A Gaussian field approach to the solvation of spherical ions in electrolyte solutions

View Online   Export Citation   CrossMark

Tiejun Xiao[1] (iD) and Xueyu Song[2,a] (iD)

AFFILIATIONS

[1] Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Synergetic Innovation Center of Scientific Big Data for Advanced Manufacturing Technology, Guizhou Education University, Guiyang People's Republic of China
[2] Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA

[a] Author to whom correspondence should be addressed: xsong@iastate.edu

ABSTRACT

In this work, the electrostatic response of an electrolyte solution to a spherical ion is studied with a Gaussian field theory. In order to capture the ionic correlation effect in concentrated solutions, the bulk dielectric response function is described by a two-Yukawa response function. The modified response function of the solution is solved analytically in the spherical geometry, from which the induced charge density and the electrostatic energy are also derived analytically. Comparisons with results for small ions in electrolyte solutions from the hyper-netted chain theory demonstrate the validity of the Gaussian field theory.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0187141

I. INTRODUCTION

The dielectric continuum theory and its generalizations are useful tools to understand the screening effect of polar species and ionic species on charged objects, which has wide applications to colloidal suspension,[1-3] electric double layer,[4-8] solvation,[9-12] and solvation dynamics[13-16] in electrolyte solutions.

In general, there are two different approaches in the dielectric continuum theories. One approach is to consider the electric potential of a solute using an electrostatic model, where the electric potential in the solution region satisfies various electrostatic models, such as the Born model,[17-19] the Poisson–Boltzmann theory[20-22] or the modified Poisson–Boltzmann theory,[23-25] and the linearized Poisson–Boltzmann theory, or equivalently, the Debye–Hückel (DH) theory[26-29] and its extension with multi-DH response modes,[30-33] extra local dielectric response,[34-36] or nonlocal dielectric response.[37-43] Once the electric potential is determined, one can use it to compute the induced charge density and electrostatic solvation energy.

The other approach is to use the linear response theory to directly determine the induced charge density around a solute. As the linear response theory can take into account the excluded volume effect of the solute, the Gaussian field theory, developed by Chandler for fluids with short-range interactions,[44] has been

extended to polar fluid systems.[14,45,46] The Gaussian field theory introduces a modified response function due to the excluded volume of a solute to evaluate the induced charge density, which can be further used to compute the electric potential and the electrostatic solvation energy.

In a previous study,[47] the Gaussian field theory was extended to electrolyte systems with a planar geometry. In order to capture the ionic correlations in concentrated electrolytes, a two-Yukawa (TY) function is used to describe the bulk dielectric response function, whereas the single Yukawa model case leads to the conventional linearized Poisson–Boltzmann theory. The modified response function in the planar geometry is determined analytically, from which the planar electric double layer problem is solved analytically. When the Stillinger–Lovett second moment condition[48] and the contact theorem[49-52] are used as constraints for the parameters of the TY response function, our theory could capture the nonlinear response effect of the electric double layer as well. This approach goes beyond the mean field theory, such as the Poisson–Boltzmann theory, by incorporating multiple screening lengths of the electrolyte solution and leads to a different perspective on the electrostatic response of ionic fluids.

In this work, the Gaussian field theory is further extended to the solvation of a spherical solute in an electrolyte solution. In particular, the Gaussian field theory is used to understand the solvation

of a spherical ion in electrolyte solutions. The bulk electrostatic response function of a concentrated solution is also described by a TY function. The modified response function in a spherical symmetry is derived analytically and is further used to evaluate the induced charge density profile and the electrostatic solvation energy. When the theory is applied to spherical ions in electrolyte solutions, good agreements with the hyper-netted chain (HNC) theory demonstrate the validity of our approach.

This paper is organized as follows: In Sec. II, the induced charge density around a spherical ion is presented with the Gaussian field theory combined with a TY response function. In Sec. III, applications to ions in electrolyte solutions are presented to demonstrate the utility of our approach. A brief summary of our findings is given in Sec. IV.

II. A GAUSSIAN FIELD APPROACH TO THE SOLVATION OF SPHERICAL IONS IN ELECTROLYTE SOLUTIONS

A. Model of an ion in a restricted primitive model (RPM) of electrolyte solutions

The electrolyte solvent is described by an RPM for the simplicity of our presentation. An ion is characterized by a charged hard sphere. The cations and anions of the electrolyte have the same diameter σ_s but opposite charges. The solute ion has a charge q_o and a hard sphere diameter σ_o, and then, $a = (\sigma_s + \sigma_o)/2$ is the radius of the solute–solvent hard sphere interaction. Both the solvent ions and the solute ions are immersed in a dielectric background with a relative dielectric constant ε_r. The electrostatic interaction potential between two ions, tagged as i and j, is $\frac{q_i q_j}{\epsilon_s r}$, where $\epsilon_s = 4\pi\epsilon_0\varepsilon_r$ and ϵ_0 is the permittivity in vacuum. Denote $q_i = \pm q_s$ the charge of cation and anion species ($i = 1, 2$), n_s the total particle number density, and $\beta = 1/(k_B T)$ the reduced inverse temperature. The molar fraction of solvent ionic species is $x_{1,2} = 1/2$. The inverse Debye length of the bulk solution reads $k_D = \sqrt{4\pi\beta q_s^2 n_s/\epsilon_s}$. The electrostatic coupling parameter is defined as $\Gamma = q_s^2/(\epsilon_s \sigma_s k_B T)$.

This work focuses on the charge distribution around a dilute solute rather than an electrolyte ion; namely, the interactions between solute ions are neglected. The solute is located at the origin and generates an external electric potential,

$$\psi(\mathbf{r}) = \frac{q_o}{\epsilon_s r}, \tag{1}$$

where $\mathbf{r} = (x, y, z)$ is the coordinate and $r = \sqrt{x^2 + y^2 + z^2}$. When q_o is nonzero, the free ions will form a spherical double layer around the solute. Considering the excluded volume effect of the solute, the induced charge density can be determined from the linear response theory,[14,53]

$$\rho_{ind}(\mathbf{r}) = \int \chi^{(m)}(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}', \tag{2}$$

where $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ is the modified response function of the bulk solvent in the presence of the solute. In general, $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ is determined by the bulk response function $\chi(|\mathbf{r} - \mathbf{r}'|)$ and the boundary condition due to the solute. In the limit $a \to 0$, $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ reduces to

the bulk response function $\chi(|\mathbf{r} - \mathbf{r}'|)$. More details about the modified response function and the Gaussian field theory are presented in Appendix A.

Due to the spherical symmetry of the system, it would be convenient to expand a function $F(\mathbf{r}, \mathbf{r}')$ with its spherical harmonics component $F_n(r, r')$,[37]

$$F(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi r r'}\sum_{n=0}^{\infty} F_n(r, r')P_n(\cos\gamma)$$
$$= \frac{1}{rr'}\sum_{n=0}^{\infty}\sum_{m=-n}^{n} F_n(r, r')Y_{nm}(\theta, \phi)Y_{nm}^*(\theta', \phi'), \tag{3}$$

where $\cos\gamma = \frac{\mathbf{r}\cdot\mathbf{r}'}{rr'}$, $P_n(x)$ is the Legendre polynomial, and $Y_{nm}(\theta, \phi)$ is the spherical harmonics function.

