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A molecular Debye-Hückel theory and its applications to electrolyte solutions: The size asymmetric case

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A molecular Debye-Hückel theory for electrolyte solutions with size asymmetry is developed, where the dielectric response of an electrolyte solution is described by a linear combination of Debye-Hückel-like response modes. As the size asymmetry of an electrolyte solution leads to a charge imbalanced border zone around a solute, the dielectric response to the solute is characterized by two types of charge sources, namely, a bare solute charge and a charge distribution due to size asymmetry. These two kinds of charge sources are screened by the solvent differently, our theory presents a method to calculate the mean electric potential as well as the electrostatic contributions to thermodynamic properties. The theory has been successfully applied to binary as well as multi-component primitive models of electrolyte solutions. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4978895]

I. INTRODUCTION

Solvation in ionic fluids is a fundamental problem and has many applications to various processes in physical and biological sciences such as protein crystallization,[1–3] surface tension of ionic fluids,[4–6] and electron transfer reactions,[7–10] to name a few. It has been known for over a century that an ion is perfectly screened by an ionic fluid as described by the Debye-Hückel (DH) theory.[11,12] Due to the mean field nature of the DH theory, its applications are limited to dilute electrolyte solutions or weak coupling ionic fluids.[13]

Naturally there are various efforts to improve the DH theory. For example, Stillinger and Lovett[14] demonstrated the existence of some general constraints for the distribution function of ions in an electrolyte solution, where the second moment constraint implies that the charge density would become oscillatory decay for a large Debye screening parameter. Such oscillatory decay behavior of electric potential is known to originate from the competition between the local packing effect and the long ranged Coulomb interaction.[15] Based on a rigorous analysis from statistical mechanics, Kirkwood and Poirier[16] and Outhwaite[17–19] demonstrated that the electric potential, $\Phi(r)$, of an ion can be expressed as a linear combination of multi Yukawa potentials, namely, $\Phi(r) = \sum_n \frac{q_{n,*} e^{-k_n r}}{\epsilon_n r}$. When the decay parameters k_n become complex numbers, one naturally have the oscillatory decayed potentials. Kjellander and coworkers[20–22] developed a dressed ion theory based on a rigorous charge renormalization process of the Poisson equation. Such a scenario can also be understood using the dispersion relations from the solutions of the Maxwell equation.[23,24]

Based upon the multi-Yukawa potential formulation, a molecular DH (MDH) theory is developed for ionic fluids with any coupling strength.[24] In our previous work,[24] the MDH theory is developed for a restricted model of ionic fluids, where the cations and anions have the same size. The physical picture of the MDH theory is that the electrostatic response of an ionic fluid can be described by a linear combination of DH-like modes, where each DH mode has its own decay parameter which depends only on the bulk dielectric function, whereas the linear combination coefficients can also be determined from the dielectric function as long as the solute size is close to the size of the solvent ions. Such a prescription has been applied successfully to the various ionic fluids.[25–28]

In this contribution, we extend the MDH theory to the size asymmetric case, so that the cation and anion of the electrolyte solutions can have different sizes. It is known that the size asymmetry leads to a border zone around a solute ion, where the charge density is nonzero even for a neutral solute.[29,30] Such an observation implies that one should account for the charge density induced by size asymmetry. In the high temperature limit, we find that the charge density around a neutral solute reduces to a universal charge density $\rho_j^{hs}(r) = \sum_j n_i q_i g_{ij}^{hs}(r)$ which can be evaluated with a radial distribution $g_{ij}^{hs}(r)$ of a hard sphere mixture. As a consequence, the solvent will respond both to the bare solute charge q_j and the charge density $\rho_j^{hs}(r)$ due to the size asymmetry. Our theory is developed based upon this physical picture.

This paper is organized as following: in Section II the MDH theory for the size asymmetric case is formulated. The electrostatic contribution to various thermodynamic properties of the ionic fluids is discussed in Section II. In Section III the MDH theory is applied to various electrolyte solution models. Finally the paper concludes with a brief summary in Section IV.

II. A MOLECULAR DEBYE-HÜCKEL THEORY FOR BINARY ELECTROLYTES WITH SIZE ASYMMETRY

A. Model description of size asymmetric electrolytes

We use the binary size asymmetric primitive model of an electrolyte solution as an illustrative example to develop a MDH theory. A central ion tagged by i (or equivalently a solute) is described by a hard sphere with a diameter σ_i and a point charge q_i. Let the elemental charge be e_0, then the central ion's charge number is $z_i = q_i/e_0$. The diameters of the ions are additive such that the radius of contact between an ion i and an ion j is $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The total particle number density is n, the reduced inverse temperature is $\beta = \frac{1}{k_B T}$ with k_B being the Boltzmann constant and T the temperature, the dielectric constant of the background is ϵ_s. The surrounding ions (or equivalently the solvent ions) are denoted as species 1 and 2. As we focus on the size asymmetry in this paper, it is assumed that 1 and 2 have the same absolute charge such that $q_1 = -q_2 \equiv q_s$. Let x_i be the mole fraction, then $x_{1,2} = 1/2$. Furthermore, it is assumed that $\sigma_1 > \sigma_2$ without loss of generality.

