

2011

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Abstract

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Keywords

Electrolytes, Electrostatics, Thermodynamic properties, Dielectric function, Perturbation theory

Disciplines

Chemistry

Comments

The following article appeared in *Journal of Chemical Physics* 135 (2011): 104104, and may be found at doi:[10.1063/1.3632052](https://doi.org/10.1063/1.3632052).

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Citation: *The Journal of Chemical Physics* **135**, 104104 (2011); doi: 10.1063/1.3632052

View online: <http://dx.doi.org/10.1063/1.3632052>

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A molecular Debye-Hückel theory and its applications to electrolyte solutions

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(Received 8 June 2011; accepted 12 August 2011; published online 9 September 2011)

In this report, a molecular Debye-Hückel theory for ionic fluids is developed. Starting from the macroscopic Maxwell equations for bulk systems, the dispersion relation leads to a generalized Debye-Hückel theory which is related to the dressed ion theory in the static case. Due to the multi-pole structure of dielectric function of ionic fluids, the electric potential around a single ion has a multi-Yukawa form. Given the dielectric function, the multi-Yukawa potential can be determined from our molecular Debye-Hückel theory, hence, the electrostatic contributions to thermodynamic properties of ionic fluids can be obtained. Applications to binary as well as multi-component primitive models of electrolyte solutions demonstrated the accuracy of our approach. More importantly, for electrolyte solution models with soft short-ranged interactions, it is shown that the traditional perturbation theory can be extended to ionic fluids successfully just as the perturbation theory has been successfully used for short-ranged systems. © 2011 American Institute of Physics. [doi:10.1063/1.3632052]

I. INTRODUCTION

Coulomb interaction is ubiquitous in nature, ranging from physical, chemical to biological systems, such as plasma, electrolyte solutions, and protein-DNA complexes. The long-ranged nature of Coulomb interaction makes it difficult to tackle compared with short-ranged interactions. On the other hand, the microscopic neutrality condition naturally leads to the Debye screening, which dramatically simplified the description of systems with Coulomb interactions as demonstrated in the Debye-Hückel (DH) theory.¹ This traditional treatment is based on the Poisson equation in combination with a mean field approximation for the radial distribution function of ionic species, which lead to the familiar Poisson-Boltzmann (PB) equation. Since PB equation is highly nonlinear, analytical solutions are hard to attain except some simple geometries, and even numerical solutions of PB are highly nontrivial. In the low coupling limit, linearization of PB equation leads to the Debye-Hückel theory¹ of electrolyte solutions. The DH theory is elegant in the sense that it reveals the universality of Debye screening in systems with Coulomb interactions. The electric potential in the traditional DH theory has one Yukawa term, and the screening parameter is simply determined by the Debye screening length, which leads to straightforward calculations of thermodynamic properties contributed from the Coulomb interactions.

Due to the simplicity of the DH theory, it became the hallmark of theoretical treatments for Coulomb systems.² Since the traditional DH is valid only for low coupling limit, naturally there are numerous works to improve this approach. For example, Kirkwood and Poirier³ utilized the concept of potential of mean force, which could be expanded in a

power series in terms of a charging parameter, and the coefficient of the expansion of potential of mean force could be derived in a systematic way using the method of semi-invariants. They demonstrated that the DH theory is a rigorous statistical mechanics theory in the low coupling limit. Outhwaite and co-workers⁴⁻⁷ had provided a modified PB approach by considering the so-called fluctuation potential, which could be solved using superposition principle. Attard and co-workers⁸⁻¹⁰ had improved the traditional DH in a self-consistent way, with the Debye screening length replaced by an effective screening length which could be determined by the Stillinger-Lovett relation.¹¹ A particular relevant approach to the current work is the dressed ion theory (DIT) by Kjellander and Mitchell,^{12,13} which keeps the Yukawa form of electrical potential as in the traditional DH theory by introducing renormalized charges and effective screening lengths, which are determined from the dielectric function of the system. Thus, a formally exact theory of Coulomb systems can be formulated using a combination of linearized PB solutions. A comprehensive review of the DH theory and its extensions can be found in Ref. 14.

Essentially, all of these works are for the static case and there is no clear route to extend to dynamical cases, where the frequency-dependent screening may play important roles such as protein-protein interaction models in electrolyte solutions¹⁵ and solvation dynamics in ionic fluids.¹⁶ With these motivations in mind, we began to develop not only static extension of the traditional DH theory, but also systematic extension to the dynamical case.¹⁷ In our previous work, it was demonstrated that the dispersion relation of the dielectric function naturally leads to the effective screening lengths, which reduced to the screening lengths in the dressed ion theory for the static case. Furthermore, such dynamical screening lengths provide a simple theory for solvation dynamics in ionic fluids.¹⁷

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There are two important concepts in the dressed ion theory,^{12,13} namely, roots of the dielectric function lead to the effective screening lengths (see also Ref. 32), and the effective charge of the dressed ion reflects the nonlinear response of the environment to the tagged ion. The dielectric function is a macroscopic property of the bulk system and could be obtained from molecular simulations or experimental measurements, while the effective charge is a microscopic property which is related to the local molecular correlations. For applications of the dressed ion theory, the radial distribution function of the system is necessary to find the effective charges and the effective screening lengths, which contain the information that is missing in the traditional DH theory. For complex systems, such as proteins in an electrolyte solution, the radial distribution functions of the whole system either from molecular simulations or from the integral equations are difficult to obtain. Furthermore, as the electric potential is expressed in terms of an asymptotic series of Yukawa terms, accurate evaluation, which is crucial for accurate thermodynamic properties, requires summation of many such terms.

Our strategy in this report is to develop a molecular DH theory, which keeps the simplicity of the traditional DH theory and at the same time thermodynamic properties of proteins can be evaluated accurately given the macroscopic dielectric function of the electrolyte solution and a molecular model of the protein. To this end, we have found that for a primitive model of electrolyte solutions, general relations between the parameters of multi-Yukawa potential form and the dielectric function can be established, where the first two relations are just the charge neutrality condition and the Stillinger-Lovett relation. From these relations, we can determine the parameters of Yukawa potential forms, and then accurate excess thermodynamic properties could be determined. Our theory is also applicable to models of electrolyte solutions with soft short-ranged interactions by introducing effective hard sphere sizes using perturbation theory. It is shown that the widely successful perturbation theory used for short-ranged interaction systems can be extended to Coulomb systems as long as our molecular DH theory is used to calculate the Coulomb contribution to thermodynamic properties. Applications to 1:1, 2:2, and 2:1 primitive models as well as models of electrolyte solutions with inverse power potential or Lennard-Jones potential are used to demonstrate the validity of our approach.

The paper is organized as follows. In Sec. II, the connection between the dispersion relations from the Maxwell equations and an extended DH theory is established. In Sec. II, a molecular DH theory is introduced to calculate the mean electric potential of a tagged ion in terms of multi-Yukawa forms. Calculations of the electrostatic contribution to thermodynamic properties from the mean electric potential are discussed in Sec. III. Applications to primitive models and models with soft short-ranged interactions are presented in Sec. IV. Some concluding remarks are given in Sec. V. For the static case, a rigorous statistical mechanics derivation and connection with the extended DH theory is presented in the Appendix to clarify the connection between our dispersion relation formulation and the dressed ion theory.

II. DISPERSION RELATIONS AND AN EXTENDED DEBYE-HÜCKEL THEORY OF IONIC FLUIDS

Recently, we have developed a theoretical framework to connect the Debye-Hückel theory to the dispersion relations in electrodynamics.¹⁷ This connection between the dispersion relation (the functional relationship between wave-vector and frequency) and an extended Debye-Hückel theory will be presented here. The purpose of this section is to rigorously derive an extended dynamical Poisson-Boltzmann, Eq. (14), which is the starting point of any extended Debye-Hückel theory.

Let's start with the Maxwell equations of a non-magnetic macroscopic system in Systeme International (SI) unit,¹⁸

$$\begin{aligned}\nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0, \\ \nabla \cdot \mathbf{D} &= \rho, \\ \nabla \times \mathbf{B} - \frac{\partial \mathbf{D}}{\partial t} &= \mathbf{J},\end{aligned}\quad (1)$$

where ρ and \mathbf{J} are the macroscopic (free) charge density and current density in the system. After a Fourier transformation with $e^{i\omega t - i\mathbf{k}\cdot\mathbf{r}}$, all quantities are transformed from $\mathbf{X}(\mathbf{r}, t)$ to $\mathbf{X}(\mathbf{k}, \omega)$, where

$$\mathbf{X}(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt \iiint_{-\infty}^{\infty} d\mathbf{r} \exp(i\omega t - i\mathbf{k} \cdot \mathbf{r}) \mathbf{X}(\mathbf{r}, t),$$

and the inverse transform is defined as

$$\begin{aligned}\mathbf{X}(\mathbf{r}, t) &= \frac{1}{(2\pi)} \int_{-\infty}^{\infty} d\omega \frac{1}{(2\pi)^3} \\ &\times \iiint_{-\infty}^{\infty} d\mathbf{k} \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r}) \mathbf{X}(\mathbf{k}, \omega).\end{aligned}$$

For brevity, we omit the arguments unless it is not clear from the context. Then the Maxwell equations become

$$\begin{aligned}\mathbf{k} \cdot \mathbf{B} &= 0, \\ \mathbf{k} \times \mathbf{E} - \omega \mathbf{B} &= 0, \\ -i\mathbf{k} \cdot \mathbf{D} &= \rho, \\ -i\mathbf{k} \times \mathbf{B} - i\omega \mathbf{D} &= \mathbf{J}.\end{aligned}\quad (2)$$

For a conducting medium such as an ionic fluid, the constitutive relations according to the linear response are

$$\mathbf{D} = \boldsymbol{\Sigma}(\mathbf{k}, \omega) \cdot \mathbf{E},\quad (3)$$

where $\boldsymbol{\Sigma}(\mathbf{k}, \omega) = \boldsymbol{\varepsilon}(\mathbf{k}, \omega) + \frac{i}{\omega} \boldsymbol{\sigma}(\mathbf{k}, \omega)$ is the generalized dielectric tensor, $\boldsymbol{\varepsilon}(\mathbf{k}, \omega)$ is the dielectric tensor, and $\boldsymbol{\sigma}(\mathbf{k}, \omega)$ is the conductivity tensor.¹⁹ If there is no external charge and current as the induced charge and current have been included in the generalized dielectric tensor $\boldsymbol{\Sigma}(\mathbf{k}, \omega)$, a combination of the equations in Eq. (2) leads to

$$\omega^2 \mathbf{D} = \omega^2 \boldsymbol{\Sigma} \cdot \mathbf{E} = \mathbf{E} k^2 - \mathbf{k}(\mathbf{k} \cdot \mathbf{E}).\quad (4)$$