The electric potential $\psi(\mathbf{r})$ can also be expanded with its spherical harmonics component $\psi_n(r)$, i.e., $\psi(\mathbf{r}) = \frac{1}{r}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\psi_n(r)Y_{nm}(\theta, \phi)$. As the solute charge is located at the origin of a spherical cavity, there is no high order multipole contribution to the electric potential. The nonzero spherical harmonics component of $\psi_n(r)$ is

$$\psi_0(r) = \frac{q_o}{\epsilon_s}, \tag{4}$$

while other components vanish, i.e., $\psi_n(r) = 0$ for $n \geq 1$.

The induced charge density depends only on a variable r such that $\rho_{ind}(\mathbf{r}) = \rho_{ind}(r)$ due to the spherical symmetry of the solute. Denote $g_{io}(r)$ ($i = 1, 2$) as the radial distribution function between the free solvent ion species i and the solute o. According to the theory of simple liquids, the induced charge density is related to a linear combination of the solute–solvent radial distribution function, i.e., $\rho_{ind}(r) = \sum_{i=1,2} q_i n_s x_i g_{io}(r)$. Using the spherical harmonics component $\chi_n^{(m)}(r, r')$ of $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$, the induced charge density can be rewritten as

$$\rho_{ind}(r) = \frac{1}{r}\int_a^{\infty} \psi_0(r')\chi_0^{(m)}(r, r')dr'. \tag{5}$$

The electric potential $\phi(r)$ in the solution region is related to $\rho_{ind}(r)$ via the Poisson equation,

$$\nabla^2\phi(r) = -\frac{4\pi}{\epsilon_s}\rho_{ind}(r), \quad r > a. \tag{6}$$

Note that there is no induced charge in the core region $r < a$; the Poisson equation reduces to

$$\nabla^2\phi(r) = -\frac{4\pi}{\epsilon_s}q_o\delta^{(3)}(\mathbf{r}), \quad r < a, \tag{7}$$

where $\delta^{(3)}(\mathbf{r})$ is the three-dimensional delta function. As long as the induced charge density $\rho_{ind}(r)$ is known, Eqs. (6) and (7) can be used to determine the electric potential $\phi(r)$.

Denote $\chi(k) = \int \chi(r)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$ as the three-dimensional Fourier transform of $\chi(r)$. The conventional DH theory can be obtained using a bulk response function $\chi(k)_{DH} = -\frac{\epsilon_s}{4\pi}\frac{k^2 k_D^2}{k^2+k_D^2}$ $= -\frac{k_D^2\epsilon_s}{4\pi}\left(1 - \frac{k_D^2}{k^2+k_D^2}\right)$. Namely, using this response function, the Gaussian field theory leads to $\phi(r > a)_{DH} = \frac{q_o}{\epsilon_s}\frac{e^{-k_D(r-a)}}{(1+k_D a)r}$, which is exactly

the same as that from the linearized Poisson–Boltzmann theory for the spherical symmetry.[54] Without breaking the presentation of our main results, details of these results are summarized in Appendix B.

B. Solvation of a spherical ion in an electrolyte solution with a TY response function

In our previous study of the planar electric double layer problem, a TY response function was used to capture the correlated response in concentrated electrolytes.[47] The TY response function reads $\chi(k)_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left(1 - \sum_{i=1,2} \frac{C_i k_i^2}{k^2 + k_i^2}\right)$ in k-space, with $C_1 + C_2 = 1$ due to the charge neutrality condition and $\kappa^2 = k_1^2 k_2^2/(C_2 k_1^2 + C_1 k_2^2)$ due to the Stillinger–Lovett second moment condition.[48] The TY response reads $\chi(\mathbf{r} - \mathbf{r}')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta^{(3)}(\mathbf{r} - \mathbf{r}') - \sum_{i=1,2} \frac{C_i k_i^2}{4\pi} \frac{e^{-k_i|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}\right]$ in r-space. The spherical harmonics component of $\chi(\mathbf{r} - \mathbf{r}')$ is[55]

$$\chi_n(r, r')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta(r - r') - \sum_{i=1,2} C_i k_i^2 g_n(r, r'; k_i)\right], \quad (8)$$

where $g_n(r, r'; k) = \sqrt{rr'} I_{n+\frac{1}{2}}(kr) K_{n+\frac{1}{2}}(kr')$ for $r < r'$ and $g_n(r, r'; k) = \sqrt{rr'} I_{n+\frac{1}{2}}(kr') K_{n+\frac{1}{2}}(kr)$ for $r > r'$. $\delta(x)$ is the one-dimensional delta function; $I_n(x)$ and $K_n(x)$ are the modified Bessel functions of the first and second kind.

The modified response function $\chi_n^{(m)}(r, r')_{TY}$ can be evaluated analytically, as shown in Appendix C. The final result reads

$$\chi_n^{(m)}(r, r')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta(r - r') - \sum_{i=1,2} C_i k_i^2 g_n(r, r'; k_i)\right.$$
$$\left. - \sum_{i,j=1,2} \alpha_{ij} K_{n+\frac{1}{2}}(k_i r) K_{n+\frac{1}{2}}(k_j r')\right], \quad (9)$$

where the coefficients α_{ij} are defined in Eq. (C6) of Appendix C.

The analytical form of $\chi_n^{(m)}(r, r')$ is used to determine the induced charge density $\rho_{ind}(r)$. It is noted that only the $n = 0$ component has a net contribution as the point charge is located at the center of the hard sphere; otherwise, other n components will be needed for off-centered charges.

After some straightforward calculations, it was found that the induced charge density reads

$$\rho_{ind}(r) = -\frac{q_o}{4\pi} \sum_{i=1,2} \frac{D_i k_i^2 e^{-k_i(r-a)}}{(1 + k_i a) r} \quad (10)$$

with the coefficient D_i defined in Eq. (C8) of Appendix C. In the k-space, the induced charge density reads

$$\rho_{ind}(k) = \int \rho_{ind}(r) \frac{\sin(kr)}{kr} 4\pi r^2 dr$$
$$= -q_o \sum_{i=1,2} \frac{D_i k_i^2 [\cos(ka) + k_i \sin(ka)/k]}{(k_i^2 + k^2)(1 + k_i a)}. \quad (11)$$

The integrated induced charge reads

$$Q_{ind} = \rho_{ind}(k = 0) = -q_o(D_1 + D_2). \quad (12)$$

One can check that $D_1 + D_2 = 1$ so that the local charge neutrality condition $Q_{ind} = -q_o$ is fulfilled.

The electrostatic energy u_e of the solute ion can be evaluated directly using the induced charge density,

$$\beta u_e = \frac{1}{2} \int_a^\infty \frac{\beta q_o \rho_{ind}(r)}{\epsilon_s r} 4\pi r^2 dr = -\frac{\beta q_o^2}{2\epsilon_s} \sum_{i=1,2} \frac{D_i k_i}{1 + k_i a}. \quad (13)$$

Due to the linear response, u_e also equals the electrostatic solvation free energy.[30]

Note that the electric potential has been widely used in studying charge solvation. With the analytical form of $\rho_{ind}(r)$ in Eq. (10), the electric potential $\phi(r)$ can be determined from Eqs. (6) and (7). Note that the electric potential satisfies $\phi(r \to \infty) = 0$ and $\frac{d\phi(r \to \infty)}{dr} = 0$. It is found that

$$\phi(r) = \frac{q_o}{\epsilon_s} \sum_{i=1,2} \frac{D_i}{1 + k_i a} \frac{e^{-k_i(r-a)}}{r}, \quad r \geq a. \quad (14)$$

The electric potential $\phi(r)$ in the range $r < a$ reads

$$\phi(r) = \frac{q_o}{\epsilon_s r} + A, \quad r < a, \quad (15)$$

with $A = -\frac{q_o}{\epsilon_s} \sum_{i=1,2} \frac{D_i k_i}{1 + k_i a}$ being the induced potential at the origin. The electrostatic energy u_e can also be evaluated as[30]

$$\beta u_e = \frac{\beta q_o A}{2} = -\frac{\beta q_o^2}{2\epsilon_s} \sum_{i=1,2} \frac{D_i k_i}{1 + k_i a}, \quad (16)$$

which is the same as Eq. (13).

