Self-consistent field model for strong electrostatic correlations and inhomogeneous dielectric media

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Electrostatic correlations and variable permittivity of electrolytes are essential for exploring many chemical and physical properties of interfaces in aqueous solutions. We propose a continuum electrostatic model for the treatment of these effects in the framework of the self-consistent field theory. The model incorporates a space-dependent dielectric permittivity and an excluded ion-size effect for the correlation energy. This results in a self-energy modified Poisson-Nernst-Planck or Poisson-Boltzmann equation together with state equations for the self energy and the dielectric function. We show that the ion size is of significant importance in predicting a finite self energy for an ion in an inhomogeneous medium. Asymptotic approximation is used to a generalized Debye-Hückel equation for effectively obtaining the self energy which has been shown to capture the ionic correlation and dielectric self energy. The model is shown to agree with particle-based Monte Carlo simulations. Numerical results for symmetric and asymmetric electrolytes demonstrate that the model predicts the charge inversion at high correlation regime in the presence of multivalent interfacial ions which is beyond the mean-field theory, and also show strong effect to double layer structure due to the space- or field-dependent dielectric permittivity.

I. INTRODUCTION

Electrostatic interaction in aqueous solution including charged interfaces is of interest in a wide range of areas such as biological macromolecules, colloidal suspensions, and nanoparticle assembly. The structure of screened ions near charged surfaces, so-called the electric double layer, controls many macroscopic properties of the system such as the zeta potential and colloidal renormalized charges [1–3], and is affected by such as the interfacial chemistry, the surface charge distribution, and the ionic specificity. In the presence of divalent ions, electrostatic correlation plays a very important role, which could lead to the over screening of counterions for highly charged surfaces, i.e., the charge inversion phenomenon [4–10]. The electrostatic correlation is probably responsible for a lot of many-body phenomena such as like-charge attraction [11, 12] and ion transport in membrane channels [13], and many-body systems such as electrodes in ionic liquids [14]. A deep understanding of correlation effects and its relation with interfacial properties are then considered to be great meaningful in many applications.

Electrostatic correlations should be seriously studied in many conditions, e.g., if a system includes highly charged surface charges, multivalent counterions, or the system is at low temperature. The correlation strength is often measured by a coupling parameter [10] defined by \( \Xi = z^3 e^2 / 8 \pi (\varepsilon k_B T)^2 \), where \( z_e \), \( \sigma_e \), \( \varepsilon \), \( \varepsilon_k \) and \( k_B T \) are the counterion valence, the average surface charge density, the electronic charge, the dielectric permittivity, and the thermal energy, respectively. The coupling parameter can be simplified to \( \Xi = z^2 e^2 / \ell_B \), the product of \( z^2 e^2 \) and the ratio of the Bjerrum length \( \ell_B \) to the Gouy-Chapman length \( \ell_{GC} \). These two length scales describe the ion-ion and ion-interface interaction strengths, respectively. Though being often used, the classical Poisson-Boltzmann (PB) theory is mean-field and works only when \( \Xi \ll 1 \) since it ignores the ion correlation, thus fails to explain correlation-induced electrostatic phenomena. Many extended theories beyond the mean field has been studied and applied for different problems, e.g., to include the steric effect or dielectric self energy [16–20]. A first-principle description of electrostatic correlation should follow the integral-equation theory [21], which turns out to be a difficulty in resolving high-dimensional obstacles. Phenomenologically, the electrostatic correlation is taken into account in a Ginzburg-Laudau-type functional which yields a modified PB equation with a biharmonic term to describe the contribution from the correlation energy [22] and a correlation length as a parameter to be accurately fitted by simulations or experiments.

In most of theoretical and computational studies under the primitive model [24, 25], a homogeneous dielectric profile for electrolytes near surfaces is often assumed, e.g., 80 for the relative dielectric constant of water solvent. This is far from a high-accurate description of dielectric properties of solvent. Water molecules are ordered near micro- or macro-ions, weakening the shielding for ion-ion interactions. This has led to models for ion-concentration- or field-dependent dielectric permittivities. Historically, the dependence of the dielectric permittivity on the ionic solution has been discussed as early as 1940s [26]. Later, Booth considered the dielectric constant of polar electrolytes as a function of the
electrostatic field strength \(27, 28\), which was followed by many related studies from molecular dynamics simulations \(29, 30\) to continuum theory \(31, 32\). Recent work also reported that the dielectric decrement is relevant to ion-specific effects \(33\). On the other hand, the Booth’s model was utilized to modify the Poisson-Boltzmann equation to predict the capacitance with effects of morphology and dielectric permittivity \(34\). Coupling with the Booth’s model, the Langevin-Poisson-Boltzmann (LPB) equation was developed to investigate the effects of polarization saturation to the contact potential at the colloid surface and the long range interactions between colloids \(35\). More recently, Bonthuis et al. \(36, 37\) and Bonthuis and Netz \(38\) through molecular dynamics simulations showed that the interfacial dielectric function is closely related to the molecular solvent structure of the surface. By incorporating the structure properties in the dielectric profile, the Bonthuis-Netz model \(38\) has been successful in predicting the ion distribution with good agreement with a bunch of physical experimental results and particle simulations.