The condition for this set of linear homogeneous equations of \mathbf{E} to have nontrivial solutions is the vanishing of the following determinant:

$$\left| k^2 \left(\mathbf{I} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) - \omega^2 \boldsymbol{\Sigma}(\mathbf{k}, \omega) \right| = 0.\quad (5)$$

This is the dispersion relation in electrodynamics,²⁰ and \mathbf{I} is the rank 2 identity tensor. For an isotropic system, the longitudinal and transverse components of the generalized dielectric tensor are scalars,¹⁹

$$\boldsymbol{\Sigma}(\mathbf{k}, \omega) = \Sigma_l(k, \omega) \left(\mathbf{I} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) + \Sigma_t(k, \omega) \frac{\mathbf{k}\mathbf{k}}{k^2}. \quad (6)$$

The dispersion relations are reduced to

$$\frac{k^2}{\omega^2} - \Sigma_t(k, \omega) = 0, \quad (7)$$

$$\Sigma_l(k, \omega) = 0. \quad (8)$$

Now let us find the solution of Eq. (1) in terms of a scalar potential $\Phi(\mathbf{r}, t)$ and a vector potential $\mathbf{A}(\mathbf{r}, t)$, i.e.,

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (9)$$

$$\mathbf{E}(\mathbf{r}, t) = -\nabla\Phi(\mathbf{r}, t) - \frac{\partial\mathbf{A}(\mathbf{r}, t)}{\partial t}. \quad (10)$$

Note that from the charge density equation we have

$$\rho = -i\mathbf{k} \cdot \mathbf{D} = \Sigma_l(k, \omega)(k^2\Phi - \omega\mathbf{k} \cdot \mathbf{A}), \quad (11)$$

and for the current we have

$$\mathbf{J} = -i\mathbf{k} \times \mathbf{B} - i\omega\mathbf{D} = [k^2\mathbf{I} - \omega^2\boldsymbol{\Sigma}(\mathbf{k}, \omega)] \cdot \mathbf{A} + \omega\Sigma_l(k, \omega)\mathbf{k}\Phi - \mathbf{k}\mathbf{k} \cdot \mathbf{A}. \quad (12)$$

It is noted that the solution will be unchanged under gauge transformations.¹⁸ For the Coulomb gauge, we have

$$\nabla \cdot \mathbf{A} = 0, \quad (13)$$

and then the scalar potential satisfies the Poisson equation,

$$k^2\Sigma_l(k, \omega)\Phi(k, \omega) = \rho(k, \omega). \quad (14)$$

If the current is split into a longitudinal part \mathbf{J}_l and a transverse part \mathbf{J}_t , i.e., $\nabla \times \mathbf{J}_l = 0$ and $\nabla \cdot \mathbf{J}_t = 0$, then the vector potential satisfies the following equation if the continuity equation for the charge density is used

$$[k^2 - \omega^2\Sigma_t(k, \omega)]\mathbf{A}(\mathbf{k}, \omega) = \mathbf{J}_t(k, \omega). \quad (15)$$

Therefore, these two potentials are decoupled, and the scalar and vector potentials are related to the longitudinal and transverse property, respectively.

For the static case $\omega = 0$, application of the dispersion relation $\Sigma_l(k) = 0$ to ionic fluids leads to extended Debye-Hückel theories as in the DIT.¹²⁻¹⁴ In general, the roots of $\Sigma_l(k) = 0$ are complex and they appear in pairs as $\Sigma_l(\omega, k) = \Sigma_l^*(-\omega, k)$.²⁰ Define an electric potential $\Phi(\mathbf{r})$ via $\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r})$, then the electric potential satisfies the following equation:

$$k^2\Sigma_l(k)\Phi(k) = \rho(k), \quad (16)$$

which is the starting point of any extended Debye-Hückel theory as exploited in the dressed ion theory¹²⁻¹⁴ as long as a microscopic expression of $\rho(k)$ is given. Therefore, above results Eqs. (14) and (15) provide a natural extension of the

Debye-Hückel theory to the dynamical domain. In order to further clarify the connection between the above formulation and the traditional Debye-Hückel theory, we will present a general formulation of the Debye-Hückel theory from the mean electrostatic potential in the Appendix.

III. A MOLECULAR DEBYE-HÜCKEL THEORY

In the Appendix, two phenomenological functions, namely, the dielectric function and the renormalized charge density in our approach are discussed at the microscopic level. In this section the average electric potential around a tagged ion, which is the starting point of thermodynamic property calculations, will be obtained from these functions.

An inverse Fourier transform of $\Phi_j(k) = \rho_j^0(k)/[k^2\varepsilon_l(k)]$, which provides a solution to Eq. (A15), leads to the average electric potential as

$$\begin{aligned} \Phi_j(r) &= \frac{1}{8\pi^3} \iiint d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \Phi_j(k) \\ &= \frac{1}{2\pi^2 r} \int_0^\infty dk [\Phi_j(k)k] \sin(kr). \end{aligned} \quad (17)$$

Suppose that the roots of $\varepsilon_l(k)$ can be found as ik_n , i.e.,

$$k^2\varepsilon_l(k) = \frac{\varepsilon_s \prod_n (k^2 + k_n^2)}{f(k)}, \quad (18)$$

where $f(k)$ is a function with no poles, then we can rewrite the electrical potential as

$$\Phi_j(k) = \frac{f(k)\rho_j^0(k)}{\varepsilon_s \prod_n (k^2 + k_n^2)}. \quad (19)$$

For an electrolyte solution, the traditional Debye-Hückel theory is equivalent to use a dielectric function $\varepsilon_l(k) = \varepsilon_s(1 + k_{\text{DH}}^2/k^2)$ and the charge density $\rho_j^0(k) = q_j$, where $k_{\text{DH}} = \sqrt{\beta \sum_i n_i q_i^2 / \varepsilon_s}$ is the conventional inverse Debye screening length.¹³

After some calculations, it can be shown that $\Phi_j(r)$ has the following asymptotic behavior:

$$\Phi_j(r) \sim \sum_n \frac{q_{\text{eff},jn}}{4\pi\varepsilon_{\text{eff},n}} \frac{e^{-k_n r}}{r}, \quad (20)$$

where $q_{\text{eff},jn} = \rho_j^0(ik_n)$ is an effective charge, and $\varepsilon_{\text{eff},n} = 1/2[kd\varepsilon_l(k)/dk]_{k=ik_n}$ is an effective dielectric constant determined from the bulk property $\varepsilon_l(k)$, and ik_n is the root with positive imaginary part. It is interesting to note that different ions in the same solution will have the same set of screen parameters k_n , but with different effective charges.

The traditional DH theory has just one Yukawa term in the electric potential outside the hard core with the conventional Debye screening length, bare charge of the tagged ion, and solvent dielectric constant ε_s . The multi-Yukawa terms in Eq. (20) motivate us to calculate the electric potential in terms of a multi-parameter DH theory, i.e., the electric potential could be a linear combination of solutions from a DH theory with different Debye length k_n , effective charge $q_{\text{eff},jn}$ and effective dielectric constant $\varepsilon_{\text{eff},n}$ from molecular properties of an electrolyte solution. A straightforward implemen-

tation of this procedure as in the dressed ion theory¹³ will require many terms to achieve accurate thermodynamic properties. Our approach is to use effective linear combination coefficients instead of $q_{\text{eff},jn}/[4\pi\epsilon_{\text{eff},n}]$, which are obtained from some rigorous constraints, to calculate the average electric potential accurately. This approach is called a *molecular DH theory*.

Consider a primitive model where ion j has a hard core with diameter σ and the bare charge density is $\rho_j^c(r) = q_j\delta(r)$. Denote $\phi_{jn}(r)$ as the solution of the DH equation with a Debye screening parameter k_n ,

$$\begin{aligned} -\epsilon_s \nabla^2 \phi_{jn}(r) &= \rho_j^c(r), & r < \sigma, \\ \nabla^2 \phi_{jn}(r) &= k_n^2 \phi_{jn}(r), & r > \sigma. \end{aligned} \quad (21)$$

Here, $\phi_{jn}(r)$ is the n th basic mode of Eq. (20), which could be used to expand the electric potential, i.e.,

$$\Phi_j(r) = \sum_n C_{jn} \phi_{jn}(r), \quad (22)$$

where C_{jn} s are the linear combination coefficients to be determined. A main advantage of this approach is the linear nature of the formulation as in the conventional DH theory, from which one can extend this approach to complex solute with arbitrary shape and arbitrary charge distribution, and the only price we need to pay is to find these coefficients C_{jn} which contain nonlinear effect via the re-normalization of the effective charge and effective dielectric constant. If appropriate C_{jn} s are used, Eq. (22) would be an approximate solution to $\Phi_j(k) = \rho_j^0(k)/[k^2\epsilon_l(k)]$. Moment conditions related to the dielectric function of the bulk system can be exploited to determine these linear combination coefficients. Conceptually, this approach is a resummation of the asymptotic series in Eq. (20) using moment conditions as constraints.

According to Eqs. (21) and (22), the mean electric potential $\Phi(r)$ outside the core is a linear combination of multi-Yukawa potential,

$$\Phi_j(r) = \sum_n \frac{q_j C_{jn}}{4\pi\epsilon_s(1+k_n\sigma)} \frac{e^{-k_n(r-\sigma)}}{r}, \quad r > \sigma. \quad (23)$$

Using the Poisson equation Eq. (A1), Eq. (23) is equivalent to assume that

$$\sum_i n_i q_i h_{ij}(r) = \sum_n \frac{q_j C_{jn} k_n^2}{4\pi\epsilon_s(1+k_n\sigma)} \frac{e^{-k_n(r-\sigma)}}{r}, \quad r > \sigma. \quad (24)$$

Inside the hard core, it is known that

$$\Phi_j(r) = \frac{q_j}{4\pi\epsilon_s r} + B, \quad r < \sigma. \quad (25)$$

Continuous conditions of Φ_j and $\epsilon_s \partial\Phi_j(r)/\partial r$ at boundary $r = \sigma$ lead to the following restriction about B and C_{jn} ,

$$\frac{q_j \sum_n C_{jn}/(1+k_n\sigma)}{4\pi\epsilon_s\sigma} = B + \frac{q_j}{4\pi\epsilon_s\sigma}, \quad \sum_n C_{jn} = 1. \quad (26)$$

It is note that the second restriction in Eq. (26) is equivalent to the charge neutrality condition. These two restrictions

lead to

$$B = \frac{q_j(\sum_n C_{jn}/(1+k_n\sigma) - 1)}{4\pi\epsilon_s\sigma} = -\frac{q_j}{4\pi\epsilon_s} \sum_n \frac{C_{jn}k_n}{1+k_n\sigma}. \quad (27)$$

As our purpose is to develop a molecular multi-parameter DH theory given the bulk dielectric function of the electrolyte solution, it can be shown that both the effective Debye screening parameter k_n and the coefficient C_{jn} could be determined from the bulk dielectric function.

