function of the solution as modified by the presence of the solute (hence the superscript \( m \)). In fact, using the inverse transform of \( \tilde{\Delta E}(\mathbf{s}) \) (Ref. 39) and the analyticity of the response function 38 we have
\[
\Delta E(t) = \frac{1}{2\pi i} \int_C ds e^{st} \Delta \tilde{E}(s) = -\frac{1}{2} \int dr \int dr' \Delta \tilde{\mathcal{E}}(r) \cdot \tilde{\chi}^{(m)}(r, r'; 0) \cdot \Delta \tilde{\mathcal{E}}(r') \\
- \frac{1}{\pi} \int_0^\infty d\omega \cos(\omega t) \int dr \int dr' \Delta \tilde{\mathcal{E}}(r) \cdot \frac{\tilde{\chi}^{(m)}(r, r'; \omega)}{\omega} \cdot \Delta \tilde{\mathcal{E}}(r') \\
= -\frac{1}{2} \int dr \int dr' \Delta \tilde{\mathcal{E}}(r) \cdot \tilde{\chi}^{(m)}(r, r'; 0) \cdot \Delta \tilde{\mathcal{E}}(r') + \frac{2}{\pi} \int_0^\infty d\omega \cos(\omega t) \frac{\tilde{E}''(\omega)}{\omega}, \quad (9)
\]

where \(\omega\) is the frequency and \(\tilde{\chi}^{(m)}(r, r'; \omega)\) is the imaginary part of the dielectric susceptibility. \(\tilde{\chi}^{(m)}(r, r'; 0)\) is the static dielectric susceptibility. The symbol \(C\) under the integral sign denotes the Bromwich integration contour of the Laplace inversion.\(^{39}\) \(E''(\psi)\) is the imaginary part of the frequency-dependent solvation energy,

\[
E(\omega) = -\frac{1}{2} \int dr \int dr' \Delta \tilde{\mathcal{E}}(r) \cdot \tilde{\chi}^{(m)}(r, r'; \omega) \cdot \Delta \tilde{\mathcal{E}}(r').
\]

(10)

Therefore, once the dielectric susceptibility function is known at different frequencies, the time-dependent solvation energy change \(\Delta E(t)\) can be obtained from Eq. (9).

The modified response function generally differs from that of the pure solvent, \(\tilde{\chi}(r, r'; \omega)\). A conventional way to estimate \(\tilde{\chi}^{(m)}(r, r'; \omega)\) in terms of \(\tilde{\chi}(r, r'; \omega)\) is to assume that the solvent outside the volume occupied by the solute remains the same as the bulk solvent, namely, behaves like an unperturbed pure isotropic solvent. The only effect of the solute is on the volume of the integration in Eq. (8). This assumption is the “uniform” or “homogeneous” dielectric approximation used in many solvation dynamics theories; see, for example, discussions of this and alternative approximations in Refs. 40 and 41. We have shown that this approximation is generally not accurate because the presence of the solute significantly affects polarization correlations outside the excluded volume.\(^{42}\)

Employing a Gaussian field model of solutions, a general relation between the modified response function \(\tilde{\chi}^{(m)}(r, r'; \omega)\) and the pure solvent \(\tilde{\chi}(r, r'; \omega)\) (Ref. 42) can be obtained,

\[
\tilde{\chi}^{(m)}(r, r'; \omega) = \tilde{\chi}(r, r'; \omega) - \int_{\text{in}} dr'' dr''' \tilde{\chi}(r, r''; \omega) \\
\cdot \tilde{\chi}^{-1}(r', r'''; \omega) \cdot \tilde{\chi}(r'', r'''; \omega). \quad (11)
\]

The ‘in’ labeling the integration symbol means that the integration is limited to the region occupied by the solute and from which the solvent dipole density is expelled. The inverse of the in matrix \(\tilde{\chi}^{-1}(r, r'; \omega)\), is defined as

\[
\int_{\text{in}} dr'' \tilde{\chi}^{-1}(r, r''; \omega) \cdot \tilde{\chi}(r', r''; \omega) = \delta(r - r') I,
\]