Let $f(k) = \int d\mathbf{r} f(r) e^{i\mathbf{k}\cdot\mathbf{r}} = \int_{r=0}^{\infty} f(r) 4\pi r^2 \frac{\sin(kr)}{kr} dr$ be the three-dimensional Fourier transform of a function $f(r)$. Let $g_{ij}(r)$ be the radial distribution function between species i and j, one can use the correlation function $h_{ij}(r) \equiv g_{ij}(r) - 1$ to evaluate the total charge density $\rho_j^t(r) = q_j \delta^{(3)}(\mathbf{r}) + \sum_{i=1,2} q_i n_i h_{ij}(r)$ around the central ion j, where $\delta^{(3)}(\mathbf{r})$ is the Dirac delta function. Hence $\rho_j^t(k) = q_j + \sum_{i=1,2} q_i n_i h_{ij}(k)$ in k-space.

A crucial observation in our formulation is that one can split the charge density $\rho_j^t(k)$ around a central ion into a hard sphere contribution $\rho_j^{hs}(k) \equiv \sum_{i=1,2} n q_i x_i h_{ji}^{hs}(k)$ due to the size asymmetry and a contribution $\rho_j'(k) \equiv \rho_j^t(k) - (q_j + \rho_j^{hs}(k))$ due to the dielectric response of surrounding ions. It is noted that in the high temperature limit $\beta \to 0$, the system is reduced to a hard sphere mixture, $h_{ji}^{hs}(k)$ can be evaluated from the system at the high temperature limit, namely, $\lim_{\beta\to 0} h_{ji}(k) \equiv h_{ji}^{hs}(k)$. Hence,

$$\lim_{\beta\to 0} \rho_j^t(k) = q_j + \sum_{i=1,2} n q_i x_i h_{ji}^{hs}(k) \equiv q_j + \rho_j^{hs}(k). \tag{1}$$

As $\rho_j^{hs}(k)$ only depends on the ion size, even a neutral solute can have a nonzero charge density $\rho_j^{hs}(k)$, an explicit example is given using the mean spherical approximation (MSA) in the Appendix. Thus, one can treat q_j and $\rho_j^{hs}(k)$ as two kinds of source charges of the solute, and then $\rho_j'(k) = \rho_j^t(k) - (q_j + \rho_j^{hs}(k))$ can be viewed as the dielectric response to the charge density $q_j + \rho_j^{hs}(k)$. Such a physical picture is the starting point to build our extended MDH theory for size asymmetric electrolytes.

Some remarks on the charge density $\rho_j^{hs}(r)$ are in order. It is known that the correlation function $h_{ij}^{hs}(r)$ of hard spheres can be evaluated using integral equations such as the Percus-Yevick (PY) closure, from which one can find that $\rho_j^{hs}(r) = \sum_{i=1,2} n q_i x_i h_{ji}^{hs}(r)$. Then a cumulative charge can be obtained $Q_j^{hs} \equiv \int_{\sigma_{j2}}^{\infty} \rho_j^{hs}(r') 4\pi r'^2 dr'$ and an electric potential at the center of the solute will be $\psi_j^{hs} \equiv \int_{\sigma_{j2}}^{\infty} \frac{\rho_j^{hs}(r')}{r'} 4\pi r'^2 dr'$ due to the Gauss theorem.[31] As such a cumulative charge exists even for a neutral solute and this charge is purely due to the size asymmetry of the charged surrounding solvent particles, this cumulative charge will be used later (see Secs. II B and II E) to capture the size asymmetry of charged solvent particles. Such an identification of two kinds of source charges for a size asymmetric system forms the foundation of our development of MDH for such systems.

B. Extended molecular Debye-Hückel theory for size asymmetric electrolytes

Let us focus on the electric potential $\Phi_j(r)$ of the central ion j, which is known to satisfy the Poisson equation[32]

$$\nabla^2 \Phi_j(r) = -\frac{4\pi}{\epsilon_s} \rho_j^t(r) = -\frac{4\pi}{\epsilon_s} [q_j \delta^{(3)}(\mathbf{r}) + \rho_j(r)]. \tag{2}$$

As indicated by the dressed ion theory, a rigorous charge renormalization process can be applied to the total charge density, and then the electric potential in k-space can be rewritten as[20,24]

$$k^2 \epsilon_l(k) \Phi_j(k) = 4\pi \rho_j^0(k), \tag{3}$$

where $\epsilon_l(k)$ is the dielectric response function of the bulk system and $\rho_j^0(k)$ is the effective charge density of the dressed ion. The interested readers can refer to Refs. 20 and 24 for more details of the charge renormalization process. An asymptotic analysis of the electric potential leads to $\Phi_j(r) \approx \sum_n \frac{q_{eff,n}}{\epsilon_{eff,n}} \frac{e^{-k_n r}}{r}$,[20,24] where k_n are the roots of $\epsilon_l(k)$. As a Yukawa potential $\frac{e^{-k_n r}}{r}$ can be viewed as a DH response mode with $\nabla^2 \phi_n(r) = k_n^2 \phi_n(r)$, the asymptotic expansion motivates us to approximate the dielectric response of an electrolyte with multi-DH-like modes, i.e., the electric potential $\Phi_j(r)$ is expanded as a linear combination of DH-like modes,

$$\Phi_j(r) = \sum_n C_{jn} \phi_{jn}(r), \tag{4}$$

where $\{C_{jn}\}$s are the linear combination coefficients to be determined. The electric potential $\phi_{jn}(r)$ is the solution of a DH equation with a decay parameter k_n,

$$\begin{aligned}
\nabla^2 \phi_{jn}(r) &= -\frac{4\pi}{\epsilon_s} q_j \delta^{(3)}(r), && r \le \sigma_{j2}, \\
\nabla^2 \phi_{jn}(r) &\approx -\frac{4\pi}{\epsilon_s} \rho_e^{hs} \delta(r - a_d), && \sigma_{j2} \le r \le b_j, \\
\nabla^2 \phi_{jn}(r) &= k_n^2 \phi_{jn}(r), && r > b_j,
\end{aligned} \tag{5}$$

where $b_j = (\sigma_j + \sigma_{12})/2$ is an effective size of the solute. Naturally such an effective size choice is not unique, but our results are not sensitive to the choice. In the above equations, a surface charge density $\rho_e^{hs} \delta(r - a_d)$ is used to mimic the hard sphere charge density $\rho_j^{hs}(r)$. We take $\rho_j^{hs}(r) \approx \rho_e^{hs} \delta(r - a_d)$, where the two parameters are determined via $\rho_e^{hs} = (\psi_j^{hs})^2/(4\pi Q_j^{hs})$ and $a_d = Q_j^{hs}/\psi_j^{hs}$.