Note that $S_{zz}(k)$ offers the connection between $h_{ij}(r)$ and $\epsilon_l(k)^{-1}$, expansions of the functions $\epsilon_l(k)^{-1}$ and $S_{zz}(k)$ in terms of k yield

$$\frac{\epsilon_s}{\epsilon_l(k)} = \sum_{n=1}^{\infty} D_n k^{2n} \quad (28)$$

and

$$1 - \frac{n\beta e_0^2}{\epsilon_s k^2} S_{zz}(k) = 1 - \frac{n\beta e_0^2}{\epsilon_s k^2} \left(\sum_i Z_i^2 x_i + \sum_0^{\infty} \frac{(-1)^{n+1}}{(2n+1)!} M_{2n} k^{2n} \right), \quad (29)$$

where $M_{2n} = \int d\mathbf{r} r^{2n} \sum_{i,j} Z_i Z_j x_i x_j n h_{ij}(r)$ is the $2n$ th moment. Using Eq. (A12) we have the following relations of moments M_{2n} ,

$$\begin{aligned} -M_0 &= \sum_i Z_i^2 x_i, \\ -\frac{1}{3!} \frac{n\beta e^2}{\epsilon_s} M_2 &= 1, \\ -\frac{1}{(2n+1)!} \frac{n\beta e^2}{\epsilon_s} M_{2n} &= (-1)^n D_{n-1} \cdot (n \geq 2). \end{aligned} \quad (30)$$

To derive Eq. (28), the perfect screening condition $\lim_{k \rightarrow 0} \epsilon_s/\epsilon_l(k) = 0$ is used. Note that the first two relations in Eq. (30) are just the charge neutrality condition and the Stillinger-Lovett relation,¹¹ and the third equality is the restriction about the high order moments.

For a restricted primitive model with element charge $e = 1$, we have $x_i = 1/2$, $q_i = Z_i e = Z_i$, $i = 1, 2$, and $Z_1 = -Z_2$. By symmetry, we also have $C_{1i} = C_{2i} = C_i$. From Eq. (A11) and Eq. (24), we can relate $S_{zz}(k)$ to k_i and C_i . After some calculations, we can find the moment M_{2n} in terms of k_i and C_i as

$$\begin{aligned} -M_0 &= \sum_i q^2 C_i, \\ -\frac{1}{3!} \frac{n\beta e^2}{\epsilon_s} M_2 &= \sum_i C_i \frac{k_{\text{DH}}^2}{k_i^2} \frac{1+k_i\sigma + k_i^2\sigma^2/2 + k_i^3\sigma^3/6}{1+k_i\sigma}, \\ -\frac{1}{(2n+1)!} \frac{n\beta e^2}{\epsilon_s} M_{2n} &= \sum_i C_i \frac{k_{\text{DH}}^2}{k_i^{2n}} \frac{\sum_{l=0}^{2n+1} (k_i\sigma)^l / l!}{(1+k_i\sigma)} \quad (n \geq 2). \end{aligned} \quad (31)$$

Combine Eqs. (30) and (31), we have a set of linear equations about $\mathbf{C} = \{C_j\}$, which reads

$$\mathbf{TC} = \mathbf{Q}, \quad (32)$$

where $\mathbf{T} = \{T_{ij}\}$ is a matrix with element $T_{ij} = [k_{\text{DH}}^2/k_i^{2j-2}][\sum_{l=0}^{2j-1} (k_i\sigma)^l / l! / (1+k_i\sigma)]$, and $\mathbf{Q} = \{Q_j\}$

is a vector with element $Q_1 = k_{\text{DH}}^2$, $Q_2 = 1$, $Q_j = (-1)^{j-1} D_{j-2}$, ($j \geq 3$). From this linear equation, we can find the solution $\mathbf{C} = \mathbf{T}^{-1}\mathbf{Q}$.

Now it is clear that we can find the electric potential given the dielectric function is known. Namely, one can first find the screening parameters k_l by finding the roots of $\epsilon_l(k)$ from numerical fitting. Second, Eq. (32) could be used to find the coefficient C_l with these screening parameters k_l . Finally, the electric potential is given by Eq. (23). This electric potential will be used in Sec. IV to evaluate the electrostatic contribution to thermodynamic properties.

IV. ELECTROSTATIC CONTRIBUTIONS TO THERMODYNAMIC PROPERTIES

As long as the mean electric potential $\Phi_j(r)$ is determined, one can calculate electrostatic contribution to the internal energy according to the following procedure. Since the induced electric potential ψ_j of ion j at origin is given by

$$\psi_j \equiv \lim_{r \rightarrow 0} \left[\Phi_j(r) - \frac{q_j}{4\pi\epsilon_s r} \right], \quad (33)$$

the electrostatic energy per particle reads

$$\frac{\beta U^{\text{ele}}}{N} = \frac{1}{n} \sum n_j \beta q_j \int_0^1 \lambda \psi_j d\lambda = \sum \frac{\beta x_j q_j \psi_j}{2}. \quad (34)$$

It is possible to find ψ_j using the definition Eq. (33); however, it is not convenient to calculate $\Phi_j(r)$ by numerical calculations because of the singularity of $\Phi_j(r)$ at the origin. Using the relation from inverse Fourier transform $f(r=0) = 1/8\pi^3 \int_0^\infty dk 4\pi k^2 f(k)$, it would be easier to evaluate ψ_j by

$$\psi_j = \frac{1}{8\pi^3} \int_0^\infty dk 4\pi k^2 \left[\Phi_j(k) - \frac{q_j}{\epsilon_s k^2} \right] = \frac{1}{2\pi^2} \int_0^\infty dk f(k), \quad (35)$$

where $f(k) = k^2[\Phi_j(k) - q_j/\epsilon_s k^2]$. According to the Poisson equation, we find that $f(k) = \sum_i n_i q_i h_{ij}(k)/\epsilon_s$. Using the local charge neutrality condition, $\sum_i q_i n_i h_{ij}(k=0) = -q_j$, it is easy to find that $f(k=0) = -q_j/\epsilon_s$, which has no singularity.

In the context of our molecular DH theory, B is the induced potential ψ_j at the origin according to Eq. (33), then the electrostatic energy per particle becomes

$$\frac{\beta U^{\text{ele}}}{N} = - \sum_j \frac{\beta n_j q_j^2}{8\pi\epsilon_s n} \sum_i \frac{C_{ji} k_i}{1 + k_i \sigma}. \quad (36)$$

For a restricted primitive model, the expression of the energy is further simplified

$$\frac{\beta U^{\text{ele}}}{N} = - \sum_j \frac{\beta n_j q_j^2}{8\pi\epsilon_s n} \sum_i \frac{C_i k_i}{1 + k_i \sigma} = - \frac{k_{\text{DH}}^2}{8\pi n} \sum_i \frac{C_i k_i}{1 + k_i \sigma}, \quad (37)$$

which should be compared with the traditional DH theory

$$\frac{\beta U^{\text{ele}}}{N} = - \frac{k_{\text{DH}}^2}{8\pi n} \frac{k_{\text{DH}}}{1 + k_{\text{DH}} \sigma}. \quad (38)$$

In the traditional DH theory or mean sphere approximation (MSA), $\epsilon_l(k)$ depends on k_{DH} only, and hence the electrostatic

energy depends only on the Debye parameter k_{DH} . However, in general, this is not necessary true. For example, $\epsilon_l(k)$ could be a function of both k_{DH} and β as indicated by hypernetted Chain (HNC) calculations. One should note that generally the coefficient C_{jl} depends on both subscripts “ j ” and “ l ” rather than only “ l .” To a good approximation, we found that the approximation $C_{jl} \approx C_l$ is always adequate when one try to evaluate the thermodynamic properties for electrolytes with size or charge asymmetry.

Note $S_{zz}(k)$ is a linear function of $h_{ij}(k)$, the electrostatic energy per particle could also be evaluated as²³

$$\begin{aligned} \frac{\beta U^{\text{ele}}}{N} &= \frac{1}{2n} \sum_{i,j} n_i n_j \beta \int_0^\infty \frac{q_i q_j}{4\pi\epsilon_s r} 4\pi r^2 h_{ij}(r) dr \\ &= \frac{\beta e_0^2}{4\pi^2 \epsilon_s} \int_0^\infty \left(S_{zz}(k) - \sum_i Z_i^2 x_i \right) dk \\ &= \frac{1}{4\pi^2 n} \int_0^\infty \left\{ \left[1 - \frac{\epsilon_s}{\epsilon_l(k)} \right] k^2 - k_{\text{DH}}^2 \right\} dk, \quad (39) \end{aligned}$$

which means that the electrostatic energy could be determined given the static structure factor or equivalently the dielectric function. It is straightforward to prove that Eqs. (34) and (39) are equal.