To test the validity of our approach, a procedure is needed to determine the parameters $\kappa, C_{1,2}$ of the solvent. The parameters $\kappa, C_{1,2}$ are chosen in such a way that the Gaussian field theory reproduces the same linear coefficients $D_{1,2}^s$ for solvent species in a self-consistent manner, which can be done with the following two steps given that $k_{1,2}$ is known.

Step 1: $D_{1,2}^s$ for solvent species are determined. Note that the Stillinger–Lovett second moment condition leads to $D_1^s f_s(k_1) + D_2^s f_s(k_2) = 1$ with $f_s(k_i) = \frac{\kappa_D^2}{k_i^2} \frac{1 + k_i \sigma_s + k_i^2 \sigma_s^2/2 + k_i^3 \sigma_s^3/6}{1 + k_i \sigma_s}$ for the solvent species.[30] One can solve $D_1^s + D_2^s = 1$ and $D_1^s f_s(k_1) + D_2^s f_s(k_2) = 1$ to determine $D_{1,2}^s$.

Step 2: We apply the Gaussian field model to solvent species by taking $a = \sigma_s$ and $q_o = q_s$, namely the solute ion being the same as a solvent ion. Then, the Gaussian field theory leads to coefficient $D_i|_{a=\sigma_s} = V_i(C_1, 1 - C_1, k_1, k_2, \sigma_s)$ for the solvent species [see Eq. (C8)]. The self-consistency condition requires that $D_i|_{a=\sigma_s} = D_i^s$, and hence, one can solve $V_1(C_1, 1 - C_1, k_1, k_2, \sigma_s) = D_1^s$ numerically to find the coefficient C_1. The other parameters are evaluated with $C_2 = 1 - C_1$ and $\kappa = \frac{k_1 k_2}{\sqrt{C_1 k_2^2 + C_2 k_1^2}}$.

It is noted that the Gaussian field theory has been used as an alternative approach to derive the Born model of ion solvation in polar fluids.[14,19] Based on the linear response theory, a generalized Stillinger–Lovett second moment condition of the polar fluids has been used by Remsing and Weeks to derive the induced charge density and the electrostatic energy of a spherical solute ion.[19] Remsing and Weeks also considered the charge solvation in electrolyte solutions and adopted a generalized DH theory to account for the higher

order moments. Their results are similar in spirit to our work, i.e., multiple screening lengths are needed to give a good description of the dielectric response function of electrolytes.

III. APPLICATIONS TO SPHERICAL IONS IN RPM IONIC FLUIDS

In this section, the Gaussian field theory is applied to spherical ions in two RPM ionic fluids. The hyper-netted chain (HNC) theory is known to be very accurate for simple electrolytes over a very large range of parameter spaces[56,57] and is chosen as the benchmark of this study. Note that the HNC theory uses reduced dimensionless parameters to characterize the electrolyte system.[58] For the sake of simplicity, symbols for real parameters of the ionic fluids are adopted for the reduced parameters.

Denote $g_{ij}(r)$ as the radial distribution function between two ion species i and j ($i, j = 1, 2$). The total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$ of the ionic species are evaluated using the HNC theory, which is further used to compute the dielectric function $\epsilon_l(k)$ of the bulk system as well as the induced charge density of a solute. Denote $h_{ij}(k) = \int h_{ij}(r) \frac{\sin(kr)}{kr} 4\pi r^2 dr$ as the Fourier transform of $h_{ij}(r)$. The function $Y(k) \equiv 1 - \frac{\epsilon_s}{\epsilon_l(k)} = \frac{4\pi\beta n_s}{k^2} \left[\sum_{i=1,2} q_i^2 x_i + n_s \sum_{i,j=1,2} q_i q_j x_i x_j h_{ij}(k) \right]$ is further fitted to a half-empirical formula $Y(k) = \frac{a_0 k^2}{k^4 + (a_1 k^2 - a_2)\cos(kb) + a_3 \sin(kb) + a_2}$. The first two roots of $\epsilon_l(k)$ are determined by numerically solving $k^4 + (a_1 k^2 - a_2)\cos(kb) + a_3 \sin(kb) + a_2 = 0$ with $k = ik_n$ ($n = 1, 2$) and $\mathrm{Re}(k_n) > 0$.[43] $k_{1,2}$ are combined with the two-step procedure to determine the parameters $\{C_{1,2}, \kappa\}$ used in the TY response function. Using these parameters, the coefficients $[D_i = V_i(C_1, C_2, k_1, k_2, (\sigma_o + \sigma_s)/2)]$ are further calculated for various solute parameters; namely, the dielectric response of the solute is linear even though some nonlinear response is captured through a charge renormalization parameter κ in a self-consistent manner. The induced charge density $\rho_{ind}(k)$ and electrostatic energy βu^e from the Gaussian field theory are evaluated with Eqs. (11) and (16).

For the first ionic fluid, the reduced parameters for the solvent are chosen as $q_s = 1, \sigma_s = 1, n_s = 0.22, \beta = 2.15, \epsilon_s = 1$. The inverse Debye length is $k_D = \sqrt{4\pi\beta q_s^2 n_s / \epsilon_s} \simeq 2.44$. The electrostatic coupling parameter is $\Gamma = \beta q_s^2 / (\epsilon_s \sigma_s) = 2.15$. This system is used to mimic a NaCl-like aqueous solution with a molar concentration of 2 M and a mean diameter of 4.5 Å, for which the relative dielectric constant is about 58 at temperature $T = 298$ K due to the dielectric decrement effect.[59] The first two roots of $\epsilon_l(k)$ are a pair of conjugate complex numbers $k_{1,2} \simeq 1.896 \pm 2.304i$. Using the two-step procedure, the parameters in the TY model are $\kappa \simeq 2.051, C_{1,2} \simeq 0.5 \pm 1.177i$.