Eqs. (4) and (5) are the main working equations for the MDH theory of size asymmetric electrolytes. According to the above equations, a central ion j is characterized by q_j and $\rho_j^{hs}(r)$, while the dielectric response of the surrounding ions is described by a set of DH-like modes with a decay parameter k_n. In general, the linear combination coefficients $\{C_{jn}\}$ are solute-dependent, so that the cations and anions of the solvent may have different $\{C_{jn}\}$. In the range of $\sigma_{j2} \le r \le b_j$ in Eq. (5), it is also possible to use the term $\rho_j(r)$ instead of $\rho_j^{hs}(r)$ to build the MDH theory, and then one may find a new set of $\{C_{jl}\}$. However, as $\rho_j(r)$ actually depends on the solute charge q_j and also contains the dielectric response of the solvent beyond the hard sphere charge accumulation due to the size asymmetry, such a convoluted effect prevents us from developing a simple MDH approach using $\rho_j(r)$.

According to Eqs. (4) and (5), the mean electric potential $\Phi(r)$ outside the core is a linear combination of multi-Yukawa potential,

$$\Phi_j(r) = \sum_{n=1}^{L} \frac{(q_j + Q_j^{hs})C_{jn}}{\epsilon_s(1 + k_n b_j)} \frac{e^{-k_n(r - b_j)}}{r}, \; r > b_j, \tag{6}$$

where L is the number of adopted DH modes, Q_j^{hs} is the cumulate charge due to asymmetric hard sphere sizes. Inside the hard core, Eq. (5) can be solved with appropriate boundary conditions

$$\begin{aligned} \Phi_j(r) &= \frac{q_j}{\epsilon_s r} + \psi_j, & 0 < r < \sigma_{j2}, \\ \Phi_j(r) &= \frac{q_j + Q_j^{hs}}{\epsilon_s r} - \frac{q_j + Q_j^{hs}}{\epsilon_s} \sum_{n=1}^{L} \frac{C_{jn} k_n}{1 + k_n b_j}, & \sigma_{j2} < r \le b_j, \end{aligned} \tag{7}$$

where the induced electric potentials ψ_j is defined as

$$\psi_j = \frac{\psi_j^{hs}}{\epsilon_s} - \frac{q_j + Q_j^{hs}}{\epsilon_s} \sum_{n=1}^{L} \frac{C_{jn} k_n}{1 + k_n b_j}. \tag{8}$$

C. Induced charge densities and the dielectric response function

According to the Poisson equation Eq. (2) and the MDH theory equations Eqs. (5)–(7), the induced charge density $\rho'_j(r) = \rho_j(r) - \rho_j^{hs}(r)$ from MDH theory is

$$\begin{aligned} \rho'_j(r) &\approx 0, & r < b_j, \\ \rho'_j(r) &= -\frac{\epsilon_s}{4\pi}\nabla^2\Phi_j(r) = -\frac{q_j + Q_j^{hs}}{4\pi} \sum_{n=1}^{L} \frac{C_{jn} k_n^2}{(1 + k_n b_j)} \frac{e^{-k_n(r-b_j)}}{r}, & r > b_j, \end{aligned} \tag{9}$$

where the weak dielectric response inside the solute cavity is neglected. The three-dimensional Fourier transform $\rho'_j(k)$ of $\rho'_j(r)$ is

$$\begin{aligned} \rho'_j(k) &= -\int_{b_j}^{\infty} \frac{q_j + Q_j^{hs}}{4\pi} \sum_{n=1}^{L} \frac{C_{jn} k_n^2}{(1 + k_n b_j)} \frac{e^{-k_n(r-b_j)}}{r} \frac{\sin(kr)}{kr} 4\pi r^2 dr \\ &= -\sum_{n=1}^{L} (q_j + Q_j^{hs}) C_{jn} f_n(b_j, k), \end{aligned} \tag{10}$$

with $f_n(\sigma, k) = \frac{k_n^2}{1 + k_n\sigma} \frac{\cos(k\sigma) + k_n \sin(k\sigma)/k}{k_n^2 + k^2}$. The charge density $\rho_j(k) = \rho'_j(k) + \rho_j^{hs}(k)$ due to the induced charge density and the cumulative charge density from size asymmetry can be evaluated as

$$\rho_j(k) = \rho_j^{hs}(k) - \sum_{n=1}^{L} (q_j + Q_j^{hs}) C_{jn} f_n(b_j, k). \tag{11}$$

It is easy to check that the perfect screening condition $\rho_j^t(k=0) = 0$ is satisfied as long as $\sum_{n=1}^{L} C_{jn} = 1$. Given the charge density $\rho_j(k)$ from other methods such as integral equations or simulations, fitting $\rho_j(k)$ using Eq. (11) will lead to a set of coefficient $\{C_{jn}\}$ for the solute j.