When moving an ion from a high-dielectric region to a lower one, it costs the solvation energy and thus favors to stay away. This explains the ion depletion near the water/air interface. So with the decrement of the double-layer dielectric permittivity by the field, ions are repelled. In contrast, we should see that the ion-ion correlation becomes stronger for lower \(\varepsilon\) since the coupling parameter \(\Xi\) is the reciprocal ratio of \(\varepsilon^2\), enhancing the ion condensation. These mutual effects to the interfacial ion structure are less understood. This is our purpose to find an appropriate model to account for both effects. We have considered the effect of inhomogeneous dielectric function which is either space-dependent or field-dependent under the continuum theory. We go one step further to couple the dielectric function with the self-consistent field (SCF) theory \(39, 40\) to incorporate the correlation energy (the self energy of a test ion). A self-consistent system composed of a self-energy modified PB equation (or Possion-Nernst-Planck equation for charge dynamics) and a generalized Debye-Hückel (DH) equation is derived, which characterizes the inhomogeneous dielectric background. This SCF model gives rise to difficult issues for numerical approximation. On one hand, the inhomogeneity of dielectric permittivity introduces the difference in the solvation energy (Born energy) which is proportional to the reciprocal of the product of the dielectric constant and the ionic radius \(47\). It is necessary to handle the exclude-volume effect of ions, essentially giving rise to a multi-scale problem. On the other hand, the solution of the generalized DH equation is always a difficult issue even when the dielectric profile is homogeneous, since it is a Green’s function equation. Numerical methods for this high-dimensional problem are computationally expensive. More efficient solution should be proposed. These technical issues will be resolved by introducing an asymptotic decomposition of the self energy, where the approximate DH equation is represented by an integral over the three-dimensional domain.

The traditional SCF equations for charged systems are based on a point-charge assumption, formulated from the variational field theory. The solution of this set of equations blows up at the high coupling parameter \(\Xi\) (see Ref. \(18\)) because the ion size effect is ignored and thus the correlation energy is divergent. This shortcoming is fixed in this paper, thus allowing us to explore new physics at the higher coupling regime. We simulate the 1:1 and 2:1 salts for electrolytes with fixed dielectric permittivity through the proposed SCF model and particle-based Monte Carlo simulations, and find excellent agreement between two approaches. Meanwhile, it is illustrated that many important features are captured by the modified SCF equations, e.g., the depletion due to the low dielectric zone and the charge inversion for strong-coupling systems. Furthermore, we find from the Booth dielectric model that the electric field causes the ordered alignment for the first few layers of water, which however greatly changes the surface potential of the charged interface near an electrolyte. These results demonstrate the attractive features of the SCF model, and then promising for the use in understanding richer physical and biological phenomena.

II. MODEL

A. Self-consistent field model with variable permittivity

Let \(\varepsilon\) be the dielectric permittivity of the solvent including a binary salt of valences \(z_\pm\). Subject to suitable boundary conditions, the electrostatic potential \(\Phi\) in the electrolyte is described by the classical Poisson equation,

\[
- \nabla \cdot \varepsilon \nabla \Phi = \sum_{i=\pm} z_i e c_i, \tag{1}
\]

where \(e\) is the elementary charge and \(c_i\) is the concentration function of the ions of species \(i\). By the mass conservation, the modified Nernst-Planck equation is used to describe the dynamics of charged particles in an electrolyte, i.e., the equation for \(c_i\) is,

\[
\begin{align*}
\frac{\partial c_i}{\partial t} &= \nabla \cdot D_i \left( \nabla c_i + \beta c_i \nabla U_i \right), \\
U_i &= z_i e \Phi + \frac{1}{2} z_i^2 e^2 u_i, \tag{2}
\end{align*}
\]

where \(D_i\) is the diffusion constant, and \(\beta = 1/k_B T\) is the inverse thermal energy. The second term in the right side is the contribution from the ion transport due to the energy gradient and \(U_i\) is the electrostatic energy of an ion at the position, called the potential of mean force as approximated by the sum of the mean potential energy and the correlation energy \(\frac{1}{2} z_i^2 e^2 u_i\), following a lot of work \(40, 41, 44, 47\). The physical meaning of the potential of mean force is the free energy cost of moving
a unit test ion from the bulk solvent region into its current position, where the correlation energy is related to a Green’s function to be discussed later on. In equilibrium, the Nernst-Planck equation Eq. (2) has an explicit formula for ionic concentration, \( c_i = c_{i0} e^{-\beta U_i} \), where \( c_{i0} \) is the concentration in bulk solution. This leads to the self-energy modified PB equation,

\[
- \nabla \cdot \varepsilon \nabla \Phi = \sum_i z_i e c_{i0} e^{-\beta U_i}. \tag{3}
\]

This equation is beyond the classical PB theory in the sense that electrostatic correlations have been included in the self energy to improve the approximation of the mean-force potential.

Equation (3) is available for cases with symmetric or asymmetric ionic sizes and valences. There is an obvious shortcoming in physical systems with high surface charge density or large surface electric potentials for which the ion density near the interface increases exponentially and does not saturate. One way to fix this issue is to consider the steric effect of finite ionic size, and one can introduce the entropic contribution of water molecules in the free energy and use the lattice gas formalism to derive the ion density distribution with maximal charge density.