(12)

where \(I\) is the \(3 \times 3\) identity matrix associated with the Cartesian coordinates of a three-dimensional system, and

\[
\tilde{\chi}(r, r'; \omega) \text{ is } \tilde{\chi}(r, r'; \omega) \text{ when both } r \text{ and } r' \text{ are within the region, and is zero otherwise.}
\]

If the pure solvent response function \(\tilde{\chi}(r, r'; \omega)\) and the region occupied by the solute are known, the solvation correlation function \(S(t)\) can be calculated from Eqs. (4), (9), and (11).

Such a strategy has been used for the solvation dynamics studies using a dielectric continuum response function for polar solvents\(^{42-44}\) and using the mean spherical approximation of the response function.\(^{45}\)

In this paper, a slightly different strategy is used to calculate the frequency-dependent solvation energy based on the success of the dielectric continuum model in polar solvents solvation dynamics studies.\(^{44}\) The expression for the frequency-dependent solvation energy in Eq. (10) can be rewritten as

\[
E(\omega) = -\frac{1}{2} \int dr \int dr' \Delta \tilde{\mathcal{E}}(r) \cdot \frac{e(r, r'; \omega) - 1}{4\pi} \cdot \tilde{E}(r'),
\]

(13)

where \(e(r, r'; \omega)\) is the dielectric tensor of the solvent and \(\tilde{E}(r)\) is the Maxwell field of the solution.\(^{38}\) From this perspective, the calculation of the solvation energy is reduced to solving the quasistatic boundary value problem of electrostatics if a dielectric continuum model is adopted. For the dielectric continuum model of polar solvents, an explicit demonstration for such a strategy was given about a decade ago.\(^{43}\) However for the ionic fluid case, the dielectric tensor is intrinsically nonlocal due to long-range correlation of free charges. If a Debye–Hückel type of dielectric model is used for the dielectric function of an ionic fluid, the solvation energy calculation can be reduced to a boundary value problem and can be solved for an arbitrary geometry of the solute.\(^{46,47}\) One of the major goals of this work is to demonstrate that an extended Debye–Hückel model can indeed be used for the studies of solvation dynamics in ionic fluids. To this end, a general formulation of the dielectric response of ionic fluids is needed.

### B. Dispersion relations and an extended Debye–Hückel theory of ionic fluids

In this section the connection between the dispersion relation (the functional relationship between wave vector and frequency) and an extend Debye–Hückel theory is presented.
Let us start with the Maxwell equations of a nonmagnetic macroscopic system,
\[ \nabla \cdot \mathbf{B} = 0, \]
\[ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0, \]
\[ \nabla \cdot \mathbf{D} = 4 \pi \rho, \] (14)
\[ \nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4 \pi}{c} \mathbf{J}. \]

Here, \( \rho \) and \( \mathbf{J} \) are the macroscopic (free) charge density and current density in the system, \( \mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \), where \( \mathbf{P} \) is the polarization. After a Fourier transformation with \( e^{-i\mathbf{k} \cdot \mathbf{r}} \), all quantities are transformed from \( \mathbf{X}(\mathbf{r}, t) \) to \( \mathbf{X}(\mathbf{k}, \omega) \). For brevity, we omit the arguments unless it is not clear from the context. Then the Maxwell equations become

\[ \mathbf{k} \cdot \mathbf{B} = 0, \]
\[ \mathbf{k} \times \mathbf{E} - \frac{\omega}{c} \mathbf{B} = 0, \] (15)
\[ ik \cdot \mathbf{D} = 4 \pi \rho, \]
\[ ik \times \mathbf{B} + \frac{i\omega}{c} \mathbf{D} = \frac{4 \pi}{c} \mathbf{J}. \]