As the first test, our theory is used to predict the induced charge density $\rho_{ind}(k)$. The solute charge is fixed at $q_o = 1$, and the solute diameter σ_o is taken as the control parameter. It is noted that $D_{1,2} = 0.5 \mp 0.1706i, 0.5 \mp 0.1422i, 0.5 \mp 0.0927i$ for $\sigma_o = 0.5, 1, 3$, respectively. One can see that the linear coefficients have a weak dependence on the solute size parameter σ_o. $\rho_{ind}(k)$ for solutes with diameters $\sigma_o = 0.5, 1, 3$ is shown in Figs. 1(a)–1(c), respectively. The conventional DH theory leads to $\rho_{ind}(k) = -q_o \frac{k_D^2 [\cos(ka) + k_D \sin(ka)/k]}{(k_D^2 + k^2)(1 + k_D a)}$,[60] which is also used for comparison.
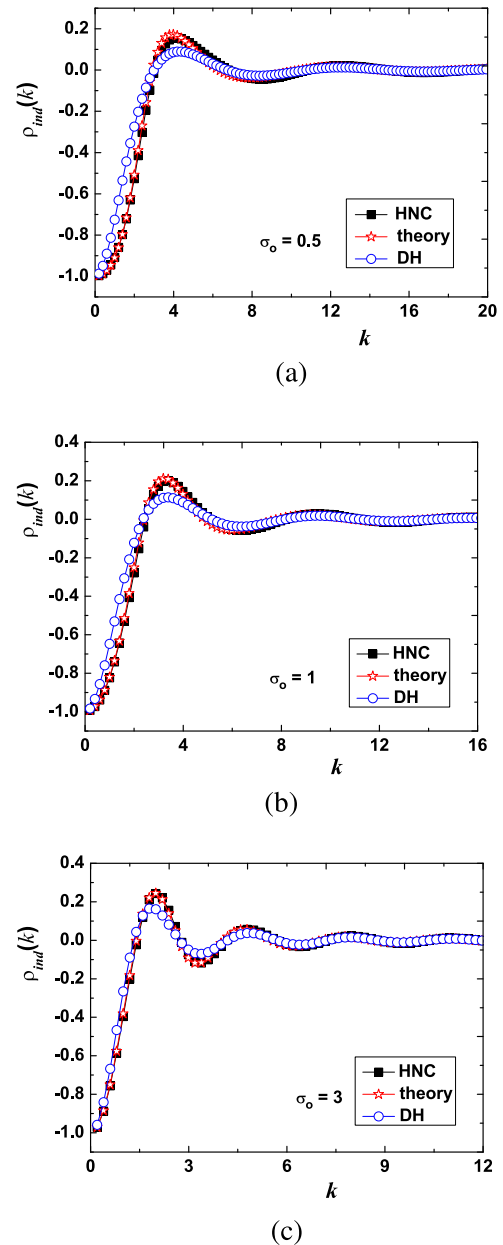
FIG. 1. Induced charge density around a spherical cation with $q_o = 1$ in an RPM electrolyte solution with $\kappa_D \simeq 2.44$, from the HNC theory (filled squares), the DH theory (hollow circles), and the Gaussian field theory (hollow stars). The lines are a guide to the eye. (a) The ion diameter is $\sigma_o = 0.5$. (b) The ion diameter is $\sigma_o = 1$. (c) The ion diameter is $\sigma_o = 3$.

As one can see, the Gaussian field theory leads to accurate induced charge densities for these three solutes, while the DH theory is a bit less accurate than the Gaussian field theory. We also test our theory for other solute size parameters in the range of $0.5 \leq \sigma_o \leq 8$, where similar good agreements between our theory and HNC theory are found.

As the second test, our theory is used to predict the electrostatic energy βu_e. The DH theory leads to $\beta u_e = -\frac{\beta q_o^2}{2\epsilon_s}\frac{k_D}{1+k_Da}$,[60] which is also used as a comparison. As one can see, the Gaussian field theory leads to very accurate electrostatic energy, while the DH theory is much less accurate. βu_e as a function of solute size σ_o for solutes with fixed charge $q_o = 1$ is shown in Fig. 2(a). In the range of $0.35 \leq \sigma_o \leq 9$, the relative energy difference between the Gaussian field theory and the HNC theory is no more than 3%, while the relative energy difference between the DH theory and the HNC theory is about 5–22%. βu_e as a function of solute charge q_o for solutes with fixed diameter $\sigma_o = 1$ is shown in Fig. 2(b). In the range of $q_o \leq 5$, the relative energy difference between the Gaussian field theory and the HNC theory is no more than 5%, while the relative energy difference between the DH theory and the HNC theory is about 17–20%. It is also noted that the Gaussian field theory becomes less accurate for solutes with smaller sizes and larger charges, i.e., the relative energy differences between the Gaussian field theory and the HNC are about 2, 3, and 5% for solutes with sizes and charge parameters $(\sigma_o, q_o) = (1, 1)$, $(1, 3)$, and $(1, 5)$, respectively. This is most likely due to the fact that the linear response becomes less accurate for a solute with a smaller
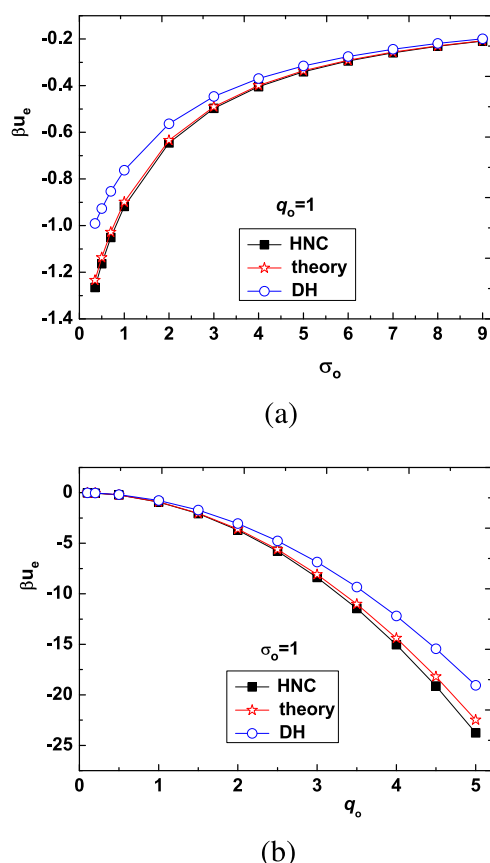
size and a larger charge, where the charge renormalization in the solution becomes different from that in the pure solvent.

For the second ionic fluid system, the parameters for the solvent are chosen as $q_s = 1, \sigma_s = 1, n_s = 0.55, \beta = 2.6, \epsilon_s = 1$. The inverse Debye length is $k_D = \sqrt{4\pi\beta q_s^2 n_s/\epsilon_s} \simeq 4.24$. The electrostatic coupling parameter is $\Gamma = \beta q_s^2/(\epsilon_s \sigma_s) = 2.6$. This system is used to mimic a NaCl-like aqueous solution with a molar concentration of 5 M and

(a)

(b)

(c)
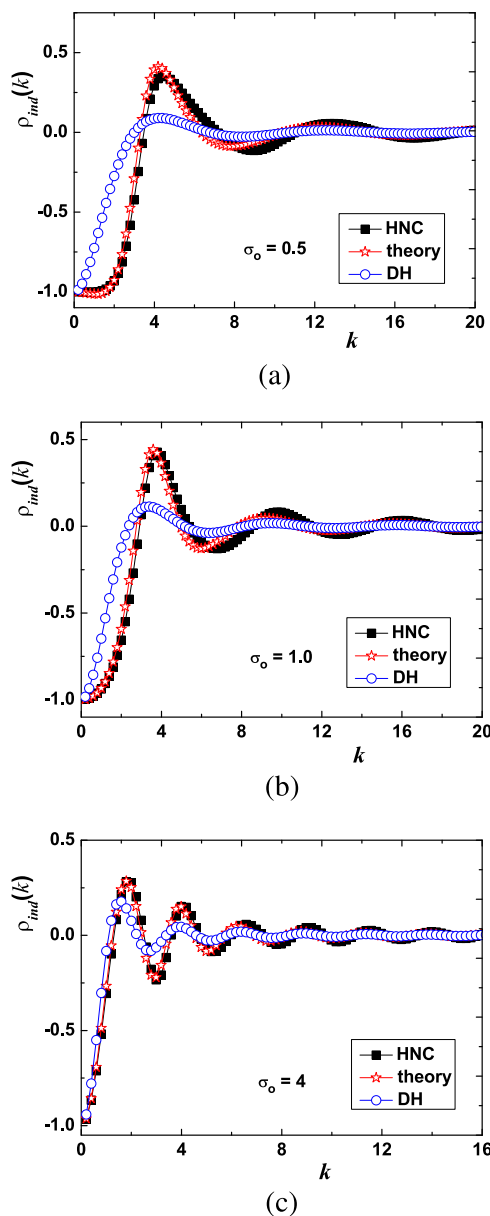
FIG. 3. Induced charge density around a spherical cation with $q_o = 1$ in an RPM electrolyte solution with $\kappa_D \simeq 4.24$, from the HNC theory (filled squares), the DH theory (hollow circles), and the Gaussian field theory (hollow stars). The lines are a guide to the eye. (a) The ion diameter is $\sigma_o = 0.5$. (b) The ion diameter is $\sigma_o = 1$. (c) The ion diameter is $\sigma_o = 4$.