In order to close the above equation system, we define the self energy \( u_i \) by following the SCF theory \cite{10,42}, where the self energy is the self-Green’s function limit,

\[
u_i = \lim_{r’ \to r} \left( G_i(r, r’) - G_0(r, r’) \right), \tag{6}
\]

and \( G_i \) is the Green’s function described by a generalized Debye-Hückel (DH) equation, and \( G_0 \) is the free-space Green’s function described by \( \frac{-\varepsilon_0 \nabla^2 G_0(r, r’)}{\varepsilon_0} = \delta(r, r’) \). In order to take into account the effect of variable dielectric permittivity, the DH equation in the SCF theory is expressed as \cite{52},

\[
- \nabla \cdot \varepsilon_i(r, r’) \nabla G_i(r, r’) + 2 I_i(r, r’) G_i(r, r’) = \delta(r, r’), \tag{7}
\]

where the dielectric permittivity \( \varepsilon_i(r, r’) \) and ionic strength \( I_i(r, r’) \) locally depends on the position of the test ion of species \( i \), which characterizes its ionic size effects to the dielectric function and excluded volume,

\[
\varepsilon_i(r, r’) = \begin{cases} 
    \varepsilon_0, & |r - r’| < a_i, \\
    -\varepsilon(r), & \text{otherwise},
\end{cases}
\tag{8}
\]

\[
I_i(r, r’) = \begin{cases} 
    0, & |r - r’| < a_i, \\
    \frac{1}{2} \beta e^2 \sum_i z_i^2 c_i, & \text{otherwise},
\end{cases}
\tag{9}
\]

where \( \varepsilon_0 \) is the effective dielectric permittivity inside the ion and we take the vacuum dielectric constant in this work, \( a_i \) is the radius of \( i \)th ion. At the point charge assumption \( a_i \to 0 \), Eq. (8) is divergent for a space-dependent \( \varepsilon \), thus this modification is essential to ensure a finite self energy \( u_i \). It can be emphasized that ionic specific effects can be accounted for by defining a species-dependent \( \varepsilon_0 \) in Eq. (8).

The large potentials usually appear near the surfaces with strong surface charges, the treatment with steric entropy is useful to control numerical stability and performs well to constrain the concentration of counterions in a physically significant regime. For the case of asymmetric ionic sizes, we take the lattice volume \( \nu \) as the volume of a counterion, considering the ion distribution is far below the saturation density and not sensitive to the size of the coions. On the other hand, we do introduce the effect of asymmetry in ion size when calculating the self energy with Eq. (8). We find this consideration is necessary when the ion-ion correlation of the coions is also strong, e.g., for 2:2 electrolytes.

### B. Nondimensionalization

Let \( L \) be a length scale to characterize the geometric length of interfaces, \( \ell_B = \beta e^2 / (4 \pi \varepsilon_0 W) \) be the Bjerrum length in water solvent, and \( \ell_D = 1 / \sqrt{4 \pi \ell_B} \sum_i z_i^2 c_{i0} \) be the Debye screening length. We follow parts of the dimensionless parameters and variables in \cite{53} and define \( \mathbf{\tilde{r}} = \mathbf{r} / L, \mathbf{\tilde{c}}_{i0} = c_{i0} / c_{i0}, \tilde{\varepsilon} = \varepsilon / \varepsilon_0, \tilde{\Phi} = \beta e \mathbf{\Phi}, \tilde{G}_i = \beta e^2 \tilde{G}_i, \) and \( \tilde{G}_0 = \beta e^2 \tilde{G}_0 \). We define the dimensionless variables for the surface charge density \( \tilde{\sigma} = \sigma L^2 / e \) and the dipole moment \( \tilde{\rho}_0 = \rho_0 / (\varepsilon L) \) for the use in next sections. We drop the tildes of all new variables and have the dimensionless modified PB and DH equations as the following,

\[
-2 \beta e^2 \nabla \cdot \varepsilon \nabla \Phi = \sum_i z_i c_{i0} e^{-\beta U_i - S}, \tag{10}
\]

\[
U_i = z_i \tilde{\Phi} + \frac{1}{2} \tilde{z}_i^2 u_i, \tag{11}
\]

\[
S = \log \left[ 1 + \sum_j \nu_j c_{j0} \left( e^{-\beta U_j} - 1 \right) \right], \tag{12}
\]

\[
u_i = \lim_{r’ \to r} \left[ G_i(r, r’) - G_0(r, r’) \right], \tag{13}
\]

\[
- \nabla \cdot \varepsilon_i \nabla G_i + I_i / (\nu_0 e^2) G_i = 4 \pi q \delta(r - r’), \tag{14}
\]
where

\[ G_0 = \frac{q}{\varepsilon_0 |r - r'|}, \]  

\[ \varepsilon_i(r, r') = \begin{cases} \varepsilon_0, & |r - r'| < a_i, \\ \varepsilon(r), & otherwise, \end{cases} \]  

\[ I_i(r, r') = \begin{cases} 0, & |r - r'| < a_i, \\ \frac{1}{2} \sum_i z_i^2 c_i, & otherwise, \end{cases} \]  

and \( \varepsilon = \ell_D/L \) and \( q = \ell_B/L \) are two dimensionless parameters, \( I_0 = \sum_i z_i^2 c_i/(2\varepsilon e^2) = z_+ (z_+ + 1)/2 \) is the scaled far field ionic strength, which is one for 1:1 electrolytes, and 3 for 2:1 electrolytes. We shall note that after the nondimensionalization the dielectric permittivities \( \varepsilon_0 = 1/80 \) and \( \varepsilon(r) \to 1 \), since they are divided by the water dielectric constant. It is not difficult to see that \( (2I_0 e^2 \varepsilon) \) denotes the effective dielectric function, and \( q \) represents the effective charge of the test ion and hence the strength of its self energy. Eqs. (10)- (13) comprises the SCF model for variable media. This system of self-consistent equations is general for different electrolytes and arbitrary surface geometries. The solution of the DH equation is however challenging, not only because of its high dimensions but also because it is a multiscale problem, i.e., the sizes of nanoparticles and mobile ions are of two different spatial scales.