For a conducting medium such as an ionic fluid, the constitutive relations are
\[ \mathbf{D} = \mathbf{\Sigma}(\mathbf{k}, \omega) \cdot \mathbf{E}, \] (16)
where \( \mathbf{\Sigma}(\mathbf{k}, \omega) = \varepsilon(\mathbf{k}, \omega) + (4\pi i/\omega) \mathbf{\sigma}(\mathbf{k}, \omega) \) is the generalized dielectric tensor, \( \varepsilon(\mathbf{k}, \omega) \) is the dielectric tensor, and \( \mathbf{\sigma}(\mathbf{k}, \omega) \) is the conductivity tensor.\(^{49}\) If there is no external charge and current as the induced charge and current have been included in the generalized dielectric tensor \( \mathbf{\Sigma}(\mathbf{k}, \omega) \), a combination of the equations in Eq. (15) leads to
\[ \frac{\omega^2}{c^2} \mathbf{D} = \frac{\omega^2}{c^2} \mathbf{\Sigma} \cdot \mathbf{E} = \mathbf{E} k^2 - \mathbf{k} \cdot \mathbf{E}. \] (17)

The condition for this set of linear homogeneous equations of \( \mathbf{\Sigma}(\mathbf{k}, \omega) \) to have nontrivial solutions is the vanishing of the following determinant:
\[ \left| k^2 \left( I - \frac{\mathbf{k} \mathbf{k}}{k^2} \right) - \frac{\omega^2}{c^2} \mathbf{\Sigma}(\mathbf{k}, \omega) \right| = 0. \] (18)

This is the dispersion relation in electrodynamics.\(^{32}\) For an isotropic system, the longitudinal and transverse components of the generalized dielectric tensor are scalars\(^{49}\)
\[ \mathbf{\Sigma}(\mathbf{k}, \omega) = \mathbf{\Sigma}(k, \omega) \left( I - \frac{\mathbf{k} \mathbf{k}}{k^2} \right) + \mathbf{\Sigma}_l(k, \omega) \frac{\mathbf{k} \mathbf{k}}{k^2}. \] (19)

The dispersion relations are reduced to
\[ k^2 \frac{\omega^2}{c^2} - \mathbf{\Sigma}_l(k, \omega) = 0, \] (20)
\[ \mathbf{\Sigma}_l(k, \omega) = 0. \] (21)

For the static case \( \omega = 0 \), the dispersion relation \( \mathbf{\Sigma}_l(k) = 0 \) leads to an extended Debye–Hückel theory as in the dressed ion theory.\(^{33,34,50}\) In general, the roots of \( \mathbf{\Sigma}_l(k) = 0 \) are complex and they appear in pairs as \( \mathbf{\Sigma}_l(\omega, k) = \mathbf{\Sigma}_l^\ast(-\omega, k) \).\(^{32}\)

Assuming that the root that is closest to the real axis is \( k_D \) and other roots are well separated from \( k_D \), we have \( (k^2 - k_D^2) \mathbf{\Sigma}_l(k) = 0 \). The longitudinal part of the homogeneous equation \( \mathbf{\Sigma}_l(k)(\mathbf{k} \mathbf{k}/k^2) \cdot \mathbf{E} = 0 \) leads to the linearized Poisson–Boltzmann equation for the potential \( \phi(k) \), \( (k^2 - k_D^2) \phi(k) = 0 \) corresponding to that root, which is the starting point of the Debye–Hückel theory.\(^{51}\) If \( k_D \) is identified as an effective Debye screening length.\(^{34}\) Naturally, other roots of the dispersion relation also lead to different solutions of the potential or longitudinal electric fields. A linear combination of these homogeneous solutions will yield the final solution of the problem when appropriate boundary conditions are used.\(^{32}\)

Let us consider that a unit external charge potential \( \phi_0(r) = 1/r \) is applied to the ionic fluid, the screened potential \( \phi(r) \) is given by
\[ \phi(k) = \frac{\phi_0(k)}{\mathbf{\Sigma}_l(k)}. \] (22)