(a)

(b)

FIG. 2. Electrostatic energy of a spherical cation in an RPM electrolyte solution with $\kappa_D \simeq 2.44$, from the HNC theory (filled squares), the DH theory (hollow circles), and the Gaussian field theory (hollow stars). The lines are a guide to the eye. (a) The ion charge is $q_o = 1$. (b) The ion diameter is $\sigma_o = 1$.

a relative dielectric constant of 48 at a temperature of T = 298 K.[59] The first two roots of $\varepsilon_l(k)$ are a pair of conjugate complex numbers $k_{1,2} \simeq 1.503 \pm 3.257i$. Using the two-step procedure, the parameters in the TY model are $\kappa \simeq 3.304$, $C_{1,2} \simeq 0.5 \pm 1.201i$.

As the third test, our theory is used to predict the induced charge density. The solute charge is fixed at $q_o = 1$, and the solute diameter σ_o is taken as the control parameter. It is noted that $D_{1,2} = 0.5 \mp 0.5019i, 0.5 \mp 0.4454i, 0.5 \mp 0.3432i$ for $\sigma_o = 0.5, 1, 4$, respectively. The results from the DH theory are also shown. $\rho_{ind}(k)$ for solutes with diameters $\sigma_o = 0.5, 1, 4$ is shown in Figs. 3(a)–3(c), respectively. As one can see, the Gaussian field theory leads to a good prediction of the location and height of the first peak and valley of induced charge densities, while the discrepancy between the DH theory and the HNC theory is evident. For the small solute with $\sigma_o = 0.5$ and $q_o = 1$, both the HNC theory and the Gaussian field theory lead to $\rho_{ind}(k) + q_o < 0$ in the range of $0.1 < k < 1$, which reveals the existence of charge inversion. This observation implies that the Gaussian field theory combined with the TY response function can be applied to study the phenomenon of charge inversion. When compared with the results for the first test system, it is noted that both the DH theory and the Gaussian field theory become less

accurate in electrolyte systems with a larger electrostatic coupling parameter $\Gamma = q_s^2/(\epsilon_s \sigma_s k_B T)$. We also test our theory for other solute size parameters in the range of $0.5 \leq \sigma_o \leq 7$, where similar results are found.

As the fourth test, our theory is used to predict the electrostatic energy. The conventional DH theory is also used as a comparison. βu_e as a function of solute size σ_o for solutes with a fixed charge $q_o = 1$ is shown in Fig. 4(a). In the range of $0.5 \leq \sigma_o \leq 7$, the relative energy differences between our theory and the HNC theory are about 3–5%, while the relative energy difference between the DH theory and the HNC theory is about 9–29%. βu_e as a function of solute charge q_o for solutes with a fixed diameter $\sigma_o = 1$ is shown in Fig. 4(b). In the range of $q_o \leq 5$, the relative energy differences between our theory and the HNC theory are no more than 6%, while the relative energy differences between the DH theory and the HNC theory are about 22–25%. So one can see that the Gaussian field theory also leads to accurate electrostatic energy for this system.

As a brief summary, our theory is applicable to spherical ions in 1:1 electrolyte solutions with moderate electrostatic coupling, as long as the solute charge number is not very large. However, it is also worth pointing out that our theory could fail for the problem of spherical double layers with a larger surface charge density. Denote $C_s = \frac{\sigma_e}{\zeta}$ as the capacitance of a spherical double layer, where $\zeta = \phi$ ($r = a$) is the zeta potential and $\sigma_e = \frac{q_o}{4\pi a^2}$ is the surface charge density. Previous studies show that C_s is a nonlinear function of the surface charge density as long as the cavity radius a is fixed.[61,62] However, the Gaussian field theory used in this study is a simple linear response theory and predicts that C_s is a constant for a fixed cavity radius of a, no matter how large the charge density is. This means that our theory cannot be used to understand the nonlinear response of the spherical double layers, especially in the case of large surface charge densities. Then the exact contact theorems may be used as constraints to improve the accuracy of the Gaussian field theory, just as in the case of the planar electric double layer.[47] The extension of the Gaussian field theory to a spherical electric double layer with a large charge density is underway. Note that in this work, we focus on RPM electrolytes with valency symmetric ions. When the cations and anions of the electrolyte have different sizes, previous studies show that the size-asymmetry leads to an extra effective charge density around a neutral solute.[63,64] It is also noted that the nonlinear response effects in electrolytes with higher valency and/or asymmetric valency will be stronger.[65–67] These effects are not included in the present Gaussian field model and deserve further study.
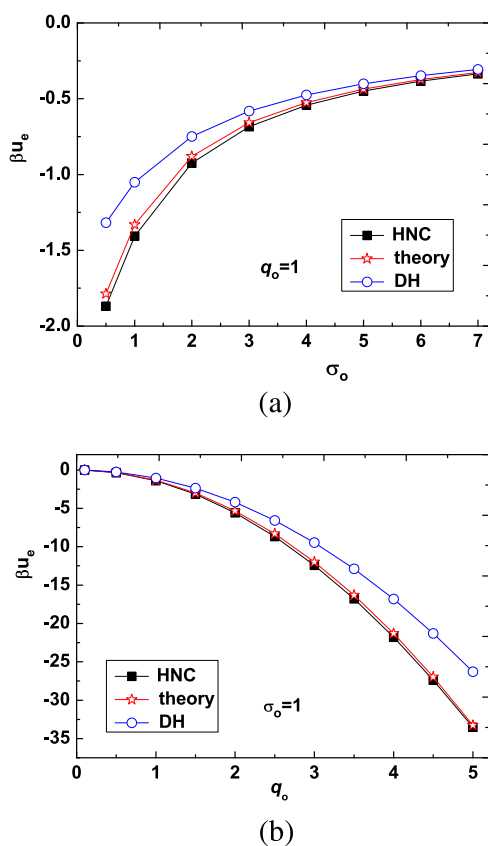
IV. CONCLUDING REMARKS

In summary, the solvation of a spherical ion in electrolyte solutions is studied using a Gaussian field theory. In order to capture the ionic correlation effect in concentrated solutions, the bulk dielectric response function is described by a two-Yukawa response function. The modified response function in the spherical symmetry is derived analytically, which is further used to evaluate the induced charge density and electrostatic energy. Applications to spherical ions demonstrate the validity of the Gaussian field theory by comparing it with the numerical HNC theory.