### C. The self-energy approximation

We consider the dimensionless DH model for finding an asymptotic self energy \( u_i \). Denote an inverse Debye length function, \( \kappa_i = \sqrt{\sum_i z_i^2 c_i/(2\varepsilon e^2)} \), then the DH equation is written as,

\[ -\nabla \cdot \varepsilon_i \nabla \varepsilon_i + \kappa_i^2 \varepsilon_i = 4\pi \delta(r - r'), \]  

where \( \varepsilon_i(r, r') \) and \( \kappa_i(r, r') \) are six dimensional and locally depend on the location of the test ion,

\[ \varepsilon_i(r, r') = \begin{cases} \varepsilon_0, & |r - r'| < a_i, \\ \varepsilon(r), & otherwise, \end{cases} \]  

\[ \kappa_i(r, r') = \begin{cases} 0, & |r - r'| < a_i, \\ \kappa(r), & otherwise, \end{cases} \]  

We recall the dimensionless \( \varepsilon \) is unitary in the bulk solvent region.

To resolve the multiscale problem in the approximation of the self energy, we decompose the solution for \( u_i \) into two parts by

\[ u_i = u_1 + u_2 = \lim_{r' \to r} G_i - G_i' + \lim_{r' \to r} (G_i' - G_0), \]  

such that \( G_i' \) satisfies,

\[ -\nabla \cdot \varepsilon_i' \nabla G_i' = 4\pi \delta(r - r'), \]  

We shall see that \( \varepsilon_i' \) is piecewise constant, which is uniform outside the ionic cavity. Then the second part of the self energy, \( u_2 \), can be evaluated locally and analytically, giving us a form of the Born energy \( [47] \),

\[ u_2 = \frac{1}{a_i} \left( \frac{1}{\varepsilon(r)} - \frac{1}{\varepsilon_0} \right), \]  

which characterizes the mutual effect of the ionic size and variable permittivity.

In the first component of the self energy \( [21] \), the solution of Green’s function depends on the boundary, global ionic concentrations and dielectric permittivity, and \( u_1 \) has no explicit expression. We consider the small \( a_i \) asymptotic and that \( \varepsilon_i' \approx \varepsilon_i \) in the locality of \( r' \). At the limit \( a_i \to 0 \), the self Green’s function

\[ \tilde{u}_1 = \lim_{r' \to r} (\tilde{G} - \tilde{G}'), \]  

and \( \tilde{G}' = 1/\varepsilon(r')|r - r'| \). Here, \( \varepsilon(r) \) and \( \kappa(r) \) do not depend on the site of the test ion, and we then remove the difficulty of solving two space scales. We shall use the far field approximation to include the excluded-volume effect in the definition of \( \kappa_i(r, r') \), which yields the expression for \( u_1 \),

\[ u_1 \approx \frac{\tilde{u}_1}{1 - \varepsilon(r)\tilde{u}_1 a_i}. \]  

The approximate expression \([20]\) is accurate in the sense that the function \( \kappa(r) \) is not rapidly varying or the ion size \( a_i \) is small.

The only expensive part is then how to solve equation \([20]\) to obtain \( \tilde{u}_1 = \lim_{r' \to r} (\tilde{G} - \tilde{G}') \). Let

\[ \mathcal{H} = \sqrt{\varepsilon(r)\varepsilon(r')\tilde{G}}. \]  

Since \( \varepsilon(r) \) and \( \kappa(r) \) are both smooth functions, we transform the Green’s function equation into the equation for \( \mathcal{H} \),

\[ -\nabla^2 \mathcal{H} + v^2 \mathcal{H} = 4\pi \delta(r - r'), \]  

where, after using the property \( g(r)\delta(r - r') = g(r')\delta(r - r') \) for any smooth \( g \), we can write,

\[ v(r) = \left[ \sqrt{\varepsilon(r)} \nabla^2 \sqrt{\varepsilon(r)} + \kappa^2 \right]^{1/2}. \]  

For the free-space Green’s function, we introduce \( \mathcal{H}_0 = \varepsilon(r)\tilde{G}' = 1/|r - r'| \). Subtracting Eq. \([22]\) and \( \mathcal{H}_0 \) into Eq. \([28]\) gives,

\[ \nabla^2 (\mathcal{H} - \mathcal{H}_0) = v^2 \mathcal{H}. \]
The solution of this equation can be represented by a Born series, widely applied for scattering theory in quantum mechanics, through the integral equation,

$$\mathcal{H} - \mathcal{H}_0 = -\frac{1}{4\pi} \int \frac{\epsilon^2(r')\mathcal{H}(r'',r')}{|r-r'|} dr''.$$  \hfill (31)