If the large \( r \) behavior of \( \phi(r) \) is of interest, then to a good approximation the pole of the above equation that is closest to the real axis, i.e., the root \( k_D \) of \( \mathbf{\Sigma}_l(k) = 0 \), will make the major contribution to \( \phi(r) \). Fourier transformation of the above equation yields
\[ \phi(r) \sim \frac{e^{ik_0 r}}{\varepsilon_0 \omega}, \] (23)
where \( \varepsilon_0 = \frac{1}{2} [k_d \mathbf{\Sigma}_l(k)/dk]_{k=k_D} \). Naturally, a complete screened potential will be determined by a summation of the contributions of all the poles. For an electrolyte solution, the Debye–Hückel theory is equivalent to a dielectric function, \( \mathbf{\Sigma}_l(k) = \varepsilon_\infty (1 + k_D^2/\omega^2) \), where \( \varepsilon_\infty \) is the dielectric constant of the pure solvent and \( k_D = 4\pi \beta \mathbf{\Sigma}_l q_i^2 \rho / \varepsilon_\infty \) is the conventional Debye screening length.\(^{34}\)

In the context of ionic fluid solvation, an interesting work by Kobrak\(^{33}\) used a modified Debye–Hückel model to study the solvation energy of ionic fluids. The asymptotic charge distribution form used can be rationalized in our work as the result of the complex Debye decay length, which can be obtained from the wave vector dependent dielectric function.\(^{34}\)

For the dynamical case, \( \mathbf{\Sigma}_l(\omega, k) = 0 \) will give the general dispersion relation \( \omega = \omega_l(k) \). \( \mathbf{\Sigma}_l(\omega, k) \) can be obtained either from theoretical calculations based on some microscopic model of the system or from experimental measurements.\(^{54}\)

In practice, a complete \( \mathbf{\Sigma}_l(\omega, k) \) is not easily accessible and judicious approximations are necessary. In this paper, based on the success of the Debye–Hückel theory and the Vlasov–Boltzmann model in plasma physics\(^{37}\) the following model dielectric function for an ionic fluid is proposed:
\[ \Sigma_i(\omega, k) = \Sigma(\omega) \left( 1 + \frac{k_{\text{DH}}^2}{k^2} \right). \]  \hspace{1cm} (24)

Namely, the traditional Debye screening length \( 1/k_{\text{DH}} = 4\pi\beta\Sigma_1q_i^2r_i/\Sigma(\omega) \) is used and the effective dielectric function \( \varepsilon_{\text{eff}}(\omega, k) \) is approximated by the dielectric function at zero wave vector. Naturally, better approximations can be obtained by using all the information of \( \Sigma_i(\omega, k) \) to extract the Debye screening length and the corresponding effective dielectric function.

As in the static case, the above approximation for the dielectric function is equivalent to the Poisson–Boltzmann equation at a particular frequency \( \omega \) under the Lorentz gauge if the transverse field is not included.48,55 Hence, the dynamical solution can be formulated in exactly the same way as the static case except that a frequency-dependent dielectric function is used.

C. Solution to the dynamical Poisson–Boltzmann equation

Consider the dielectric cavity spanned by the molecular surface of a solute (see Fig. 1). There are \( N \) charges \( q_i \) at points \( r_i \) inside the dielectric cavity. Inside the dielectric cavity the dielectric constant is \( \varepsilon_1 = 1 \), which satisfies the

\[
\frac{1}{2} \left( 1 + \frac{\varepsilon_1}{\Sigma(\omega)} \right) \varphi_i(r) + \int \int L_1(r_1, r) \varphi_i(r_1) d\mathbf{r}_1 + \int \int L_2(r_1, r) \frac{\partial \varphi_i}{\partial n_1}(r_1) d\mathbf{r}_1 = \sum_{i=1}^{N} \frac{q_i}{\varepsilon_1} F(r_i, r),
\]