With the electric potential, we can also evaluate electrostatic contributions to other thermodynamic properties. For example, the excess chemical potential μ_i^{ex} of species i could be evaluated from a Kirkwood coupling process,²¹

$$\beta \mu_i^{\text{ex}} = \beta n \sum_j x_j \int_0^1 d\xi \int d\mathbf{r} \frac{\partial u_{ij}(r; \xi)}{\partial \xi} g_{ij}(r; \xi), \quad (40)$$

where ξ is the coupling parameter to define $u_{ij}(r; \xi)$ which is the pair interaction between a partially coupled ion of species j and another ion of species i , while the other particles interact fully with each other. Here, $g_{ij}(r; \xi)$ is the radial distribution function of species j around the partially coupled i ion. As during the coupling process, both the short-ranged and Coulomb interactions from the charges will change, this coupling could be realized in two stages. During the first stage, ξ_1 is used to specify the coupling strength of the short-ranged potential, $u^s(r, \xi_1)$. For example, if the short-ranged interaction is hard sphere interaction with diameter σ , then when ξ_1 goes from 0 to 1, the tagged hard sphere will grow from 0 to σ . Here, $g_{ij}^s(r; \xi_1)$ is the radial distribution function between i and j particles when their interaction is $u^s(r, \xi_1)$. During the second stage, charge $\xi_2 q_j$ at the center of the sphere j grows linearly from 0 to q_j while keeping the full short-ranged interactions, and $g_{ij}(r; \xi_2)$ denotes the radial distribution function between i and j ions. Then the excess Gibbs free energy per particle can be written as²⁴

$$\begin{aligned} \frac{\beta \Delta G^{\text{ex}}}{N} &= \beta n \sum_{i,j} x_i x_j \int_0^1 d\xi_1 \int d\mathbf{r} \frac{\partial u_{ij}^s(r; \xi_1)}{\partial \xi_1} g_{ij}^s(r; \xi_1) \\ &\quad + \beta n \sum_{i,j} x_i x_j \int_0^1 d\xi_2 \int d\mathbf{r} \frac{q_i q_j}{4\pi\epsilon_s r} g_{ij}(r; \xi_2) \\ &= \frac{\beta \Delta G^s}{N} + \frac{\beta \Delta G^{\text{ele}}}{N}. \quad (41) \end{aligned}$$

For concreteness, the short-ranged interaction is taken as hard sphere with a diameter σ . Introducing the cavity function $y_{ij}^s(r; A) = g_{ij}^s(r; A)e^{\beta u_{ij}^s(r)}$, where A is the distance between two hard spheres; one can evaluate the integral in the first term of Eq. (41),

$$\begin{aligned} & \beta \int d\mathbf{r} \frac{\partial u_{ij}^s(r; A)}{\partial A} g_{ij}^s(r; A) \\ &= \beta \int d\mathbf{r} \frac{\partial u_{ij}^s(r; A)}{\partial A} e^{-\beta u_{ij}^s(r)} y_{ij}^s(r; A) \\ &= - \int d\mathbf{r} \frac{\partial e^{-\beta u_{ij}^s(r; A)}}{\partial A} y_{ij}^s(r; A) \\ &= \int d\mathbf{r} \delta(r - A) y_{ij}^s(r; A) = 4\pi A^2 y_{ij}^s(A; A) \\ &= 4\pi A^2 g_{ij}^s(A; A), \end{aligned} \quad (42)$$

and then we have

$$\begin{aligned} \frac{\beta \Delta G^s}{N} &= \beta n \sum_{i,j} x_i x_j \int_0^\sigma dA \int d\mathbf{r} \frac{\partial u_{ij}^s(r; A)}{\partial A} g_{ij}^s(r; A) \\ &= 4\pi n \sum_{i,j} x_i x_j \int_0^\sigma dA A^2 g_{ij}^s(A; A). \end{aligned} \quad (43)$$

Since in the first stage the particle i is neutral, the reversible work performed to grow this hard sphere should be not relevant to the Coulomb interactions between the other particles and thus can be evaluated using the Gibbs free energy of a hard sphere system with size A . Generally, this term could be evaluated by the Canahan-Starling formulas.²⁵ The second term in Eq. (41) is the contribution from Coulomb interactions,

$$\begin{aligned} \frac{\beta \Delta G^{\text{ele}}}{N} &= \frac{\beta n}{\epsilon_s} \sum x_i x_j q_i q_j \int_0^1 d\xi \int_0^\infty r g_{ij}(r; \xi_2) dr \\ &= - \sum_j \beta x_j \int_0^1 d\xi_2 \int_0^\infty \nabla^2 \Phi_j(r; \xi_2) dr, \end{aligned} \quad (44)$$

where $\Phi_j(r; \xi_2)$ is obtained from $-\epsilon_s \nabla^2 \Phi_j(r; \xi_2) = q_j \xi_2 \delta(r) + \sum q_i n_i g_{ij}(r; \xi_2)$. During the charging process, only the charge of tagged j th particle is changed, and thus the bulk property $\epsilon_l(k)$ or k_l in Eq. (23) can be used. Assuming that the coefficient C_l keeps constant during the charging process, then $\Phi_j(r; \xi_2) = \xi_2 \Phi_j(r)$. Using Eqs. (23) and (44), we have

$$\begin{aligned} \frac{\beta \Delta G^{\text{ele}}}{N} &= \frac{\beta}{\epsilon_s} \sum_{i,j} n_i n_j q_i q_j \int_0^1 d\xi_2 \int_0^\infty \xi_2 r h_{ij}(r) dr \\ &= - \sum_j \frac{\beta n_j q_j^2}{8\pi \epsilon_s n} \sum_i \frac{C_{ji} k_i}{1 + k_i \sigma}. \end{aligned} \quad (45)$$

In this case, we have $\beta \Delta G^{\text{ele}}/N = \beta U^{\text{ele}}/N$, which is similar to the case of traditional DH or MSA. Now the solvation energy, which is defined as the excess Gibbs free energy per particle (excess chemical potential), reads

$$E_{\text{sol}} = \frac{\beta \Delta G^s}{N} + \frac{\beta U^{\text{ele}}}{N}. \quad (46)$$

Using the virial equation, we can find the pressure as

$$\frac{\beta P}{n} = 1 + \frac{2\pi n \sigma^3}{3} \sum_{i,j} x_i x_j g_{ij}(\sigma) + \frac{\beta U^{\text{ele}}}{3N}. \quad (47)$$

From the thermodynamic relations, the excess Helmholtz free energy reads which is

$$\begin{aligned} \frac{\beta \Delta A^{\text{ex}}}{N} &= \frac{\beta \Delta G^{\text{ex}}}{N} - \left(\frac{\beta P}{n} - 1 \right) = \frac{\beta \Delta G^s}{N} \\ &\quad - \frac{2\pi n \sigma^3}{3} \sum_{i,j} x_i x_j g_{ij}(\sigma) + \frac{2}{3} \frac{\beta U^{\text{ele}}}{N}. \end{aligned} \quad (48)$$

In general, the contact value $g_{ij}(\sigma)$ depends on Coulomb interaction and could be determined by other theories such as exponential approximation.²⁶ When the electrostatic coupling is not strong, the contact value $g_{ij}(\sigma)$ could be approximated by the contact value $g^s(\sigma)$ of a reference hard sphere system with size σ , and then we have

$$\begin{aligned} 1 + \frac{2\pi n \sigma^3}{3} \sum_{i,j} x_i x_j g_{ij}(\sigma) &\simeq 1 + \frac{2\pi n \sigma^3}{3} \sum_{i,j} x_i x_j g^s(\sigma) \\ &= 1 + \frac{2\pi n \sigma^3}{3} g^s(\sigma) = \frac{\beta P^s}{n}, \end{aligned} \quad (49)$$

where P^s is the pressure of the reference hard sphere system. Then the pressure equation reads

$$\frac{\beta P}{n} \simeq \frac{\beta P^s}{n} + \frac{\beta U^{\text{ele}}}{3N}, \quad (50)$$

and the excess Helmholtz free energy is reduced to

$$\frac{\beta \Delta A^{\text{ex}}}{N} \simeq \frac{\beta \Delta G^s}{N} - \frac{\beta P^s}{n} + \frac{2}{3} \frac{\beta U^{\text{ele}}}{N} = \frac{\beta \Delta A^s}{N} + \frac{2}{3} \frac{\beta U^{\text{ele}}}{N}, \quad (51)$$

where $\beta \Delta A^s/N = \beta \Delta G^s/N - \beta P^s/n$ is the Helmholtz free energy of the reference hard sphere system, which could also be evaluated by Carnahan-Starling formula. If the short-ranged interaction is not hard sphere type, straightforward generalization can be obtained for any short-ranged interactions.

Therefore, all Coulomb contributions to the excess thermodynamic properties could be found in terms of k_l and C_l and the short-ranged interaction contributions can be evaluated either from direct calculations, such as virial expansions or perturbation theory.²² Since the matrix equation Eq. (32) has infinite elements, it is not very useful in practical calculations. On the other hand, a screened Coulomb potential mode with large k_i would make small contribution, i.e., when k_i is very large, the coefficient C_i in Eq. (36) would be very small; the first few modes with small k_i would dominate the electrostatic contribution calculations. When the concentration of the electrolyte solution is not large, k_1 is a real number that close to but different from k_{DH} . Taking $C_1 = 1$ and neglect other $C_i (i \geq 2)$, then we recover the results of Attard and co-workers.^{9,10} In Sec. V, we will show that it is possible to obtain very accurate results using the first few terms in the expansion of Eq. (36).

V. APPLICATIONS TO ELECTROLYTE SOLUTIONS

In this section, we will apply our theory to simple models of electrolyte solutions with various short-ranged interactions. To illustrate these applications, we will calculate the excess internal energy and the solvation energy of these model systems in the context of MSA (Ref. 27) and HNC approximation, where analytically or numerically exact results are known for these approximations. As noted in Sec. V, the electric potential is determined by multi-Yukawa modes. When k_{DH} is not too large, typically for $k_{\text{DH}}\sigma < 2$, the first two Yukawa modes would make dominant contributions to the electric potential, and the excess internal energy could be well described by the first two C_i s and k_i s. As k_{DH} further increases, more Yukawa parameters are required to obtain accurate thermodynamic properties.

A. Tests against the mean spherical approximation

Using the mean spherical approximation,²⁷ analytical results for the dielectric function, excess energy and other excess thermodynamic properties are available for primitive models, hence, a natural test case for the application of our theory.

For a 1:1 primitive model, the static charge-charge structure factor is

$$S_{zz}(k) = 1 + n[h_{11}(k) - h_{12}(k)] = \frac{k^4}{4\Gamma^2 F(k)}, \quad (52)$$

Using these k_n and C_n , we can calculate electrostatic contribution to the excess energy $\beta U^{\text{ele}}/N$ via Eq. (37) and other thermodynamic properties. From these calculations, we found that the electrostatic energy converges very rapidly as the number L increases. As shown in Fig. 2, we take $L = 2$ when $k_{\text{DH}} < 1.0$ and take $L = 4$ for $k_{\text{DH}} \geq 1.0$. Our results are in very good agreements with the analytical MSA results. Even for very strong coupling cases such as $k_{\text{DH}} = 100$, our theory prediction has only 5% error compared to MSA analytical results, while the traditional DH theory has an error of about 42%.