For a pure solvent, when $\rho_1(k)$ and $\rho_2(k)$ of the solvent species are fitted to Eq. (11), one can get the coefficients $\{C_{1n}\}$ and $\{C_{2n}\}$. Using Eq. (11) for the charge density, one can find an analytical expression for the response function $\chi(k) \equiv 1 - \epsilon_s/\epsilon_l(k)$. It is known that $\chi(k) = \frac{4\pi\beta n e_0^2}{\epsilon_s k^2} S_{zz}(k)$, where $S_{zz}(k)$ is the static charge structure factor $S_{zz}(k) = \sum_i z_i^2 x_i + n \sum_{i,j} x_i x_j z_i z_j h_{ij}(k) = \sum_i z_i^2 x_i + \sum_i z_i x_i \; \rho_i(k)$.[15] With these relations, it is straightforward to find that

$$\chi(k) = \frac{4\pi\beta n}{\epsilon_s k^2} \sum_{i=1,2} q_i x_i [q_i + \rho_i^{hs}(k) - \sum_{n=1}^{L} (q_i + Q_i^{hs}) C_{in} f_n(b_i, k)], \tag{12}$$

which can be shown to reduce the results of Ref. 24 for size symmetric cases.

D. Electrostatic contributions to thermodynamic properties: I

As long as the mean electric potential $\Phi_j(r)$ is determined, one can calculate electrostatic contribution to the excess thermodynamic properties. With the induced electric potential ψ_j at the center of the ion j given by $\psi_j \equiv \lim_{r\to 0}[\Phi_j(r) - \frac{q_j}{\epsilon_s r}]$, the excess internal energy u_j^{ex} for the ion j can be evaluated as[24]

$$\beta u_j^{\mathrm{ex}} = \frac{\beta}{2} \int_0^{\infty} \frac{q_j \rho_j(r)}{\epsilon_s r} 4\pi r^2 dr = \frac{\beta q_j \psi_j}{2}. \tag{13}$$

Combining Eqs. (8) and (13), the excess internal energy reads

$$\beta u_j^{\mathrm{ex}} = \frac{\beta q_j \psi_j^{hs}}{2\epsilon_s} - \frac{\beta q_j}{2\epsilon_s} \sum_{n=1}^{L} \frac{(q_j + Q_j^{hs}) C_{jn} k_n}{1 + k_n b_j}. \tag{14}$$

An interesting observation is that the mean spherical approximation (MSA) of electrolyte solutions leads to similar functional dependence of the excess internal energy as $\beta u_j^{ex} = -\frac{\beta q_j}{\epsilon_s}(\frac{q_j\Gamma}{1 + \Gamma\sigma_i} + \psi'_j)$, where Γ is the energy parameter, ψ'_j is an induced potential which is independent of the ion charge.[33] For the convenience of the readers, some main results for thermodynamic properties from MSA theory are summarized in the Appendix.

Let us consider the dilute limit where $h_{ij}^{hs}(r) = -1$ for $r < \sigma_{ij}$ and $h_{ij}^{hs}(r) = 0$ for $r > \sigma_{ij}$. The first decay parameter

k_1 is reduced to the conventional Debye parameter $k_D = \sqrt{\frac{4\pi\beta n \sum_{i=1,2} x_i q_i^2}{\epsilon_s}}$. By using $a_d = b_j$, $\psi_j^{hs} = 2\pi q_2 n_2(\sigma_{j1}^2 - \sigma_{j2}^2)$, and $Q_j^{hs} = \psi_j^{hs} b_j$, the excess internal energy reads

$$\beta u_j^{\mathrm{ex}} = \frac{\beta\pi n_2 q_j q_2(\sigma_1 - \sigma_2)}{\epsilon_s}\frac{b_j}{1+k_D b_j} - \frac{\beta q_j^2}{2\epsilon_s}\frac{k_D}{1+k_D b_j}. \tag{15}$$

As a comparison, the excess internal energy from conventional DH theory is given by[11]

$$\beta u_j^{\mathrm{ex}} = -\frac{\beta q_j^2}{2\epsilon_s}\frac{k_D}{1+k_D b_j}, \tag{16}$$

where the contribution of solvent size asymmetric is absent. As one can expect, DH theory is valid only in the dilute limit where the effect of size asymmetry can be neglected.

With the electric potential from MDH theory, electrostatic contributions to other thermodynamic properties can also be evaluated. For the primitive model, the van der Waals interactions are neglected and then the excess chemical potential of the solute j can be written as[21,32]

$$\beta\mu_j^{\mathrm{ex}} = \beta\mu_j^{\mathrm{hs}} + \beta\mu_j^{\mathrm{ele}}, \tag{17}$$

where μ_j^{hs} is the cavity formation free energy of a neutral solute in the solution, which can be evaluated either from direct calculations such as virial expansions, perturbation theory,[15] scaled particle theory,[34,35] or the morphological thermodynamics theory.[36,37]