To solve it, initially we could take the leading asymptotic for \(\mathcal{H}\),

$$\mathcal{H}^{(1)}(r, r') = \frac{\exp[n(r)r_{12}]}{r_{12}},$$  \hfill (32)

where \(r_{12}\) is the distance between \(r\) and \(r'\), then a series solution is iteratively defined by,

$$\mathcal{H}^{(n)} - \mathcal{H}_0 = -\frac{1}{4\pi} \int \frac{\epsilon^2(r'')\mathcal{H}^{(n-1)}(r'', r')}{|r-r''|} dr''.$$  \hfill (33)

In principle, the solution is obtained upon the convergence of the iteration. Each step includes a multiplication of two dense matrices, which is too expensive to implement. However, \(\mathcal{H}^{(1)}\) is actually pretty good asymptotic approximation to the Green’s function, and we could expect that \(\mathcal{H}^{(2)}\) may include enough information to understand the Green’s function. In this point, the expression for \(\tilde{u}_1\) is,

$$\tilde{u}_1 = \frac{1}{\bar{\epsilon}(r)} \lim_{r' \to r} \left[ \mathcal{H}^{(2)}(r,r') - \mathcal{H}_0(r,r') \right] = -\frac{1}{4\pi \bar{\epsilon}(r)} \int \frac{\epsilon^2(r'')\mathcal{H}^{(1)}(r'', r)}{|r-r''|} dr''.$$  \hfill (34)

Finally, we find an approximate solution for the self-energy,

$$u_i = \frac{\tilde{u}_1}{1 - \bar{\epsilon}(r)\tilde{u}_1a_i} + \frac{1}{a_i} \left[ \frac{1}{\bar{\epsilon}(r)} - \frac{1}{\epsilon_0} \right],$$  \hfill (35)

where \(\tilde{u}_1\) is an integral expression given in Eq. (31). The global dielectric and ionic strength variations due to dielectric interfaces are included in \(\bar{\epsilon}\).

It should be remarked the convergence of the Born series depends on the smoothness of the dielectric permittivity. The accuracy may be low when a large change is present in the dielectric profile. When the interface is regular such as planes or spheres, this can be tackled by taking the integral region as the solvent region and introducing a WKB-type approximation by using the image charge method; see (54) for planar interfaces. For a general geometry, an efficient approximation remains an open question.

### D. Field-dependent dielectric permittivity

In this section, we introduce the dipolar model for the dielectric permittivity. The solvent molecules of the solution generally contain permanent dipoles. When an external electric field is applied, the dipoles are oriented against the field and the solvent is polarized. As aforementioned in the Introduction, the dependence of polarization and dielectric permittivity on the electric field strength were systematically discussed by Booth (27, 28) in the 1950s. In the dimensional form, the Booth’s relation is expressed by the formula,

$$\varepsilon(E) = \varepsilon_0 + \frac{p_0n_d(\beta p_0 E)}{E},$$  \hfill (36)

with the field strength \(E = |\nabla \Phi|\), the Langevin function \(\mathcal{L}(x) = \coth x - 1/x\) and the dipolar density \(n_d(x) = c_d \sinh x/x\), where \(p_0\) and \(c_d\) are the permanent dipole moment of a solvent molecule and its number density. Considering the case of water solvent, we have the limit in bulk electrolytes \(\varepsilon(E \to 0) = \varepsilon_0 + \beta p_0^2 c_d/3 = \varepsilon_W\), which gives \(\beta p_0^2 c_d = 3(\varepsilon_W - \varepsilon_0)\). Substituting this field-dependent dielectric constant into classical PB model leads to the so called dipolar PB (DPB) equation, which has been derived by Abrashkin et al. (54). Usually, it is also reasonable for water solvent to neglect the small change in the dipolar density, i.e., assume \(n_d(\beta p_0 E) = c_d\), which yields the Langevin PB equation (35).

We follow the simplified version for ignoring the density fluctuation of water, and include the self-energy contribution due to the dielectric inhomogeneity and the electrostatic correlation. In dimensionless form, the Langevin-SCF equation (SCF-L) reads,

$$-2\beta p_0^2 \varepsilon \cdot \varepsilon(|\nabla \Phi|) \nabla \Phi = \sum_i \varepsilon_i c_i \exp[-U_i - S],$$  \hfill (37)

where \(U_i\) and \(S\) are expressions described in Eqs. (11) and (12) and \(\varepsilon(1)\) is an integral expression described in Eq. (51). The global dielectric and ionic strength variations due to dielectric interfaces are included in \(\varepsilon\).

We have \(\varepsilon_0 = 1/80\) and \(\varepsilon(E \to 0) = 1\).