An interesting observation is that we can also evaluate C_{jn} in terms of effective charges and effective dielectric constants as prescribed in Sec. III. By comparing Eqs. (20) and (23), we have

$$C_{jn} = \frac{q_{\text{eff},jn}/q_j}{\epsilon_{\text{eff},n}/\epsilon_s} (1 + k_l\sigma) e^{-k_n\sigma}. \quad (56)$$

Under the context of MSA, k_n can be determined numerically, and the effective charges and dielectric constants can also be

where function $F(k) = 2\Gamma^2[1 - \cos(k\sigma)] + 2k\Gamma \sin(k\sigma) + k^2 \cos(k\sigma) + k^4/(4\Gamma^2)$ and $2\sigma\Gamma = \sqrt{1 + 2\sigma k_{\text{DH}}} - 1$. The dielectric function reads

$$\epsilon_s/\epsilon_l(k) = 1 - \frac{k_{\text{DH}}^2 S_{zz}(k)}{k^2} = \frac{4\Gamma^2 F(k) - k_{\text{DH}}^2 k^2}{4\Gamma^2 F(k)}. \quad (53)$$

The roots $k = ik_n$ of $\epsilon_l(k) = 0$ are determined by equation $F(ik_n) = 0$. Since the equation $F(ik_n) = 0$ is highly non-linear and no analytical solutions are available, we need to solve this equation numerically. For $\sigma = 1$, the first two roots $k_{1,2}$ are shown in Fig. 1, where $\text{Re}(k_{1,2})$ denotes the real part of $k_{1,2}$, and $\text{Im}(k_1)$ denotes the imaginary part of k_1 . It is noted that $k_{1,2}$ are real numbers when the coupling is weak, and then become complex conjugate after some critical value $k_{\text{DH}}\sigma \simeq 1.23$, which is related to the fact that the mean electric potential becomes oscillatory decay when the electric coupling is strong enough.²⁸ Other roots (k_n for $n \geq 3$) appear in complex conjugates for all value of k_{DH} (not shown).

The first few k_n ($n=1,2,\dots,L$) are calculated via $F(ik_n) = 0$, and then C_n is evaluated via Eq. (32), where the element of Q_j ($j \geq 3$) or equivalently D_{j-2} could be found by expanding $\epsilon_s/\epsilon_l(k) = \sum_j D_j k^{2j}$. The first four elements of Q_j are

$$\begin{aligned} Q_1 &= k_{\text{DH}}^2, & Q_2 &= 1, & Q_3 &= D_1 \\ &= \frac{-k_{\text{DH}}^2(-3 + 3\Gamma\sigma + 3\Gamma^2\sigma^2 + \Gamma^3\sigma^3)}{48\Gamma^4(1 + \Gamma\sigma)^3}, \end{aligned} \quad (54)$$

$$Q_4 = -D_2 = \frac{k_{\text{DH}}^2(15 - 30\Gamma\sigma - 15\Gamma^2\sigma^2 + 20\Gamma^3\sigma^3 + 15\Gamma^4\sigma^4 + 6\Gamma^5\sigma^5 + \Gamma^6\sigma^6)}{960\Gamma^6(1 + \Gamma\sigma)^4}. \quad (55)$$

found

$$\begin{aligned} q_{\text{eff},jn}/q_j &= k_n^2/k_{\text{DH}}^2, \\ \epsilon_{\text{eff},n}/\epsilon_s &= -2\Gamma^2[(2\Gamma^2\sigma + 2\Gamma - k^2\sigma) \sin(k\sigma)/k \\ &\quad + 2(1 + \Gamma\sigma) \cos(k\sigma) + k^2/\Gamma^2]/k_{\text{DH}}^2|_{k=ik_n}. \end{aligned} \quad (57)$$

Equation (56) is then used to calculate C_{jn} , and electrostatic contribution to the excess energy is determined by Eq. (36). Our calculation shows that this approximation could give us very accurate results as long as we collect enough terms into the summation. However, this strategy is not very satisfactory because of its slow convergency for high coupling cases. For inverse Debye length $k_{\text{DH}} = 1.0$, the error is less than 2% when we take the first two k_n for evaluation; while for $k_{\text{DH}} = 3.0$, the error is about 3% if the first eight k_n are taken into account. The strategy proposed in Sec. III to evaluate C_n is equivalent to a resummation of the above series using moment conditions, thus a faster convergent calculation of excess thermodynamic properties.

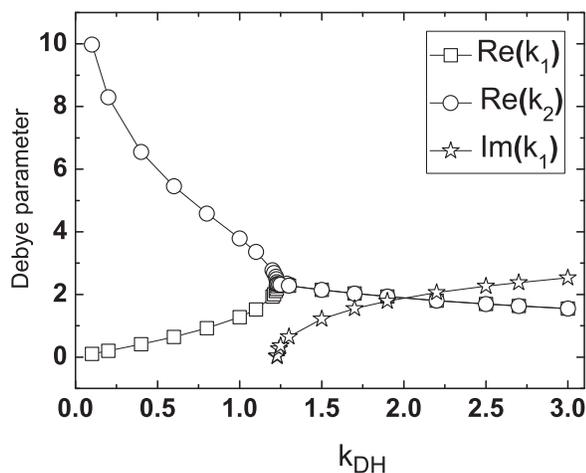


FIG. 1. The first two roots from the MSA dielectric function (symbols). The lines are guides to the eye.

B. Applications to binary electrolyte solutions

Consider a binary primitive model of electrolyte solutions with hard sphere diameter $\sigma = 1$, reduced inverse temperature $\beta = 1$, and dielectric constant $\epsilon_s = 1/4\pi$. We will test our theory using HNC approximation, which is known to yield very accurate thermodynamic properties of primitive models.²⁷ In this case, only numerical results rather than analytical form of the dielectric function can be obtained. In order to find the first few screened constants k_n ($n = 1, 2, \dots, L$), a Padé polynomial

$$\frac{P_1(k)}{P_2(k)} = \frac{\sum_{n \geq 1} a_n k^{2n}}{\sum_{m \geq 0} b_m k^{2m}} \quad (58)$$

is introduced to fit $\epsilon_l(k)^{-1}$, from which we can find k_n as well as the expansion coefficient D_n . Similar to the MSA case, the first two Debye parameters $k_{1,2}$ under HNC are also real numbers when the coupling is not strong, and then become complex conjugate after $k_c \sigma \simeq 1.3$.¹⁰

As long as we have k_n and D_n , we can solve Eq. (32) to find C_n and thermodynamic properties. $L = 2$ is used for

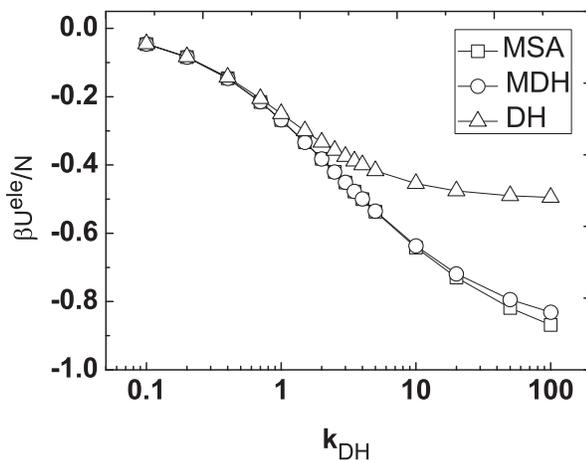


FIG. 2. Electrostatic contribution to the excess internal energies of a symmetric 1:1 primitive model of an electrolyte solution from MSA (square), our molecular Debye Hückel approximation (circle), and traditional DH theory (triangle). The lines are guide to the eye.

$k_{DH} < 2$, and $L = 4$ is used for $k_{DH} > 2$. In this study, the function $\chi(k) \equiv 1 - \epsilon_s/\epsilon_l(k)$ is fitted by

$$\chi(k) = \frac{a_0 + a_1 k^2}{a_0 + k^2 + a_2 k^4} \quad \text{for } L = 2,$$

$$\chi(k) = \frac{a_0 + a_1 k^2}{2} \left[\frac{1}{a_0 + k^2 + a_2 k^3 + a_3 k^4} + \frac{1}{a_0 + k^2 - a_2 k^3 + a_3 k^4} \right] \quad \text{for } L = 4. \quad (59)$$

The electrostatic contribution to excess energies $\beta U^{ele}/N$ of the electrolyte solutions with $(q_1, q_2) = (1, -1), (2, -2), (2, -1)$ have been calculated according to our molecular DH theory and are shown in Figs. 3(a)–3(c), respectively.

The number density n for $k_{DH} = 3.0$ is about 0.72, 0.18, and 0.36 for the 1:1, 2:2, and 2:1 electrolyte solutions, respectively. Again, very good agreements between our theory and HNC calculations are found. For example, when $k_{DH} \simeq 3$, the error from our theory is 3%, while the traditional DH theory is about 25%. We have also calculated the excess Gibbs free energy, where the hard sphere contribution to excess Gibbs free energy is derived from the Carnahan-Starling formulas.²² As shown in Fig. 4, again very satisfactory results are found. Previous simulations show that HNC is accurate when compared with Monte Carlo simulations for $n < 0.3$,²⁷ hence our theory should provide accurate thermodynamic properties as well when compared with molecular simulation results.

Note that for the 1:1 electrolyte in high density region (e.g., $k_{DH} > 2.5$ which roughly corresponding to $n > 0.5$ in Fig. 4(a)), our prediction has significant difference when compared with HNC results. This is most probably due to the fact that HNC is not good enough at high densities to yield accurate hard sphere contribution to excess Gibbs free energy $\beta \Delta G^s/N$. When $\beta \Delta G^s/N$ comes from HNC calculations, rather than the Carnahan-Starling formulas which is used in our molecular DH calculations, much better agreement between our theory prediction and HNC is found, e.g., the error is smaller than 2% for number densities up to $n = 0.7$.

In this study, our main focus is on the electrolyte solutions with size symmetry cases, i.e., all the ions have the same size. However, one should note that we can extend our theory to a binary electrolyte solution with size asymmetry without difficulty, where the coefficients of multi-Yukawa potential will satisfy a similar linear equation as in Eq. (32), but with the element of \mathbf{T} and \mathbf{Q} modified as functions of sizes. We have also calculated the excess thermodynamic properties for a binary electrolyte system with size asymmetry, where satisfactory results are found as well (not shown).