The electrostatic part of the excess chemical potential μ_j^{ele} of species j can be evaluated from a Kirkwood coupling process,[32]

$$\begin{aligned}\beta\mu_j^{ele} &= \beta n \sum_i x_i \int_0^1 d\xi \int d\mathbf{r}\, u_{ij}^{ele}(r) g_{ij}(r;\xi)\\ &= \beta\int_0^1 d\xi q_j \psi_j(\xi q_j),\end{aligned} \tag{18}$$

where $0 \le \xi \le 1$ is a coupling parameter and ξq_j is the charge of the partially charged j ion. $u_{ij}^{ele}(r;\xi) = \xi\frac{q_i q_j}{\epsilon_s r}$ is the pair interaction between a partially charged solute ion j and a solvent ion of species i, while other solvent particles interact fully with each other. $g_{ij}(r;\xi)$ denotes the radial distribution function of solvent species i around the partially charged j ion, and $\psi_j(\xi q_j) \equiv \beta n \sum_i x_i \int d\mathbf{r}\, u_{ij}^{ele}(r) g_{ij}(r;\xi)$ denotes the induced potential of the partial charged j ion. Unfortunately, the evaluation of $\psi_j(\xi q_j)$ cannot be done by using the linear combination coefficients $\{C_{jn}\}$ obtained in Sec. II C since the coefficients $\{C_{jn}\}$ come from the dielectric response of two different kinds of charge sources, namely, the bare charge of the solute and the cumulative charge due to the size asymmetry of charged solvent particles. Sec. II E will present a detailed discussion and a resolution on the two kinds of dielectric responses.

E. Two sets of response coefficients as a consequence of two types of charge sources

In general, the MDH theory can be used to predict the thermodynamic properties of a single ion. As one can see from Sec. II D, the excess internal energy βu_j^{ex} is a simple linear function of $\{q_j C_{jn}\}$ while the excess chemical potential $\{\beta\mu_j^{ex}\}$ cannot be expressed as a simple function of $\{q_j C_{jn}\}$.

To illustrate two different kinds of dielectric responses to the two types of charge sources q_j and $\rho_j^{hs}(r)$, let us consider a pair of conjugate solutes tagged by j and j_c, where the solute size is $\sigma_j = \sigma_{j_c}$ and the solute charge is $q_j = -q_{jc}$. The asymmetric and symmetric part of the charge density and the electric potential can be evaluated as $\rho_j^{a,s}(k) = (\rho_j^t(k) \mp \rho_{j_c}^t(k))/2$ and $\Phi_j^{a,s}(k) = (\Phi_j(k) \mp \Phi_{j_c}(k))/2$. It is easy to check that electric potential $\Phi_j^{a,s}(k)$ satisfies the Poisson equation as $\nabla^2\Phi_j^a(r) = -\frac{4\pi}{\epsilon_s}[q_j\delta^{(3)}(\mathbf{r}) + \rho_j^a(r)]$ and $\nabla^2\Phi_j^s(r) = -\frac{4\pi}{\epsilon_s}\rho_j^s(r)$. Following the procedure of MDH theory, one can introduce two sets of coefficients as $\{C_{jl}^{a,s}\}$, and the induced charge density can be evaluated as $\rho_j^a(k) = -\sum_n q_j C_{jn}^s f_n(b_j,k)$ and $\rho_j^s(k) = \rho_j^{hs}(k) - \sum_n Q_j^{hs} C_{jn}^s f_n(b_j,k)$, namely, the symmetric response is due to the charges from the size asymmetry whereas the asymmetric response is due to the bare charge of the solute. Note that $\rho_j(k) = \rho_j^s(k) + \rho_j^a(k)$, one should have $\rho_j^{hs}(k) - \sum_n (q_j + Q_j^{hs}) C_{jn} f_n(b_j,k) = \rho_j^{hs}(k) - \sum_n Q_j^{hs} C_{jn}^s f_n(b_j,k) - \sum_n q_j C_{jn}^a f_n(b_j,k)$ and then we can find the following relation:

$$(q_j + Q_j^{hs})C_{jn} = q_j C_{jn}^a + Q_j^{hs} C_{jn}^s. \tag{19}$$

Combining Eqs. (8) and (19), the induced potential can be written as

$$\psi_j = \frac{\psi_j^{hs}}{\epsilon_s} - \frac{1}{\epsilon_s}\sum_{n=1}^{L}\frac{(q_j C_{jn}^a + Q_j^{hs} C_{jn}^s)k_n}{1+k_n b_j}. \tag{20}$$

According to the procedure to derive Eqs. (19) and (20), one may need to introduce a fictitious four-component system for a binary pure solvent. So we adopt an approximate solution presented below to simply the application. For a solvent with moderate size asymmetry, we assume that $C_{jn}^{a,s}$ for the solvent ions $j = 1,2$ are the same, i.e., $C_{1n}^a = C_{2n}^a = C_n^a$, $C_{1n}^s = C_{2n}^s = C_n^s$, then one can find the following constraints for $C_n^{a,s}$ as

$$\begin{aligned}(q_1 + Q_1^{hs})C_{1n} &= q_1 C_n^a + Q_1^{hs} C_n^s,\\ (q_2 + Q_2^{hs})C_{2n} &= q_2 C_n^a + Q_2^{hs} C_n^s.\end{aligned} \tag{21}$$

This linear equation can be used to evaluate $C_n^{a,s}$. Such a strategy is not confined to the pure solvent case, but to any tagged pair of charges ions. In Sec. III we will show that such a strategy works very well.

F. Electrostatic contributions to thermodynamic properties: II

Now with the two sets of response coefficients, we are able to evaluate the electrostatic part of the excess chemical potential μ_j^{ele},

$$\begin{aligned}\beta\mu_j^{ele} = \beta\int_0^1 d\xi q_j\psi_j(\xi q_j) &= \frac{\beta q_j \psi_j^{hs}}{\epsilon_s}\\ &- \frac{\beta q_j}{2\epsilon_s}\sum_n \frac{(q_j C_{jn}^a + 2Q_j^{hs} C_{jn}^s)k_n}{1+k_n b_j},\end{aligned} \tag{22}$$

where $\psi_j(\xi q_j) \equiv \beta n \sum_i x_i \int d\mathbf{r}\, u_{ij}^{ele}(r) g_{ij}(r;\xi) = \frac{\psi_j^{hs}}{\epsilon_s} - \frac{1}{\epsilon_s}\sum_{n=1}^{L}\frac{(\xi q_j C_{jn}^a + Q_j^{hs} C_{jn}^s)k_n}{1+k_n b_j}$ denotes the induced potential of the partial coupled j ion. In the above derivation, we use the assumption that $\{C_{jn}^{a,s}\}$ is independent of the solute charge.