\[
\frac{1}{2} \left( 1 + \frac{\varepsilon_1}{\Sigma(\omega)} \right) \frac{\partial \varphi_i}{\partial n}(r) + \int \int L_3(r_1, r) \varphi_i(r_1) d\mathbf{r}_1 + \int \int L_4(r_1, r) \frac{\partial \varphi_i}{\partial n_1}(r_1) d\mathbf{r}_1 = \sum_{i=1}^{N} \frac{q_i}{\varepsilon_1} \frac{\partial F(r_i, r)}{\partial n},
\]

where

\[ L_1(r_1, r_1) = \frac{\partial F(r, r_1)}{\partial n} - \frac{\partial P(r, r_1)}{\partial n} \Sigma(\omega)/\varepsilon_1, \]  \hspace{1cm} (25)

\[ L_2(r, r_1) = P(r, r_1) - F(r, r_1), \]  \hspace{1cm} (26)

\[ L_3(r_1, r) = \frac{\partial^2 F}{\partial n_0 \partial n}(r_1) - \frac{\partial^2 P}{\partial n_0 \partial n}(r, r_1), \]  \hspace{1cm} (27)

\[ L_4(r, r_1) = -\frac{\partial F}{\partial n_0}(r, r_1) + \frac{\partial P}{\partial n_0}(r, r_1) \varepsilon_1/\Sigma(\omega), \]  \hspace{1cm} (28)

and

\[ F(r, r_1) = \frac{1}{4\pi |r - r_1|}; \]  \hspace{1cm} (29)

\[ P(r, r_1) = \frac{e^{-r_{\text{DH}}|r - r_1|}}{4\pi |r - r_1|}; \]  \hspace{1cm} (30)

For brevity, the frequency dependence of the potential and other functions in the above equation is not shown. The numerical method to solve the integral equation (25) over a molecular surface is based on collocation methods by Atkinson.58 Basis functions prescribed in Ref. 58 are set up over the surface by triangulation, and the integral equation is converted to a system of linear equations. From the solution of these integral equations, the potential outside the dielectric cavity is

\[ \varphi_i(r) = \frac{1}{\Sigma(\omega)\varepsilon_1} \int \int L_1(r_1, r) \varphi_i(r_1) d\mathbf{r}_1 + \int \int L_2(r_1, r) \frac{\partial \varphi_i}{\partial n_1}(r_1) d\mathbf{r}_1 + \sum_{i=1}^{N} \frac{q_i}{\varepsilon_1} F(r_i, r). \]  \hspace{1cm} (31)

Using the above potential, the Maxwell field in the solution can be obtained and hence the frequency-dependent solva-
tion energy from Eq. (13). Hence, the solvation correlation function calculation in an ionic fluid is reduced to the calculation of its dielectric function.

III. APPLICATIONS TO SOLVATION DYNAMICS OF NaCl MELT AND THE RTIL [BMIM+]PF$_6$

A. Dielectric functions from simulations

A formalism for the calculation of the dielectric function of an ionic fluid has been developed by Caillol et al.\textsuperscript{59-66} and later extended and elaborated by several other groups.\textsuperscript{61-63} $P(t)$ is the total dipole moment at time $t$. For each ionic species the dipole moment is defined with respect to the center of mass of that ionic species. $J(t)$ is the current of the ions. Then the dielectric function $\Sigma(\omega)$ can be written as

$$\Sigma(\omega) - 1 = \frac{4\pi}{3VkB_T} \left[ \langle P(0) \cdot P(0) \rangle + i\omega \int_{0}^{\infty} \langle P(0) \cdot P(i) \rangle e^{i\omega t} dt ight. \right.$$

$$\left. + \int_{0}^{\infty} (\langle P(i) \cdot J(0) \rangle - \langle P(0) \cdot J(i) \rangle) e^{i\omega t} dt \right]$$

$$\left. + \frac{i}{\omega} \int_{0}^{\infty} \langle J(0) \cdot J(t) \rangle e^{i\omega t} dt \right], \quad (33)$$