C. Applications to multi-component electrolyte solutions

In this section, our molecular DH theory will be applied to multi-component electrolyte solutions. By assuming that the coefficient C_{jn} is independent of j which is the index for ions, i.e., $C_{jn} = C_n$, the application of our molecular DH

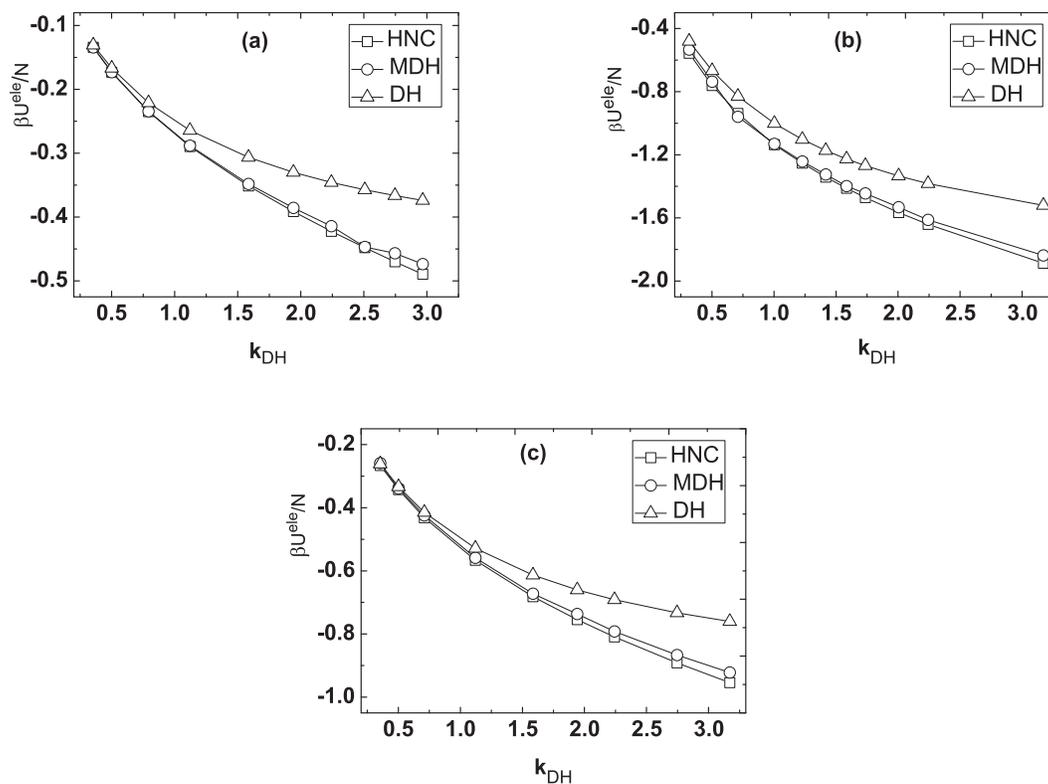


FIG. 3. Electrostatic contribution to excess energies of binary electrolyte solutions from HNC calculation (square), our molecular Debye Hückel approximation (circle), and traditional DH theory (triangle). The lines are guides to the eye.

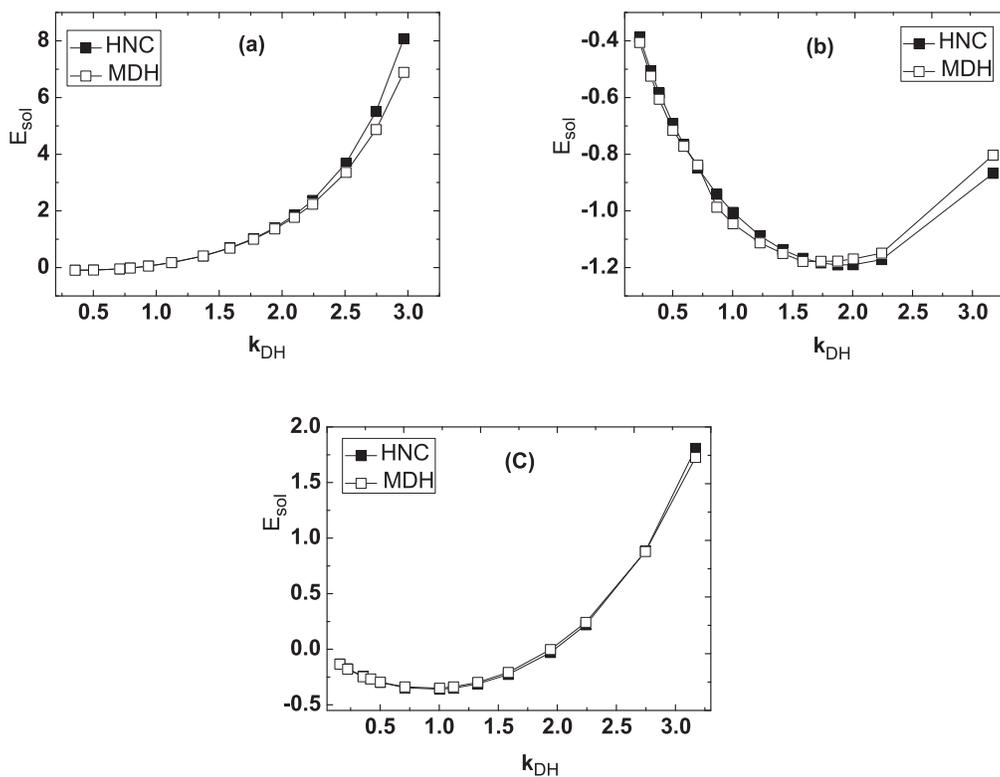


FIG. 4. Solvation energy E_{sol} of binary electrolyte solutions from direct HNC calculation (filled squares), our molecular Debye Hückel approximation (open squares). The lines are guides to the eye.

theory will be straightforward. Based on this assumption, which will be substantiated next from theoretical arguments and calculations of model systems, it is interesting to note that excess thermodynamic properties of the dilute solute can be evaluated from properties of pure solvent (majority components of ions). For multi-component systems without a minority component, the dielectric function of the whole system is needed to calculate the electrostatic contributions to thermodynamic properties from straightforward generalizations of the method presented in Sec. III. As our interests are for the systems with a clear minority component, such as proteins in an electrolyte solution, this section is used to illustrate applications of our theory to such systems.

Consider a four-component system with $q_A : q_A$ solvent A and $q_B : q_B$ solute B. The anion and cation of A has the same size σ_A , while the anion and cation of B has the same size σ_B . The molar fraction of B is $x_B = n_B/n$. In the dilute limit $x_B \rightarrow 0$, this four-component system reduces to an effective binary system. The electrostatic contribution to the internal energy per solvent particle of A is

$$\frac{\beta U_A^{\text{ele}}}{N_A} = -\frac{\beta q_A^2}{8\pi\epsilon_s} \sum_n \frac{C_{An}k_n}{1+k_n\sigma_A}, \quad (60)$$

where k_n and C_{An} are evaluated from the pure solvent dielectric function. According to Eq. (36), electrostatic contribution to the internal energy per particle of solute B reads

$$\frac{\beta U_B^{\text{ele}}}{N_B} = -\frac{\beta q_B^2}{8\pi\epsilon_s} \sum_n \frac{C_{Bn}k_n}{1+k_n\sigma_{AB}}, \quad (61)$$

where $\sigma_{AB} = (\sigma_B + \sigma_A)/2$ is the average size. When B is the same as A, naturally we have $C_{Bn} = C_{An}$; but when B has different charge and size, it is still a good approximation to evaluate electrostatic energy using $C_{Bn} \simeq C_{An}$, which could be tested using the data from HNC or molecular simulations.

For the MSA case,²⁷ we found that C_{jn} is not sensitive to the charges and sizes. When MSA is applied to this four-component system, we can find that the electrostatic energy of the solute in the dilute limit reads

$$\frac{U_B^{\text{ele}}}{N_B} = -\frac{q_B^2\Gamma}{4\pi\epsilon_s(1+\sigma_B\Gamma)}, \quad (62)$$

where parameter $\Gamma = (\sqrt{1+2\sigma_A k_{\text{DH}}} - 1)/\sigma_A$ depends only on the inverse Debye length $k_{\text{DH}} = \sqrt{\beta n_A q_A^2/\epsilon_s}$ and is the property of the pure solvent. This analytical form is similar to that of the solvent

$$\frac{U_A^{\text{ele}}}{N_A} = -\frac{q_A^2\Gamma}{4\pi\epsilon_s(1+\sigma_A\Gamma)}. \quad (63)$$

This result implies that the analytical form for the electrostatic energy of the solvent is applicable to the dilute solute when the charge q_A and size σ_A is replaced by that of the solute. It should be noted that the electrostatic energy from MSA indicates that C_{Bn} should be close to C_{An} .

In the limit $x_B \rightarrow 0$, we can approximate C_{Bn} by C_{An} , and then we have

$$\frac{\beta U_B^{\text{ex}}}{N_B} = -\frac{\beta q_B^2}{8\pi\epsilon_s} \sum_l \frac{C_{Al}k_l}{1+k_l\sigma_{AB}}. \quad (64)$$

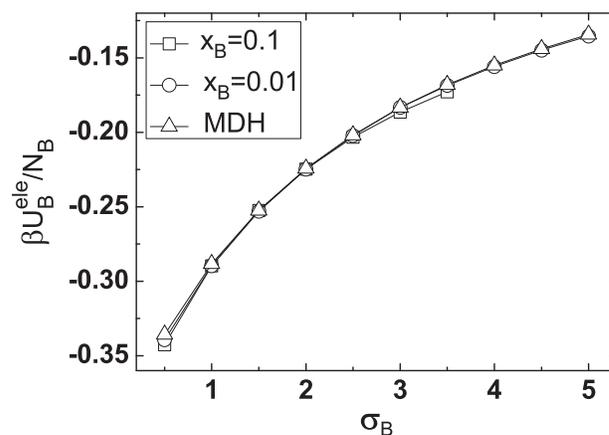


FIG. 5. Electrostatic energies of solute B from HNC under different diameter σ_B , with $x_B = 0.1$ (square), $x_B = 0.01$ (Circle), and our molecular Debye-Hückel approximation (triangle). The lines are guides to the eye.

From the electrostatic energy, we can evaluate other excess thermodynamic properties of the solute B following the thermodynamic relations derived in Sec. IV.