FIG. 4. Electrostatic energy of a spherical cation in an RPM electrolyte solution with $\kappa_D \simeq 4.24$, from the HNC theory (filled squares), the DH theory (hollow circles), and the Gaussian field theory (hollow stars). The lines are a guide to the eye. (a) The ion charge is $q_o = 1$. (b) The ion diameter is $\sigma_o = 1$.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tiejun Xiao: Conceptualization (equal); Funding acquisition (equal); Investigation (lead); Writing – original draft (lead); Writing – review & editing (equal). **Xueyu Song**: Conceptualization (equal); Funding acquisition (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

APPENDIX A: MODIFIED RESPONSE FUNCTION FROM A GAUSSIAN FIELD APPROACH

For the solvation problem with a spherical symmetry, the "in" region is defined for the excluded volume $r < a$, while the "out" region is defined for $r > a$. Denote $\chi_n^{(m)}(r,r')$, $\Delta\chi_n^{(m)}(r,r')$, and $\chi_{in,n}^{-1}(r,r')$ as the expansion component of $\chi^{(m)}(\mathbf{r},\mathbf{r}')$, $\Delta\chi^{(m)}(\mathbf{r},\mathbf{r}')$, and $\chi_{in}^{-1}(\mathbf{r},\mathbf{r}')$, respectively. Then, it is found that

$$\chi_n^{(m)}(r,r') = \chi_n(r,r') - \Delta\chi_n(r,r'), \qquad (A1)$$

with

$$\Delta\chi_n(r,r') = \int_0^a dr'' \int_0^a dr''' \chi_n(r,r'')\chi_{in,n}^{-1}(r'',r''')\chi_n(r''',r'), \qquad (A2)$$

and the inverse function $\chi_{in,n}^{-1}(r,r')$ is defined as

$$\int_0^a \chi_{in,n}^{-1}(r,r'')\chi_n(r'',r')dr'' = \delta(r-r'), r < a \text{ and } r' < a. \qquad (A3)$$

It is easy to check that

$$\chi_n^{(m)}(r,r') \equiv 0, r < a \text{ or } r' < a, \qquad (A4)$$

which is related to the fact that solvent species cannot enter the excluded volume. Given the spherical harmonics component $\chi_n(r,r')$ of the bulk response function, one can use these relations to determine $\chi_n^{(m)}(r,r')$ in the "out" region $r, r' > a$.

Denote $f(k) = \int f(r)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$ as the three-dimensional Fourier transform of $f(r)$. Define $t(k) = 1/\chi(k)$ and $t(r)$ as the inverse Fourier transform of $t(k)$. The relation $t(k)\chi(k) \equiv 1$ leads to

$\int t(\mathbf{r}-\mathbf{r}'')\chi(\mathbf{r}''-\mathbf{r}')d\mathbf{r}'' = \delta^{(3)}(\mathbf{r}-\mathbf{r}')$. Denote $t_n(r,r')$ is the spherical harmonics component of the function $t(|\mathbf{r}-\mathbf{r}'|)$. It is easy to check that $\int_0^\infty \chi_n(r,r'')t_n(r'',r')dr'' = \delta(r-r')$. So, $\chi_n(r,r')$ is the inverse function of $t_n(r,r')$ in the space $r, r' < \infty$. It is noted that the modified response function can also be determined via

$$\int_a^\infty \chi_n^{(m)}(r,r'')t_n(r'',r')dr'' = \delta(r-r'), r,r' > a. \qquad (A5)$$

This equation implies that $\chi_n^m(r,r')$ is the functional inversion of $t_n(r,r')$ in the out region. Note that the application of Eq. (A5) is a bit simpler than that of Eqs. (A1)–(A3) (for a more detailed discussion, see Ref. 47). In this work, Eq. (A5) will be used to determine the modified response function $\chi_n^m(r,r')$.

APPENDIX B: MODIFIED RESPONSE FUNCTION $\chi_n^{(m)}(r,r')$ AND INDUCED CHARGE DENSITY FROM THE DH RESPONSE FUNCTION

Consider a dilute electrolyte solution. The DH theory leads to $\chi(k)_{DH} = -\frac{\epsilon_s}{4\pi}\frac{k^2 k_D^2}{k^2+k_D^2} = -\frac{k_D^2\epsilon_s}{4\pi}\left(1 - \frac{k_D^2}{k^2+k_D^2}\right)$ and $t(k)_{DH} \equiv 1/\chi(k)_{DH} = -\frac{4\pi}{k_D^2\epsilon_s}\left(1 + \frac{k_D^2}{k^2}\right)$. In r-space, the DH response function leads to $\chi(\mathbf{r}-\mathbf{r}')_{DH} = -\frac{k_D^2\epsilon_s}{4\pi}\left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \frac{k_D^2}{4\pi}\frac{e^{-k_D|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right]$. The spherical harmonics component of $\chi(\mathbf{r}-\mathbf{r}')_{DH}$ is[55]

$$\chi_n(r,r')_{DH} = -\frac{k_D^2\epsilon_s}{4\pi}\left[\delta(r-r') - k_D^2 g_n(r,r';k_D)\right], \qquad (B1)$$

with

$$\begin{aligned} g_n(r,r';k) &= \sqrt{rr'}I_{n+\frac{1}{2}}(kr)K_{n+\frac{1}{2}}(kr') \text{ for } r < r', \\ g_n(r,r';k) &= \sqrt{rr'}I_{n+\frac{1}{2}}(kr')K_{n+\frac{1}{2}}(kr) \text{ for } r > r'. \end{aligned} \qquad (B2)$$

As discussed in Appendix A, a different way to derive the modified response function is to evaluate the functional inversion $t_{out}^{-1}(r,r')$ of the new response function $t_n(r,r')$. In the r-space, the new response function $t(\mathbf{r}-\mathbf{r}')_{DH}$ reads $t(\mathbf{r}-\mathbf{r}')_{DH} = -\frac{4\pi}{k_D^2\epsilon_s}\left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') + \frac{k_D^2}{4\pi}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]$. The spherical harmonics component $t_n(r,r')_{DH}$ of $t(\mathbf{r}-\mathbf{r}')_{DH}$ is[55]

$$t_n(r,r')_{DH} = -\frac{4\pi}{k_D^2\epsilon_s}\left[\delta(r-r') + k_D^2 g_n(r,r')\right], \qquad (B3)$$

with

$$\begin{aligned} g_n(r,r') &= \frac{\sqrt{rr'}}{2n+1}\left(\frac{r}{r'}\right)^{n+\frac{1}{2}} \text{ for } r < r', \\ g_n(r,r') &= \frac{\sqrt{rr'}}{2n+1}\left(\frac{r'}{r}\right)^{n+\frac{1}{2}} \text{ for } r > r'. \end{aligned} \qquad (B4)$$

The trial solution of the modified response function $\chi_n^{(m)}(r,r')_{DH}$ in the range of $r, r' > a$ reads[55]

$$\chi_n^{(m)}(r,r')_{DH} = -\frac{k_D^2 \epsilon_s}{4\pi}\left[\delta(r-r') - k_D^2\left(g_n(r,r';k_D)\right.\right.$$
$$\left.\left. - \nu_n \frac{g_n(r,a;k_D)g_n(a,r';k_D)}{g_n(a,a;k_D)}\right)\right]. \quad \text{(B5)}$$

Equation (B5) is inserted into Eq. (A5). By matching the coefficient of $K_{n+\frac{1}{2}}(k_D r)K_{n+\frac{1}{2}}(k_D r')$ in the two sides, it is found that

$$\nu_n = \frac{K_{n-\frac{1}{2}}(k_D a)}{K_{n+\frac{3}{2}}(k_D a)}. \quad \text{(B6)}$$