As the response to the bare charge q_j and the response to the $\rho_j^{hs}(r)$ are different in general, introduction of $\{C_{jn}^{a,s}\}$ is crucial for the chemical potential calculation. If we simply assume that $\{C_{jl}\}$ is independent of the solute charge q_j, the predicted chemical potentials would not be accurate. Furthermore, one can see that our MDH theory leads to a chemical potential calculation procedure using a single thermodynamic state, i.e., for a fixed solvent density and fixed temperature, we only need to know $\{C_{jn}^{a,s}\}$ and $\{k_n\}$ and will be able to predict the chemical potential $\beta\mu_{1,2}^{ex}$. Such an idea can be easily extended to a solute with arbitrary geometry. As a comparison, the conventional method for chemical potential calculation needs to know the excess internal energies $U^{ex}(\beta)$ for a series of inverse temperature β (or different coupling strength via the Kirkwood coupling route). $U^{ex}(\beta)$ can be used to construct the excess Helmholtz free energy βA^{ex} based on the thermodynamic relation $\beta A^{ex} = \int_0^\beta U^{ex}(\beta)d\beta$, and then the chemical potential $\beta\mu_j^{ex}$ can be determined via $\beta\mu_j^{ex} = \frac{\partial \beta A^{ex}}{\partial n_j}$. Though other theories such as the mean field lattice gas theory,[38–41] the Poisson-Boltzmann theory, the integral equation theory, and the density functional theories can also be applied to solvation problems, the route could be different. The correlation functions need to be solved first and then one can calculate the solvation energy. One may also note that the application of these theories is much more numerically involved once the solute geometry goes beyond spherical, planar, or cylindrical.

It would be of interest to see the main difference between the mean field lattice gas theory and our MDH theory. The mean field lattice gas theories are essentially the modified Poisson-Boltzmann theory with appropriate boundary conditions. Therefore, they are mean field in nature unless some loop expansion is included using field theory techniques, but it is not clear to these authors how other mean field solutions can be included in this kind of approach. Our MDH theory is a formulation to use multiple mean field solutions to approximate the exact solution of a solvation problem in an ionic fluid. In this case, the solvation problem is reduced to a linear combination of electrostatic boundary problems with Debye screening lengths determined by the response function of the neat ionic fluids. Our MDH theory is applicable to the solutes with general geometry and charge density and has been tested for several systems.[25–28]

With the above excess properties, it is possible to evaluate other thermodynamic properties of an electrolyte solution. The averaged excess internal energy per particle is

$$\frac{\beta U^{ex}}{N} \equiv \beta\bar{u}^{ex} = \sum_i x_i \beta u_i^{ex}. \tag{23}$$

The average excess chemical potential reads

$$\frac{\beta G^{ex}}{N} \equiv \beta\bar{\mu}^{ex} = \sum_i x_i \beta\mu_i^{ex}. \tag{24}$$

The pressure can be evaluated by the virial equation as

$$\frac{\beta P}{n} = 1 + \frac{\pi}{6}\sum_{i,j=1,2} x_i x_j g_{ij}(\sigma_{ij})\sigma_{ij}^3 + \frac{\beta\bar{u}^{ex}}{3}, \tag{25}$$

where $g_{ij}(\sigma_{ij})$ can be evaluated by the exponential approximation or integral equation method.[15]

G. Prescriptions to determine the linear coefficient $\{C_n^{a,s}\}$ of the pure solvent

With the above equations, one can build the MDH theory using the following procedure:

(1) $\{k_n\}$ is determined with the dielectric function $\epsilon_l(k)$ or equivalently $\chi(k) \equiv 1 - \frac{\epsilon_s}{\epsilon_l(k)}$ of the bulk system, which can be calculated using $h_{ij}(r)$ from various theories such as integral equation theory or molecular dynamics simulations. Note that $\chi(k)$ in most case is not analytically known, an empirical function $\chi(k) = \frac{a_0k^2}{k^4 + (a_1k^2 - a_2)Cos(kb) + a_3Sin(kb) + a_2}$ can be used to fit the response function $\chi(k)$, and then the pole $k = ik_n$ can be determined by solving $k^4 + (a_1k^2 - a_2)\mathrm{Cos}(kb) + a_3\mathrm{Sin}(kb) + a_2 = 0$ numerically.[27,28]

(2) The hard sphere contribution to the charge density $\rho_j^{hs}(k) = n\sum_i q_i x_i h_{ij}^{hs}(k)$ can be evaluated using the analytical correlation function $h_{ij}^{hs}(k)$ from the Percus-Yevick (PY) theory or other integral equation theory for hard sphere mixtures,[15] and then the cumulate charge $Q_j^{hs} \equiv \int \rho_j^{hs}(r)4\pi r^2 dr$ and the electric potential $\psi_j^{hs} \equiv \int \frac{\rho_j^{hs}(r)}{r}4\pi r^2 dr$ can be determined. The parameters ρ_e^{hs} and a_d of the effective surface charge are evaluated by $\rho_e^{hs} = (\psi_j^{hs})^2/(4\pi Q_j^{hs})$ and $a_d = Q_j^{hs}/\psi_j^{hs}$. Furthermore, we chose $b_j = (\sigma_j + \sigma_{12})/2$.