Although in this report, our focus is on the ions with spherical symmetry, one should note that this molecular approach could be extended to molecules with arbitrary shape such as biomolecules. The key difference is that the mean potentials in Eqs. (21) and (22) are obtained from solving the corresponding linearized Poisson-Boltzmann equations with screening length k_n using appropriate boundary conditions; therefore, our approach may find broad applications in studying biomolecules solvation in electrolyte solutions.

To test Eq. (64), a four-component primitive model of electrolyte solutions with 1:1 solvent A and 1:1 solute B is considered. The diameter of A is fixed as $\sigma_A = 1$, while σ_B , the diameter of B is used as a parameter. For a dilute solution, the molar fraction of solute B is small. As shown in Fig. 5, for $n = 0.1$ the electrostatic energy $\beta U_B^{\text{ele}}/N_B$ for B is obtained from HNC calculations. It is noted that $\beta U_B^{\text{ele}}/N_B$ is not sensitive to the exact value of x_B as long as it is small. For example, the results for $x_B = 0.1$ and $x_B = 0.01$ only have a difference up to 3% for $\sigma_B = 3.5$ from the electrostatic energy of solute B calculated from Eq. (64). Furthermore, our theory is also in very good agreement with the excess thermodynamic properties directly calculated from HNC. We have also calculated $\beta U_B^{\text{ele}}/N_B$ for other values of number density n and size σ_B , where good agreements between our theoretical predictions and direct HNC calculations are found (not shown). These results indicate that excess thermodynamic properties of the solute can be obtained from the pure solvent dielectric properties in dilute electrolyte solutions.

D. Applications to electrolyte solutions beyond primitive models

As models of an electrolyte solution with soft short-ranged interactions are more realistic than a primitive model extension of our approach beyond primitive models will be useful. Consider a simple binary 1:1 soft electrolyte model with pair additive interaction $u_{ij}(r) = u_s(r) + q_i q_j / \epsilon_s r$.

Similar to the case of primitive models, the solvation energy (excess chemical potential) of soft electrolyte solution can be evaluated from a summation of the Gibbs free energy $\beta\Delta G^s/N$ of a simple fluid with pair interaction $u_s(r)$ and the electrostatic energy $\beta U^{\text{ele}}/N$ evaluated from the dielectric function of the soft electrolyte model, i.e.,

$$E_{\text{sol}} = \frac{\beta\Delta G^s}{N} + \frac{\beta U^{\text{ele}}}{N}. \quad (65)$$

Then the problem reduces to find Gibbs free energy of the short-ranged system and the Coulomb contribution to excess internal energy.

In general, perturbation theory can be used to calculate the thermodynamic properties of a simple fluid with short-ranged interactions such as Weeks-Chandler-Anderson (WCA) theory,²⁹⁻³¹ where the effective size of the reference hard sphere system is determined by the short-ranged repulsive part of the interaction. With the effective size and the dielectric function of the soft system, we can evaluate $\beta U^{\text{ele}}/N$ in the same way as for primitive models accurately. In this sense, our approach essentially extends the perturbation theory to systems of long-ranged interactions with the same accuracy as the successful perturbation theory widely used for short-ranged systems.

Namely, using the concept of effective size, the traditional perturbation theory is extended to soft electrolyte models if an effective primitive model is used as a reference system of the soft electrolyte model. The dielectric function of the soft system can be approximated by that of the reference primitive model, and $\beta U^{\text{ele}}/N$ is evaluated from the electrostatic energy $\beta U_{\text{eff}}^{\text{ele}}/N$ of the effective primitive model, i.e.,

$$\frac{\beta U^{\text{ele}}}{N} \cong \frac{\beta U_{\text{eff}}^{\text{ele}}}{N}. \quad (66)$$

As in the traditional perturbation theory for short-ranged systems, the evaluation of other thermodynamic properties of the soft electrolyte model would be similar.

Validity of Eq. (65) is tested for a binary electrolyte with various soft interactions once an effective size of the soft ion can be found. For one test, the short-ranged interaction for the soft ion is taken as an inverse 12 power potential, i.e., $\beta u_s(r) = \beta\epsilon(\sigma/r)^{12}$ and the parameters

TABLE I. Coulomb excess internal energy $\beta U^{\text{ele}}/N$ for 1:1 soft electrolyte model with r^{-12} potential, where parameters used are $\beta = 1$, $\epsilon = 1$, $\epsilon_s = 1/4\pi$, $\sigma = 1$.

n	Soft	SD	BH	WCA
0.01	-0.1326	-0.1342	-0.1324	-0.1319
0.02	-0.1707	-0.1731	-0.1704	-0.1696
0.05	-0.2315	-0.2350	-0.2306	-0.2294
0.1	-0.2855	-0.2896	-0.2836	-0.2822
0.2	-0.3477	-0.3514	-0.3437	-0.3413
0.3	-0.3891	-0.3915	-0.3831	-0.3815
0.4	-0.4216	-0.4223	-0.4135	-0.4133
0.5	-0.4491	-0.4479	-0.4389	-0.4386
0.6	-0.4732	-0.4700	-0.4609	-0.4627
0.7	-0.4951	-0.4897	-0.4806	-0.4828

$\beta = 1$, $\epsilon = 1$, $q_1 = 1$, $q_2 = -1$, $\epsilon_s = 1/4\pi$, $\sigma = 1$ are used in the calculations. As the choice of an effective size is not unique from various versions of perturbation theories, for the r^{-12} potential, the effective size is determined by the widely used WCA prescription³¹ in our calculations. The effective size decreases from about 1.07 to 1.04 when the number density increases from 0.1 to 0.7. The set of C_n , k_n are directly calculated using the dielectric function $\epsilon_l(k)$ for soft electrolyte model from HNC calculation or the effective primitive model. As a comparison, the effective size is also used in the traditional DH theory to evaluate the electrostatic energy. As shown in Fig. 6(a), our theory works much better than the traditional DH in the high coupling region. The excess Gibbs free energy $\beta\Delta G^s/N$ of short-ranged system is evaluated from the WCA theory and the result for solvation energy is shown in Fig. 6(b). Again satisfactory agreements between our theoretical model and HNC calculation are found.

Even though the choice of reference hard sphere diameter is crucial for the perturbation theory calculation of short-ranged systems, for the effective primitive model used in the Coulombic systems the hard sphere diameter is not that sensitive. Hence the effective parameters C_n , k_n can be obtained easily from the effective primitive model using molecular simulations or accurate integral equations such as HNC. To demonstrate this, Eq. (66) is tested for two soft electrolyte models, one with short-ranged r^{-12} potential and the other with Leonard-Jones (LJ) potential

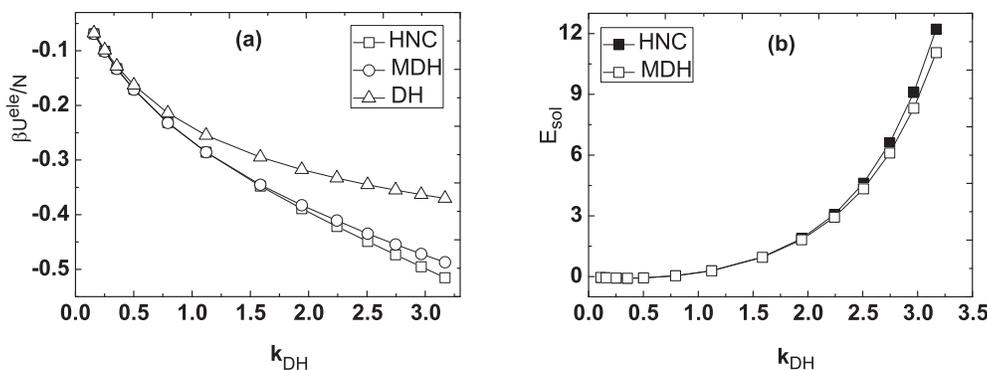


FIG. 6. Comparisons for electrostatic energies and solvation energies of soft electrolyte solution model with $1/r^{12}$ potential.

TABLE II. Coulomb excess internal energy $\beta U_i^{ex}/N$ for 1:1 soft electrolyte model with Leonard-Jones potential, where the parameters used are $\beta = 0.5$, $\epsilon = 1$, $\epsilon_s = 1/4\pi$, $\sigma = 1$.

n	Soft	SD	BH	WCA
0.01	-0.0531	-0.0507	-0.0508	-0.0507
0.05	-0.0989	-0.0935	-0.0938	-0.0936
0.1	-0.1244	-0.1180	-0.1184	-0.1182
0.2	-0.1528	-0.1466	-0.1472	-0.1470
0.3	-0.1707	-0.1656	-0.1663	-0.1661
0.4	-0.1843	-0.1804	-0.1811	-0.1810
0.5	-0.1959	-0.1928	-0.1935	-0.1935
0.6	-0.2062	-0.2036	-0.2043	-0.2044
0.7	-0.2157	-0.2133	-0.2140	-0.2142
0.8	-0.2247	-0.2221	-0.2228	-0.2232

$u_s(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. Three kinds of effective size are used for comparison. The first one is simply taken from the soft sphere diameter as an effective one, i.e., $\sigma_{\text{eff}} = \sigma$ (denoted by SD). The second one takes the Barker-Henderson (BH) prescription $\sigma_{\text{eff}} = \int_0^\infty (1 - e^{-\beta V_s(r)}) dr$ (denoted by BH); and the third one is calculated from WCA perturbation theory (denoted by WCA). The short-ranged strong repulsive part of $u_s(r)$, $V_s(r)$, is used for both BH diameter and WCA diameter calculation. For r^{-12} potential, $V_s(r) = \epsilon(\sigma/r)^{12}$; while for LJ potential, $V_s(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon$ for $r < r_m = 2^{1/6}\sigma$ and $V_s(r) = 0$ for $r > r_m$. These three kinds of effective hard sphere diameters are used as input of the effective primitive model. Electrostatic energy $\beta U^{\text{ele}}/N$ for the same soft electrolyte models directly calculated from HNC (denoted by Soft) with r^{-12} and LJ core are also shown in Tables I and II. It is found that the electrostatic energy from these three kinds of reference systems does not have significant difference from that of the soft electrolyte models. This implies that Eq. (66) is a good approximation even if the effective diameter is not very accurate. This property is different from that of short-ranged systems, i.e., when the perturbation theory is applied to a short-ranged system, the free energy is sensitive to the small difference in effective sizes.²³

It should be noted that the above results may not be universal, especially for the cases where the charge is off-center and close to the dielectric boundary. Further studies should be performed to test the best strategy to determine the dielectric boundary for a solute with general geometry.