$\chi_0^{(m)}(r,r')$ is used to determine the induced charge density, which reads

$$\rho_{ind}(r) = \frac{1}{r}\int_a^\infty \psi_0(r')\chi_0^{(m)}(r,r')_{DH}\,dr' = -\frac{qk_D^2}{4\pi}\frac{e^{-k_D(r-a)}}{(1+k_D a)r}. \quad \text{(B7)}$$

These results from the Gaussian field theory are also exactly the same as those from the linearized Poisson–Boltzmann theory in the spherical symmetry.[54]

APPENDIX C: DETAILS FOR $\chi_n^{(m)}(r,r')$ FOR A TY RESPONSE FUNCTION

Consider an electrolyte solution with a TY response function $\chi(k)_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left(1 - \frac{C_1 k_1^2}{k^2+k_1^2} - \frac{C_2 k_2^2}{k^2+k_2^2}\right)$. The new response function, defined as $t(k)_{TY} \equiv 1/\chi(k)_{TY}$, can be rewritten as[47]

$$t(k)_{TY} = -\frac{4\pi}{\kappa^2 \epsilon_s}\left(1 + \frac{C_3}{k^2+k_3^2} + \frac{C_4}{k^2+k_4^2}\right) \quad \text{(C1)}$$

with $k_3 = \sqrt{C_2 k_1^2 + C_1 k_2^2}$, $k_4 = 0$, $C_3 = C_1 k_1^2 + C_2 k_2^2 - \kappa^2$, and $C_4 = \kappa^2$.

The response function and the new response function in the r-space, respectively, read[55]

$$\chi(\mathbf{r}-\mathbf{r}')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \frac{C_1 k_1^2}{4\pi}\frac{e^{-k_1|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right.$$
$$\left. - \frac{C_2 k_2^2}{4\pi}\frac{e^{-k_2|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right],$$
$$t(\mathbf{r}-\mathbf{r}')_{TY} = -\frac{4\pi}{\kappa^2 \epsilon_s}\left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') + \frac{C_3}{4\pi}\frac{e^{-k_3|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right.$$
$$\left. + \frac{C_4}{4\pi}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]. \quad \text{(C2)}$$

The spherical harmonics component of $\chi(\mathbf{r}-\mathbf{r}')_{TY}$ and $t(\mathbf{r}-\mathbf{r}')_{TY}$ reads[55]

$$\chi_n(r,r')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta(r-r') - \sum_{i=1,2}C_i k_i^2 g_n(r,r';k_i)\right],$$
$$t_n(r,r')_{TY} = -\frac{4\pi}{\kappa^2 \epsilon_s}\left[\delta(r-r') + C_3 g_n(r,r';k_3) + C_4 g_n(r,r')\right], \quad \text{(C3)}$$

with $g_n(r,r';k)$ and $g_n(r,r')$ defined in Eqs. (B2) and (B4).

Note that $\chi_n(r,r')_{TY}$ is the inverse function of $t_n(r,r')_{TY}$ in the whole space. The trial solution of $\chi_n^{(m)}(r,r')_{TY}$ can be constructed by adding terms proportional to $K_{n+\frac{1}{2}}(k_i r)K_{n+\frac{1}{2}}(k_j r)$ to $\chi_n(r,r')_{TY}$,

$$\chi_n^{(m)}(r,r')_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi}\left[\delta(r-r') - \sum_{i=1,2}C_i k_i^2 g_n(r,r';k_i)\right.$$
$$\left. + \sum_{i,j=1,2}\alpha_{ij}K_{n+\frac{1}{2}}(k_i r)K_{n+\frac{1}{2}}(k_j r')\right], \quad r,r' > a. \quad \text{(C4)}$$

When the trial solution Eq. (C4) is inserted into Eq. (A5), both sides of the equation are linear combinations of exponential terms. By matching the coefficients of $K_{n+\frac{1}{2}}(k_i r)K_{n+\frac{1}{2}}(k_j r)$ to $t_n(r,r')_{TY}$, the constraints for the parameters $\{\alpha_{ij}\}$ are derived. After some lengthy calculations, it was found that

$$\begin{aligned}
\alpha_{ij} &= C_i k_i^2 T_{ij}/T,\\
T &= f_3(a;k_1,k_3)f_4(a;k_2) - f_3(a;k_2,k_3)f_4(a;k_1),\\
T_{11} &= f_1(a;k_1,k_3)f_4(a;k_2) - f_3(a;k_2,k_3)f_2(a;k_1),\\
T_{12} &= f_3(a;k_1,k_3)f_2(a;k_1) - f_1(a;k_1,k_3)f_4(a;k_1),\\
T_{21} &= f_1(a;k_2,k_3)f_4(a;k_2) - f_3(a;k_2,k_3)f_2(a;k_2),\\
T_{22} &= f_3(a;k_1,k_3)f_2(a;k_2) - f_1(a;k_2,k_3)f_4(a;k_1))
\end{aligned} \quad \text{(C5)}$$

with

$$\begin{aligned}
f_1(r;k_i,k_3) &= \frac{1}{k_3^2 - k_i^2}\left[k_3 r I_{n+\frac{1}{2}}(k_i r)I_{n+\frac{3}{2}}(k_3 r)\right.\\
&\quad \left. - k_i r I_{n+\frac{1}{2}}(k_3 r)I_{n+\frac{3}{2}}(k_i r)\right],\\
f_2(r;k_i) &= \frac{1}{k_i}r^{n+\frac{3}{2}}I_{n+\frac{3}{2}}(k_i r),\\
f_3(r;k_i,k_3) &= \frac{1}{k_3^2 - k_i^2}\left[k_3 r I_{n+\frac{3}{2}}(k_3 r)K_{n+\frac{1}{2}}(k_i r)\right.\\
&\quad \left. + k_i r I_{n+\frac{1}{2}}(k_3 r)K_{n+\frac{3}{2}}(k_i r)\right],\\
f_4(r;k_i) &= -\frac{1}{k_i}r^{n+\frac{3}{2}}K_{n+\frac{3}{2}}(k_i r). \quad \text{(C6)}
\end{aligned}$$

One can check that $\alpha_{12} = \alpha_{21}$ so that the symmetry condition $\chi_{in,n}^{-1}(r,r')_{TY} = \chi_{in,n}^{-1}(r',r)_{TY}$ is fulfilled.

The term $\chi_0^{(m)}(r,r')$ is used to determine the induced charge density in the solvent region,

$$\begin{aligned}
\rho_{ind}(r) &= \frac{1}{r}\int_a^\infty \psi_0(r')\chi_0^{(m)}(r,r')_{TY}\,dr' = -\frac{q\kappa^2}{4\pi}\sum_{i=1,2}\frac{w_i e^{-k_i r}}{r}\\
&= -\frac{q}{4\pi}\sum_{i=1,2}\frac{D_i k_i^2 e^{-k_i(r-a)}}{(1+k_i a)r}, \quad r > a, \quad \text{(C7)}
\end{aligned}$$

with

$$w_i = C_i \cosh(k_i a) + \sum_{j=1,2} \frac{\pi \alpha_{ij} e^{-k_j a}}{2 k_j \sqrt{k_i k_j}},$$

$$D_i = V_i(C_1, C_2, k_1, k_2, a) \equiv \frac{\kappa^2}{k_i^2} \frac{1 + k_i a}{e^{k_i a}} \left(C_i \cosh(k_i a) \right.$$

$$\left. + \sum_{j=1,2} \frac{\pi \alpha_{ij} e^{-k_j a}}{2 k_j \sqrt{k_i k_j}} \right). \tag{C8}$$

REFERENCES

[1] J.-P. Hansen and H. Löwen, Annu. Rev. Phys. Chem. **51**, 209 (2000).