(3) The coefficient $\{C_n^{a,s}\}$ can be determined using the MDH theory as prescribed in Sec. II. Namely, fitting $\rho_{1,2}(k)$ of the solvent species with Eq. (11) leads to C_{1n} and C_{2n}, which can be further used to evaluate $\{C_n^{a,s}\}$ according to Eq. (21). In both cases, the charge neutrality condition $\sum_{n=1}^{L} C_{jn} = 1$ should be implemented as a constraint.

After these three steps, all the parameters of the MDH theory of the pure solvent are determined. As will be shown in Sec. III, this strategy leads to very satisfactory charge density profiles as well as excess thermodynamic properties.

III. APPLICATIONS TO ELECTROLYTE SOLUTIONS

To demonstrate the validity of our MDH theory, we apply our theory to the electrolytes with moderate size asymmetry. Specifically we test our theory against the mean spherical approximation (MSA)[33] and hyper-netted chain (HNC) approximation of electrolyte solutions, where the excess internal energy βu_j^{ex} and the excess chemical potential $\beta\mu_j^{ex}$ are known. We follow the procedure described in Sec. II to evaluate the parameters in MDH theory, which is further used to evaluate the thermodynamic properties according to Eqs. (14) and (22). We will show that typically two or four DH modes are capable of predicting the excess thermodynamic properties accurately. When the electrostatic coupling becomes very strong, one may need more DH modes in the MDH calculation given that there is no higher order poles or branch cut in the response function.

A. Tests against the mean spherical approximation

As the first test case, we consider the mean spherical approximation[33] for primitive models, which leads to analytical results for the dielectric function, excess energy, and other excess thermodynamic properties. As shown in the Appendix, one may also note that there are two routes to compute the excess electrostatic chemical potential $\beta\mu_j^{ex}$ as shown in Eqs. (A10) and (A11). Due to the thermodynamic inconsistency of the MSA theory, these two routes lead to different results. Even though our numerical calculation shows that the results from these two routes are in excellent agreement with each other, e.g., for an electrolyte solution with $q_s = 1, \epsilon_s = 1, \beta = 1, \sigma_{1,2} = 1, 0.5$, the relative difference between the result from Eq. (A10) and that from Eq. (A11) is no more than 1 percent in the range of $0.002 < n < 1.4$. Such an observation implies that one can either use Eq. (A10) or use Eq. (A11) to evaluate the chemical potential from MSA. In this study, we chose Eq. (A11) from MSA as a benchmark to test the accuracy of our MDH theory.

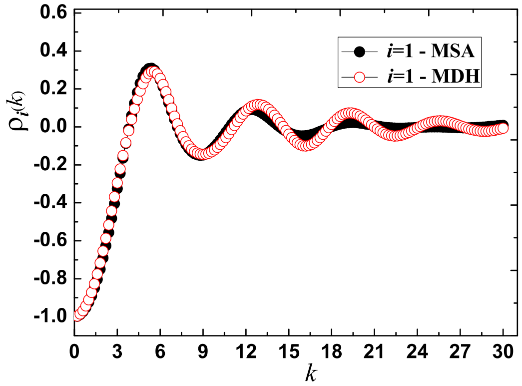
Consider a binary solvent with parameters $q_s = 1$, $\epsilon_s = 1$, $\beta = 1$, and $\sigma_{1,2} = 1, 0.5$. The total particle number density n is taken as a control parameter, with which the Debye parameter is evaluated as $k_D = \sqrt{\frac{4\pi\beta n q_s^2}{\epsilon_s}}$. For $0.002 < n < 1.4$, one can find that $0.159 < k_D < 4.19$. Two DH modes $L = 2$ are used for $k_D < 2$ and four DH modes $L = 4$ are used for $k_D > 2$ during our calculations.

To demonstrate that our MDH theory is capable of evaluating the induced charge density, we calculated $\rho_{1,2}(k)$ for total particle density $n = 0.7$ where the Debye parameter is $k_D \approx 2.97$. Using the dielectric response function $\chi(k)$ evaluated using $h_{ij}(r)$ from MSA theory, the first four decay parameters are found to be $k_{1,2} = 3.319 \pm 3.643i$ and $k_{3,4} = 6.085 \pm 14.914i$. Using the PY theory, it is found that $Q_{1,2}^{hs} = -0.488, -0.237$ and $\psi_{1,2}^{hs} = -0.726, -0.531$.

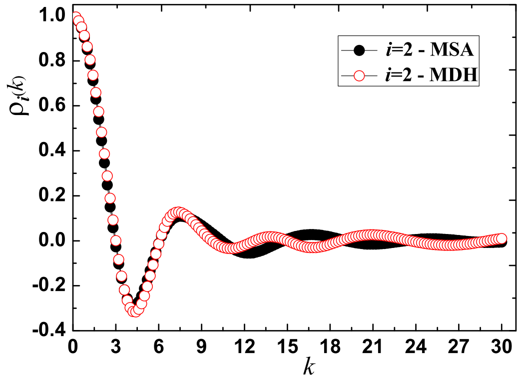
Given the two charge densities $\rho_{1,2}(k)$ from MSA, we evaluate the coefficients of solvent species $i = 1$, 2 according to the MDH theory. It is found that $C_{1,2}^{a} = 0.435 \pm 0.238i$, $C_{3,4}^{a} = 0.065 \mp 0.170i$ and $C_{1,2}^{s} = 0.415 \pm 0.834i$, $C_{3,4}^{s} = 0.085 \mp 0.231i$. These parameters lead to $\beta u_{1,2}^{ex} = -0.642, -0.461$ and $\beta\mu_{1,2}^{ele} = -0.813, -0.308$. The MSA theory gives $\beta u_{1,2}^{ex} = -0.644, -0.464$ and $\beta\mu_{1,2}^{ele} = -0.815, -0.308$, which are almost indistinguishable from our MDH results, namely, the difference between the MDH theory and the MSA results is no more than 1 percent.