where $V$ and $T$ are the volume and temperature of the simulation box and $k_B$ is the Boltzmann constant. From molecular dynamics simulations using DL_POLY,\textsuperscript{64} time-dependent current-current and dipole-dipole correlation functions are computed to obtain the frequency-dependent dielectric function. The NaCl force field is the widely used Born–Mayer–Huggins potential with Tosi–Fumi parameters.\textsuperscript{65} The [BMIM$^+$][PF$_6$] force field used is that developed by Margulis et al.\textsuperscript{66} We also used the [BMIM$^+$][PF$_6$] force field developed by Lopes et al.\textsuperscript{67} to test the sensitivity of our results and found that our solvation dynamics results are not sensitive to the force field used.

Figures 2–4 are the dielectric functions calculated from our simulations. The dielectric functions are presented as effective ones that eliminate the divergence at zero frequency, which are widely used in presenting experimental measurements of dielectric functions of ionic fluids.\textsuperscript{17}
of C153 in the excited state, the solvation correlation function can be obtained within the linear response theory as

$$ C(t) = \frac{\langle \delta \Delta E(t) \delta \Delta E(0) \rangle}{\langle \delta \Delta E(0) \delta \Delta E(0) \rangle}, $$

where $\delta \Delta E(t) = \Delta E(t) - \langle \Delta E(t) \rangle$ and $\Delta E(t)$ is the interaction energy difference between C153 in its excited state and ground state with the surrounding solvent at time $t$. In this work, we used the normalized solvation correlation function as the simple continuum model used here is not expected to lead to right absolute solvation energy, just as the situation in solvation dynamics studies in dipolar solvents.

Using the dielectric functions calculated from Sec. III A, the solvation correlation function can be calculated from Eqs. (13), (25), and (32) using our extended Debye–Hückel dielectric continuum model equation (24). A direct comparison between these two routes will provide a reliable way to test the validity of our dielectric continuum model for solvation dynamics.

Figures 5–7 are the results of such comparisons. From the above comparisons, it is reasonable to conclude that an extended Debye–Hückel dielectric continuum model can be used to interpret the solvation dynamics of ionic fluids.

IV. CONCLUDING REMARKS

Motivated by our recent proposition on the possibility to interpret experimental measurements of solvation dynamics in RTILs, some detailed simulation studies are performed to test the validity of our proposition. From our simulation studies, it seems to be justified that an extended Debye–Hückel dielectric continuum model can be used to understand the solvation dynamics of ionic fluids. The theoretical underpinning of such an extended Debye–Hückel model is presented from the general dispersion relation in electrodynamics. The connection with the static extension from the dressed ion theory of electrolyte solutions is discussed. This connection between the Debye–Hückel theory and the dispersion relation may be exploited to enhance our understanding of the electric double layer problem not only for the static case but also for dynamic situations.

In the present work, a simple dynamical extension to the traditional Debye–Hückel theory is used to interpret the solvation dynamics from simulations. Such a model is chosen for its simplicity (only zero wavevector dielectric function is used) and for its direct connection to the static Debye–Hückel model. As a matter of fact, it is clear from the discussion in Sec. II B that this model will break down as $k \rightarrow 0$ and $\omega \rightarrow 0$. The right way to extract the Debye decay length is to use the $\Sigma(k, \omega)$ function from simulations or experimental measurements in combination with the dispersion relation. Given the simplest dynamical extension already yielded a reasonable interpretation of the solvation dynamics from simulations, we will expect more detailed model will certainly improve our understanding of solvation dynamics in ionic fluids.

ACKNOWLEDGMENTS

The author is grateful for many insightful discussions with Jake Petrich, whose experimental work motivated the current work, and for the financial support from a Petroleum
Research Foundation Grant No. 46451AC5 administered by the American Chemical Society and from an NSF Grant No. CHE-0809431.

64 W. Smith, www.ccp5.ac.uk/DL_POLY/.
68 M. Kobrak, the data files are provided by Mark Kobrak.