Besides the above field-dependent or Booth’s model for dielectric permittivity, there have been many discussions for other effects to local variations of the dielectric permittivity. With the simple dipole moment model, one can see that ions in electrolytes undergo solvation shells and prevent the surrounding water molecules from being oriented against the external field. The dielectric permittivity of the solution will be decreased when ions are added to it, and one can obtain equations for the salt-concentration-dependent dielectric permittivity for electrolytes (21, 38, 57, 58). Furthermore, the ionic polarization also plays a role in the dielectric function because it acts as induced dipole moments in an external field (59). When these effects are considered, the potential of mean force \(U_i\) in the SCF model has to be modified again. However, we will limit the discussion to Eq. (37) and save them as future work if these effects have to be included to describe unexplored physics.
is simplified as,

$$\bar{u}_1 = \frac{1}{\varepsilon} \lim_{r' \to r} \left[ \mathcal{H}^{(2)}(r, r') - \mathcal{H}_0(r, r') \right]$$

$$= -\frac{1}{2\varepsilon} \int_0^\infty \rho^2(r') e^{-\rho(r')^2 r^2 + r - 2\rho(r') \cos \theta} r' e^r d\theta d\rho$$

$$= -\frac{1}{2\varepsilon} \int_0^\infty \rho^2(r') r' dr' \int (r''+r') e^{-\rho(z)} r' dr' d\rho.$$

The exponential integral is a special function and can be pre-computed, and the computational cost of evaluating $\delta \mathcal{H}(r \to r')$ for each point $r'$ becomes only a one-dimensional integral for $r''$.

We propose a self-consistent iterative algorithm to solve the SCF and SCF-L models. The algorithm is composed of two alternating steps: (1) For given $c_i^{(k)}$ and $\Phi^{(k)}$, we update $u_i^{(k)}$; and (2) for given $u_i^{(k)}$, we solve the modified PB equation for $\Phi^{(k+1)}$ subject to given boundary conditions. The iterative scheme for time steps is as follows,

$$u_i^{(k)} = \frac{-\bar{u}_i^{(k)}}{1 - \varepsilon u_i^{(k)} a_i} + \frac{1}{a_i} \left[ \frac{1}{\varepsilon(i)} - \frac{1}{\varepsilon_0} \right], \quad (42)$$

$$\bar{u}_1^{(k)} = -\int \left[ \rho(k)(r')^2 \exp \left( \rho(k)(r') - r'' \right) \right] dr'$$

$$-2I_0 e^2 \nabla \cdot \varepsilon(k+1) \nabla \Phi^{(k+1)} = \sum_i z_i c_i^{(0)} e^{-U_i^{(k+1)} - S^{(k-1)}}, \quad (44)$$

$$U_i^{(k+1)} = z_i \Phi^{(k+1)} + \frac{1}{2} \sum_j \nu_j c_j^{(0)} (e^{-U_j^{(k+1)} - 1}), \quad (45)$$

$$S^{(k+1)} = \log \left[ 1 + \sum_j \nu_j c_j^{(0)} (e^{-U_j^{(k+1)} - 1}) \right], \quad (46)$$

for $k = 0, 1, 2, ..., K$ and the iterative steps are performed until the convergence criteria $|u_i^{(k+1)} - u_i^{(k)}| < \delta$ is arrived, where $\delta$ is a small tolerant value. Here, we shall note that $\varepsilon$ and $\nu$ are functions of $\Phi$ and $c_i$. This numerical scheme follows a recent work [18] for solvents of uniform dielectric function where the self-Green’s function in the DH equation can be efficiently solved by a method of the selected inversion. Differently, in this paper a numerical integration is used for the self energy, and thus we can work on more general geometries.

The sub-level of the iterative scheme is embodied in the solution of the modified PB equation [43], which shows high nonlinearity. We could in general use the iterative scheme at the $(k)$th loop as

$$-2I_0 e^2 \nabla \cdot \varepsilon(k) \nabla \Phi^{[k+1]} - \gamma(k) \Phi^{[k+1]} = \sum_i z_i c_i^{[k]} - \gamma(k) \Phi_i^{[k]},$$

where $c_i^{[k]}$ means the potential in $U_i$ and $S$ uses the value from the $i$th step, and the relaxation function $\gamma(r)$ is defined as

$$\gamma(r) = |\sum_i z_i c_i^{[i]}/(|\Phi| + \delta_0)|, \quad (48)$$
with $\delta_0 = 10^{-8}$. Here we use the index $[\cdot]$ to represent the sub-iteration of the $(k)$th loop of the self-consistent iteration. This iteration stops when the convergence criteria $|\Phi^{[k+1]}_i - \Phi^{[k]}_i| < \delta$ is arrived.

For the physical setting with one macroion, the mean potential is spherically symmetric, hence the space discretization for Eq. (47) can be done by the central difference scheme for one-dimensional equation along the radial direction. The composite trapezoidal rule is used to approximate the integral in computing Eq. (41) for $\psi_1$.

We have not mentioned the direct numerical method for solving the Green’s function. Interestingly, solving the diagonal elements of lattice Green’s function from the generalized DH equation can be done by the use of selected inversion [61, 62], which has been shown to reduce the computational cost a lot with point charge limit [48, 53]. However, direct solvers of problems with inhomogeneous dielectric constant and size effect still remains challenging since it is a two-scale problem and we have to use a mesh size much smaller than an ion radius.

IV. RESULTS

In this section, we present numerical results for different systems of binary electrolytes surrounding a spherical macroion. We study the position-dependent dielectric constant $\varepsilon(r)$, compared with results from the MC simulations. We then perform calculation for the SCF model with field-dependent dielectric function. We use 1:1 and 2:1 salts, where anions are coions and always monovalent. Divalent counterions are used for strongly correlated systems, for which a correct treatment of electrostatic self energy is essential. Without specific statement, ions have radius of $a = 0.225 \text{ nm}$, the simulations are performed at room temperature and the relative dielectric constant 80 for the bulk water, so the Bjerrum length $\ell_B = 7.14 \text{ nm}$. The dimensional dipole moment is chosen as $p_0 = 4.8 \text{ D}$. For keeping the bulk water density $c_d = 55 \text{ M}$. Surface charge density is varied within $0 < -\sigma < 3 \text{ e/nm}^2$, which describes most of the environments in biological or physical systems.