[2] C. J. Van Oss, *Interfacial Forces in Aqueous Media* (CRC Press, 2006).

[3] J. Mewis and N. J. Wagner, *Colloidal Suspension Rheology* (Cambridge University Press, 2012).

[4] H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, L. L. Zhang, A. H. MacDonald, and R. S. Ruoff, Nat. Commun. **5**, 3317 (2014).

[5] S. Zhou, J. Chem. Phys. **151**, 064710 (2019).

[6] C. Pan, S. Yi, and Z. Hu, Phys. Chem. Chem. Phys. **21**, 14858 (2019).

[7] M. V. Fedorov and A. A. Kornyshev, Electrochim. Acta **53**, 6835 (2008).

[8] J. P. De Souza and M. Z. Bazant, J. Phys. Chem. C **124**, 11414 (2020).

[9] A. Rosspeintner, B. Lang, and E. Vauthey, Annu. Rev. Phys. Chem. **64**, 247 (2013).

[10] A. M. Rahimi, S. Jamali, J. P. Bardhan, and S. R. Lustig, J. Chem. Theory Comput. **18**, 5539 (2022).

[11] T. Xiao and Y. Zhou, J. Phys. Chem. Lett. **12**, 6262 (2021).

[12] A. Alibakhshi and B. Hartke, Nat. Commun. **12**, 3584 (2021).

[13] J. S. Bader and B. J. Berne, J. Chem. Phys. **104**, 1293 (1996).

[14] X. Song and D. Chandler, J. Chem. Phys. **108**, 2594 (1998).

[15] B. Bagchi and B. Jana, Chem. Soc. Rev. **39**, 1936 (2010).

[16] P. K. Ghorai and D. V. Matyushov, J. Phys. Chem. B **124**, 3754 (2020).

[17] M. Born, Z. Phys. **1**, 45 (1920).

[18] D. Bashford and D. A. Case, Annu. Rev. Phys. Chem. **51**, 129 (2000).

[19] R. C. Remsing and J. D. Weeks, J. Phys. Chem. B **120**, 6238 (2016).

[20] P. Attard, D. J. Mitchell, and B. W. Ninham, J. Chem. Phys. **88**, 4987 (1988).

[21] D. Andelman, *Handbook of Biological Physics* (Elsevier, 1995), Vol. 1, pp. 603–642.

[22] L. B. Bhuiyan and C. W. Outhwaite, J. Colloid Interface Sci. **331**, 543 (2009).

[23] C. W. Outhwaite, M. Molero, and L. B. Bhuiyan, J. Chem. Soc., Faraday Trans. **89**, 1315 (1993).

[24] L. Bhuiyan, C. Outhwaite, and D. Henderson, J. Chem. Phys. **123**, 034704 (2005).

[25] C. W. Outhwaite and L. B. Bhuiyan, Condens. Matter Phys. **22**, 23801 (2019).

[26] P. Debye and E. Hückel, Z. Phys. **24**, 185 (1923).

[27] R. Kjellander, J. Phys. Chem. **99**, 10392 (1995).

[28] T. Xiao, ChemPhysChem **16**, 833 (2015).

[29] G. V. Bossa and S. May, Membranes **11**, 129 (2021).

[30] T. Xiao and X. Song, J. Chem. Phys. **135**, 104104 (2011).

[31] T. Xiao, Electrochim. Acta **178**, 101 (2015).

[32] R. Kjellander, Phys. Chem. Chem. Phys. **18**, 18985 (2016).

[33] R. Kjellander, Phys. Chem. Chem. Phys. **22**, 23952 (2020).

[34] R. I. Slavchov and T. I. Ivanov, J. Chem. Phys. **140**, 074503 (2014).

[35] R. I. Slavchov, J. Chem. Phys. **140**, 164510 (2014).

[36] T. Xiao and X. Song, J. Phys. Chem. A **125**, 2173 (2021).

[37] A. Kornyshev, A. Rubinshtein, and M. Vorotyntsev, J. Phys. C: Solid State Phys. **11**, 3307 (1978).

[38] A. A. Kornyshev and G. Sutmann, J. Chem. Phys. **104**, 1524 (1996).

[39] R. Kjellander and D. J. Mitchell, J. Chem. Phys. **101**, 603 (1994).

[40] P. A. Bopp, A. A. Kornyshev, and G. Sutmann, Phys. Rev. Lett. **76**, 1280 (1996).

[41] I. G. Medvedev, Electrochim. Acta **49**, 207 (2004).

[42] R. Ramirez and R. Kjellander, J. Chem. Phys. **119**, 11380 (2003).

[43] T. Xiao and Y. Zhou, Electrochim. Acta **392**, 139040 (2021).

[44] D. Chandler, Phys. Rev. E **48**, 2898 (1993).

[45] X. Song, D. Chandler, and R. Marcus, J. Phys. Chem. **100**, 11954 (1996).

[46] H. Berthoumieux, J. Chem. Phys. **148**, 104504 (2018).

[47] T. Xiao and X. Song, J. Chem. Phys. **158**, 174104 (2023).

[48] F. H. Stillinger, Jr. and R. Lovett, J. Chem. Phys. **49**, 1991 (1968).

[49] D. Henderson and W. R. Smith, J. Stat. Phys. **19**, 191 (1978).

[50] D. Henderson, L. Blum, and J. L. Lebowitz, J. Electroanal. Chem. Interfacial Electrochem. **102**, 315 (1979).

[51] M. Holovko, J. Badiali, and D. Di Caprio, J. Chem. Phys. **123**, 234705 (2005).

[52] M. Holovko, J. Badiali, and D. Di Caprio, J. Chem. Phys. **127**, 014106 (2007).

[53] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[54] T. Xiao and X. Song, J. Chem. Phys. **141**, 134104 (2014).

[55] M. Vorotyntsev, J. Phys. C: Solid State Phys. **11**, 3323 (1978).

[56] E. Gutiérrez-Valladares, M. Lukšič, B. Millán-Malo, B. Hribar-Lee, and V. Vlachy, Condens. Matter Phys. **14**, 33003 (2011).

[57] H. Jiang and H. Adidharma, Mol. Simul. **41**, 727 (2015).

[58] E. Lomba and J. S. Høye, Comput. Phys. Commun. **69**, 420 (1992).

[59] J. B. Hasted, D. M. Ritson, and C. H. Collie, J. Chem. Phys. **16**, 1 (1948).

[60] T. Xiao and Y. Zhou, Chin. J. Chem. Phys. **36**, 553 (2023).

[61] E. Keshavarzi, M. Abareghi, and A. Helmi, Electrochim. Acta **313**, 303 (2019).

[62] D. L. Caetano, S. J. De Carvalho, G. V. Bossa, and S. May, Phys. Rev. E **104**, 034609 (2021).

[63] B. Forsberg, J. Ulander, and R. Kjellander, J. Chem. Phys. **122**, 064502 (2005).

[64] T. Xiao and X. Song, J. Chem. Phys. **146**, 124118 (2017).

[65] A. McBride, M. Kohonen, and P. Attard, J. Chem. Phys. **109**, 2423 (1998).

[66] R. Kjellander and J. Ulander, Mol. Phys. **95**, 495 (1998).

[67] J. J. Elisea-Espinoza, E. González-Tovar, and G. I. Guerrero-García, J. Chem. Phys. **158**, 224111 (2023).