VI. CONCLUDING REMARKS

In conclusion, a molecular Debye-Hückel theory for ionic fluids is developed. Starting from the macroscopic Maxwell equation for bulk systems, an application of the dispersion relations to electrolyte solutions leads to a molecular Debye-Hückel theory which is related to the dressed ion theory in the static case. The two phenomenological functions, namely, the dielectric function and the effective charge density are discussed at the microscopic level. Generally, the dielectric function has many poles, which leads to multi-Yukawa forms for the electric potential around a single ion. Parameters of these multi-Yukawa potentials, such as the linear combination coefficients and effective Debye lengths, can

be obtained from general relations such as charge neutrality condition, Stillinger-Lovett relation and other high order moment restrictions. Namely, these parameters can be obtained as long as we know the bulk dielectric function and the hard sphere diameter of primitive models. Using these parameters, the excess thermodynamic properties of primitive models can easily be evaluated accurately. For electrolyte solution models with soft short-ranged interactions, it is shown that the traditional perturbation theory can be extended to ionic fluids successfully just as the perturbation theory has been successfully used for short-ranged systems.

ACKNOWLEDGMENTS

We thank Qiang Zhang for discussions and contributions at the early stage of this work. The authors are grateful to the financial support from a Petroleum Research Foundation Grant No. 46451AC5 administrated by the American Chemical Society, and from a National Science Foundation (NSF) Grant No. CHE-0809431.

APPENDIX: THE DEBYE-HÜCKEL THEORY FROM THE MEAN ELECTRIC POTENTIAL

Consider a simple model of isotropic electrolyte solutions, where the solvent is treated as a continuum medium with dielectric constant ϵ_s and a solute particle, say “ j ,” is treated as a sphere with a point charge q_j at the center. The pair potential between i and j reads $u_{ij}(r) = u_{ij}^s(r) + u_{ij}^l(r)$, where $u_{ij}^s(r)$ is a short-ranged potential, while $u_{ij}^l(r) = q_i q_j / \epsilon_s r$ is the long-ranged Coulomb potential. The average electric potential $\Phi_j(r)$ around ion j , satisfies the following Poisson equation:²¹

$$-\epsilon_s \nabla^2 \Phi_j(r) = \rho_j^c(r) + \rho_j^{\text{ind}}(r) = \rho_j^{\text{tot}}(r), \quad (\text{A1})$$

where $\rho_j^c(r) = q_j \delta(r)$ is the bare charge density of the particle j , n_i is the particle number density of species i , $\rho_j^{\text{ind}}(r) = \sum n_i q_i g_{ij}(r) = \sum n_i q_i h_{ij}(r)$ is the induced charge density around j ; $g_{ij}(r)$ is the radial distribution function between i and j , $h_{ij}(r) = g_{ij}(r) - 1$ is the correlation function, and $\rho_j^{\text{tot}}(r)$ is the total charge density. Note that the information of dielectric response has been included in the induced charge density, one can derive the traditional Debye-Hückel theory from this Poisson equation after a mean field approximation of the induced charge density.²¹

In an isotropic equilibrium fluid, the total correlation function $h_{ij}(r)$ and the direct correlation function $c_{ij}(r)$ satisfies the conventional Ornstein-Zenike (OZ) equation

$$h_{ij}(r) = c_{ij}(r) + \sum_l \int d\mathbf{r}' c_{il}(|\mathbf{r} - \mathbf{r}'|) n_l h_{lj}(r'), \quad (\text{A2})$$

where $\mathbf{r} = (x, y, z)$ is the three-dimensional coordinate of the particle and $r = |\mathbf{r}|$ is the distance from the origin.

As noted in the dressed ion theory,¹² a renormalization of charge density could be realized by splitting the function $f(r) = h(r)$, $c(r)$, $\rho(r)$ into a well-defined long-ranged part $f^l(r)$ and a short-ranged part $f^0(r)$. Note that the asymptotic behavior of the direct correlation function behaves as

$c(r) \sim -\beta q_i q_j / \epsilon_s r$, we can define

$$c_{ij}^l(r) = -\frac{\beta q_i q_j}{\epsilon_s r} \quad (\text{A3})$$

and

$$c_{ij}^0(r) = c_{ij}(r) + \frac{\beta q_i q_j}{\epsilon_s r}. \quad (\text{A4})$$

The short-ranged part $h_{ij}^0(r)$ of $h_{ij}(r)$ is determined via the OZ equation

$$h_{ij}^0(r) = c_{ij}^0(r) + \sum_l \int d\mathbf{r}' c_{il}^0(|\mathbf{r} - \mathbf{r}'|) n_l h_{lj}^0(r'), \quad (\text{A5})$$

and then the short-ranged part of induced charge reads

$$\rho_j^{\text{ind},0}(r) = \sum_i n_i q_i h_{ij}^0(r). \quad (\text{A6})$$

It is noted that the long-ranged part of correlation function and charge density, defined via $h_{ij}^l(r) = h_{ij}(r) - h_{ij}^0(r)$ and $\rho_j^{\text{ind},l}(r) = \rho_j^{\text{ind}}(r) - \rho_j^{\text{ind},0}(r)$, are linearly related to the averaged electric potential,¹² i.e.,

$$h_{ij}^l(r) = -\beta \int d\mathbf{r}' \rho_i^0(|\mathbf{r} - \mathbf{r}'|) \Phi_j(r'), \quad (\text{A7})$$

$$\rho_j^{\text{ind},l}(r) = \sum_i n_i q_i h_{ij}^l(r) = - \int d\mathbf{r}' \alpha(|\mathbf{r} - \mathbf{r}'|) \Phi_j(r'), \quad (\text{A8})$$

where $\alpha(r) = \beta \sum_i n_i q_i \rho_i^0(r)$. Introduce an effective charge density as $\rho_j^0(r) = \rho_j^c(r) + \rho_j^{\text{ind},0}(r)$, then from Eq. (A1), we have

$$-\epsilon_s \nabla^2 \Phi_j(r) = \rho_j^0(r) - \int d\mathbf{r}' \alpha(|\mathbf{r} - \mathbf{r}'|) \Phi_j(r'). \quad (\text{A9})$$

In the Fourier space, Eq. (A9) reduces to the following equation for potential $\Phi_j(k)$,

$$k^2 \left[\epsilon_s + \frac{\alpha(k)}{k^2} \right] \Phi_j(k) = \rho_j^0(k), \quad (\text{A10})$$

where $\alpha(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \alpha(r) = \sum_i q_i n_i \rho_{ij}^0(k)$ is a screened response function, since the potential is a response to a local charge density $\rho_j^0(r)$ rather than an external charge density $q_j \delta(r)$.²² When we apply this equation to a multi-component system with solvent and solute, note $\alpha(k) = \sum_i q_i n_i \rho_{ij}^0(k)$ and $\sum_i q_i n_i h_{ij}^0(r)$ are proportional to the particle density n_i , then in the dilute limit of solute, i.e., $n_j \rightarrow 0$ for all the solute species, only the solvent will contribute to these two quantities. This means one can use the dielectric function of the pure solvent to evaluate the properties of a dilute solute, while the effective charge is still related to the cross correlation function $h_{ij}^0(k)$ between solute and solvent species.

When we compare Eq. (A10) with Eq. (16), similar structures are apparent. Introduce the static charge structure factor $S_{zz}(k)$ as

$$S_{zz}(k) = \sum_i Z_i^2 x_i + n \sum_{i,j} Z_i Z_j x_i x_j h_{ij}(k), \quad (\text{A11})$$

where $n = \sum_i n_i$ is the total number density, $x_i = n_i/n$ is the molar fraction of i th type particle, e is the element charge, and

$Z_j = q_j/e$ is the charge number of the j th ion. Then according to the linear response theory in ionic fluids,²² $\Sigma_l(k)$ could be replaced by the bulk dielectric function $\epsilon_l(k)$, which is related to the $S_{zz}(k)$ by the relation

$$\epsilon_l(k)^{-1} = \epsilon_s^{-1} \left[1 - \frac{\beta n e^2}{\epsilon_s k^2} S_{zz}(k) \right]. \quad (\text{A12})$$

Note that the screened response function $\alpha(k)$ defined in the dressed ion theory is also related to the charge structure factor,¹⁴ i.e.,

$$S_{zz}(k) = \frac{\epsilon_s k^2 \alpha(k)}{\beta n e^2 [\epsilon_s k^2 + \alpha(k)]}, \quad (\text{A13})$$

and it is straightforward to verify that

$$\epsilon_l(k) = \epsilon_s + \frac{\alpha(k)}{k^2}. \quad (\text{A14})$$

For a macroscopic system where the macroscopic Maxwell equations are used, the charge density ρ in Eq. (16) is always interpreted as free charge density, which is a macroscopic quantity.¹⁸ However, we should be careful when we apply this equation to the microscopic level, e.g., to a single ion. For a macroscopic system of interest, the linear response is applicable, since the scale we care about is much larger than the molecular scale, e.g., typically order of 1 mm, where the external field is always weak enough. However, when we consider the potential of a single ion, we are interested in the scale that is comparable with molecular size, where the Coulomb interaction may be not weak enough, then linear response would not be satisfactory, and the nonlinear effect should be taken into account. So at the molecular level, it would be essential to interpret the charge density in Eq. (16) as an effective one, which should be derived from statistical mechanics calculations of a microscopic model as the derivation of Eq. (16).²¹ As noted by Kjellander,¹³ the nonlinear response can be included in the effective charge density $\rho_j^0(k)$. When the dielectric function is replaced by the term from linear response, i.e., $\Sigma_l(k) = \epsilon_l(k)$, the charge density is interpreted as $\rho(k) = \rho_j^0(k)$, and then we have a rigorous electric potential equation that is applicable to the ionic fluids at molecular level,

$$k^2 \epsilon_l(k) \Phi_j(k) = \rho_j^0(k). \quad (\text{A15})$$

Therefore, a rigorous statistical mechanics derivation of the Poisson equation with a renormalized charge density is obtained for a molecular model with pair additive interactions. The solution of the above equation can be obtained as a superposition of linearized PB equations with effective screening lengths and charges, which forms the starting point of our molecular DH theory presented in Sec. III. Dynamical extension of the above result can be formulated in a similar fashion, namely, a rigorous statistical mechanics derivation of the macroscopic Maxwell Eqs. (14) and (15) from the microscopic ones is needed just as how Eq. (16) is derived. Since a time-dependent Ornstein-Zernike equation has not been formulated rigorously thus a rigorous dynamical extension of the DH theory is still an open question.

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