A. Space-dependent dielectric function

In the following two groups of simulations, we consider simulated systems with given space-dependent dielectric functions. We take the radius of macroion $R = 2 \text{ nm}$, and the grid size for the SCF approximation is $3.75 \times 10^{-3} \text{ nm}$.

Electrolyte with 1:1 salts. We first consider that the macroion is surrounded by an electrolyte of 50 mM 1:1 salts. A ramp shape of radial function is used to describe the dielectric permittivity, given by the following formula,

$$\varepsilon(r) = \varepsilon_W + \frac{\varepsilon_C - \varepsilon_W}{1 + \exp[(r - 0.25)/\lambda]}$$ \hspace{1cm} (49)
to obtain accurate MC results. As aforementioned, the Born series for the self energy has slow convergence for the sharp dielectric variation and Eq. (11) fails when it integrates over the whole domain. In order to make the Born series work, we take the lower limit of integral Eq. (41) as 

\[
\sum_{\ell=1}^{L} z_{\ell} \exp(\tilde{u}_{\ell} D_{\ell}) \tilde{u}_{\ell}^{\prime} = \tilde{u}_{1} + \sum_{\ell=1}^{L} z_{\ell} \exp(\tilde{u}_{\ell} D_{\ell}) \tilde{u}_{\ell}, 
\]

(50)

where index \( \ell \) means the \( \ell \)th image charges, \( z_{\ell} \) is its strength due to a unit source charge, and \( D_{\ell} \) is its distance to the source charge; for these parameters see Eqs. (11)-(12) in Ref. [71]. Both SCF and MC simulations use three image charges.

The results are presented in Fig. 3 for both weak and strong surface charge densities. From the left panel, we shall see that the WKB type approximation is very accurate for the dielectric effect, and the SCF and MC results are in a perfect agreement. For the weak-coupling system (Fig. 3(a)), the image charges repel the mobile ions and a depletion zone is formed near the surface. For the strong-coupling system (Fig. 3(b)), they are screened by the surface charge since the image charges are dipole effect. The MC simulation does not predict a depletion zone, while the SCF result has a short interval for the depletion due to the steric effect applied to the double-layer ions in the vicinity of the surface. Both results show much higher counterion density near the surface than the bulk region with a factor of \( \sim 300 \) times (15 M vs. 50 mM). Both the coion distribution profiles are slightly nonmonotonic, indicating an overscreening inside the double layer. These nonmonotonic curves are important signals for the correlation-induced charge inversion widely studied in literature [6, 7, 13, 17, 24]. The results shown in the two panels demonstrate that the SCF model can accurately capture the dielectric-boundary effect and the ion-ion electrostatic correlation.

B. Field-dependent dielectric function

We have seen that the SCF theory can accurately capture the effects of electrostatic correlation, dielectric boundary and varying dielectric permittivity by a comparison with particle-base MC simulations with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function. In this section, we study equilibrium properties for systems of field-dependent dielectric function using the Langevin-SCF model. We consider both 1:1 and 2:1 salts with a fixed space-dependent dielectric function.
\[ \sigma = -0.5, -1.5 \text{ and } -2.5 \text{ e/nm}^2 \] are given. Correspondingly, the coupling parameters for 1:1 salts are \( \Xi = 1.6, 4.8 \text{ and } 8.0 \), and those for 2:1 salts are \( \Xi = 12.8, 38.4 \text{ and } 64.1 \). The upper and middle panels show the cation and anion density distributions, (a)(b) for 1:1 salts, and (c)(d) for 2:1 salts. The bottom panels, (e)(f), are the electric potentials for 2:1 salts from both the SCF-L and classical PB predictions.

For monovalent ions, since the electric field only slightly changes the nearby permittivity at the surface, the Born-energy repulsion to mobile ions is weak and not enough to overcome the electrostatic attraction from the macroion surface. On the other side, The electrostatic correlation between monovalent ions is weak too, and the entropic effect leads to a monotonic neutralization of the surface charge along the radial direction. Therefore, with the increase of the surface charge, both cation and anion ion densities of monovalent salts remain monotonic curves.

For divalent ions, the situations are different. The electric strength is high near the surface. This produces the decrement of the dielectric permittivity as an output. The Born solvation energy is repulsive and has a quadratic relation with the ion valence. Although the surface-charge attraction is strong, a depletion zone can be observed for high surface charge densities \( \sigma = -1.5 \text{ and } -2.5 \text{ e/nm}^2 \), demonstrating that the zone is difficult to access by mobile ions due to the repulsion from the Born solvation energy. On the other hand, for these two surface densities, coions have a sharp increase up to a maximum at the one-ion-diameter distance, then decay to the bulk value monotonically. Observed from the distributions of electric potentials, the curves reverse the sign at the nearby distance, predicting a positive potential at the far field. This is the result of the correlation and the strange charge inversion phenomenon for multivalent counterions has been confirmed theoretically \([74, 76, 77]\) and experimentally by electrophoresis mobility \([78–80]\). This clearly demonstrates again that the SCF model describes the electrostatic correlation. Ignoring the many-body correlation, the classical PB theory does not predict the charge inversion and as shown in Fig. 4(f) that the electric potentials are always negative with the increase of \( \sigma \).

2. Effects of the field-dependent permittivity

In Fig. 4(a)(b), the relative dielectric functions for 1:1 and 2:1 salts are illustrated in the cases of \( \sigma = -0.5, -1.5 \text{ and } -2.5 \text{ e/nm}^2 \). We shall see that the relative dielectric function is rapidly increased from \( \sim 55 \) to \( \sim 75 \) for a distance less than one ion radius. In order to probe the effect of the dielectric variation in this small region, we present comparisons for the SCF calculations using this field-dependent dielectric function with using uniform water dielectric constant \( \varepsilon _W = 80 \varepsilon _0 \). We call both results as the SCF-L and SCF, respectively.

3. Effect of the ionic size

At last, let us see how the ionic size asymmetry affects the double-layer structure. We remain the anion radius of \( a_− = 0.225 \text{ nm} \), and consider two different cation (counterion) radii \( a_+ = 0.225 \text{ nm} \) and \( a_+ = 0.18 \text{ nm} \). The effect of ionic size is minor at the weak coupling regime. So we consider valence-symmetric electrolytes for the strong-coupling regime by setting the Bjerrum length \( \ell _B = 2.856 \text{ nm} \), a four times larger than the water Bjerrum length at room temperature. We can think this large Bjerrum length is because of a low temperature or
(d) The electric potentials for \( \sigma \) of 1:1 salts with a low bulk dielectric constant or multivalent ion species.

Fig. 6 plots the curves of both symmetric and asymmetric cases with three surface charge densities \( \sigma = -0.2, -0.3 \) and \(-0.4 \) e/nm\(^2\). We shall note that for a large \( \ell_B \), the electrostatic correlations between ions are strong and thus the nonmonotonic concentration should be predicted when \( \sigma \) is not very low. On the other hand, the smaller counterion radius greatly increases the correlation self energy which is negative and thus is favorable for the ion congregation in the double layer. Both counterion and coion nearby densities of the asymmetric case (smaller counterions) are higher than the symmetric case, and this effect is enlarged with the increase of the surface charge density. From Fig. 6(d), we have observed the charge inversion for the asymmetric case other from the symmetric case.

V. CONCLUSIONS

We have introduced a modified version of the self-consistent field model for electrostatic interaction, and developed a hybrid numerical method for the numerical solution of the resulted system of PDEs. In particular, we proposed a new and efficient way to deal with the solution of self Green’s function for a test ion as a charged hard sphere in a dielectrically inhomogeneous medium. As a result, the expensive direct numerical implementation for a multiscale (macroion and small ions) and high-dimensional Green’s function problem (i.e., 6D problem for a 3D geometry) is avoided.

The numerical results are shown to capture many-body effects, such as the effect of inhomogeneous dielectric permittivity (the Born energy), size effect and ionic correlations. These effects are thought to be significant in many biological and physical phenomena near aqueous electrolyte interfaces. The strong ionic correlations lead to the charge inversion which has also been well reproduced by the SCF model. The numerical results are shown to quantitatively match the results from MC simulations. We shall notice the drawback of the approximation with Born series is obvious for irregular surfaces and remain the challenges of overcoming this issue by developing fast and accurate numerical methods as our future work. The effect of correlation to charge dynamics shall be an important direction to be addressed in the future, which will be studied in the framework of modified Poisson-Nernst-Planck equations.

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[1] Y. Levin, Rep. Prog. Phys. 65, 1577 (2002).
[2] R. J. Hunter, Zeta Potential in Colloidal Sciences: Principles and Applications (Academic, London, 1981).
[3] L. Joly, C. Ybert, E. Trizac, and L. Boquet, Phys. Rev. Lett. 93, 257805 (2004).
[4] R. H. French, V. A. Parsegian, R. Podgornik, R. F. Rajter, A. Jagota, J. Luo, D. Asthagiri, M. K. Chaudhury, Y.-M. Chiang, S. Granick, et al., Rev. Mod. Phys. 82, 1887 (2010).
[5] D. A. Walker, B. Kowalczyk, M. O. de la Cruz, and B. A. Grzybowski, Nanoscale 3, 1316 (2011).
[6] K. Besteman, M. A. G. Zevenbergen, H. A. Heering, and S. G. Lemay, Phys. Rev. Lett. 93, 170802 (2004).
[7] J. Pittler, W. Bu, D. Vaknin, A. Travesset, D. J. McGillivray, and M. L"osche, Phys. Rev. Lett. 97, 046102 (2006).
[8] M. Lozada-Cassou, R. Saavedra-Barrera, and D. Henderson, J. Chem. Phys. 77, 5150 (1982).
[9] M. Deserno, F. Jiménez-Ángeles, C. Holm, and M. Lozada-Cassou, J. Phys. Chem. B 105, 10983 (2001).
[10] A. Y. Grosberg, T. T. Nguyen, and D. Grier, Nature 385, 230 (1997).
[11] T. E. Angelini, H. Liang, W. Wriggers, and G. C. L. Wong, Proc. Nat. Acad. Sci. USA 100, 8634 (2003).
[12] B. Eisenberg, Adv. Chem. Phys. 31, 117 (2011).