Furthermore, the microscopic structures of the electrolyte solutions can also be evaluated using the MDH theory. As long as $\{k_n\}$ and $\{C_n^{a,s}\}$ are determined, $\rho_{1,2}(k)$ can be evaluated using Eq. (11). The calculated charge density profile $\rho_{1,2}(k)$ is shown in Fig. 1. As one can see, the MDH theory does lead to charge density profiles that are in good agreement with the ones from the MSA theory and hence confirm our fitting strategy for $\{C_n^{a,s}\}$.

The excess internal energies βu_i^{ex} and excess electrostatic chemical potentials $\beta\mu_i^{ele}$ as a function of the Debye parameter k_D are shown in Fig. 2. As one can see, MDH theory are in very good agreement with MSA theory, i.e., in the range of $0.159 < k_D < 3.54$, the relative difference between MDH theory and MSA is less than 4 percent for solvent species $i = 1$, 2. As a comparison, the results from conventional DH theory are also shown. DH is not reliable for electrolytes with strong electrostatic coupling, where the difference between DH theory and MSA can be as large as 41 percent and 18 percent for solvent species $i = 1$, 2 at $k_D \approx 3.54$. One should also note that MSA and MDH theories indicate that $\beta u_1^{ex} < \beta u_2^{ex}$ for large k_D, while DH predicts that $\beta u_1^{ex} > \beta u_2^{ex}$ and hence is qualitatively wrong.



(a) The induced charge density $\rho_i(k)$ for the cation $i = 1$

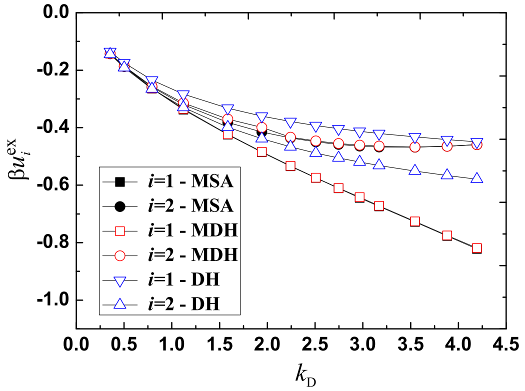


(b) The induced charge density $\rho_i(k)$ for the anion $i = 2$

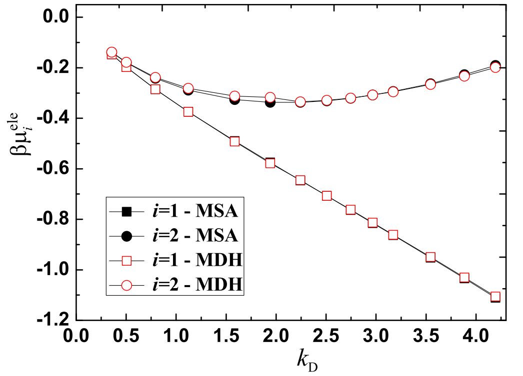
FIG. 1. Induced charge densities around the solvent species in the k-space. The results from MSA are denoted by filled symbol, while results from our MDH theory are denoted by hollow symbol. The lines are guides to the eyes.

B. Test against HNC theory of electrolyte solutions

In this section, we present the test of our theory against the HNC approximation, which is known to yield very accurate thermodynamic properties of primitive models.[33] HNC theory is used as an input to evaluate the response function $\chi(k)$ and the charge density $\rho_{i=1,2}(k)$, which is further used as an input to evaluate $\{k_n\}$ and $\{C_n^{a,s}\}$. The excess internal energies βu_j^{ex} from MDH theory are evaluated according to Eq. (14). The excess electrostatic chemical potential $\beta\mu_j^{ele}$ from HNC can be determined with two routes. The first route is to use Eq. (17). Denote $\beta\mu_j^{ex}$ and $\beta\mu_j^{hs}$ as the excess chemical potential of an ion and a neutral hard sphere with the same diameter. Then with $\beta\mu_j^{ex}$ and $\beta\mu_j^{hs}$ from HNC theory, the excess electrostatic chemical potential can be evaluated as $\beta\mu_j^{ele} = \beta\mu_j^{ex} - \beta\mu_j^{hs}$. The second route is to use the Kirkwood charging process as discussed in Secs. II D and II F. The induced potential $\psi_j(\xi q_j)$

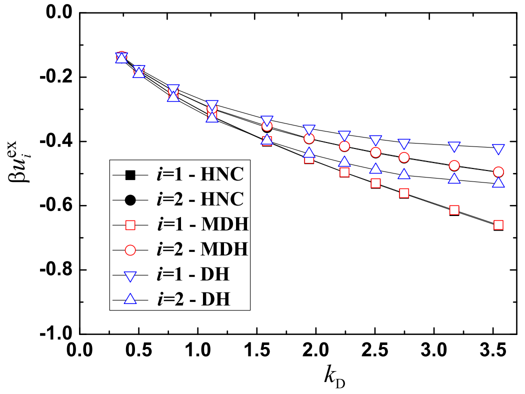


(a)Excess internal energies βu_i^{ex}

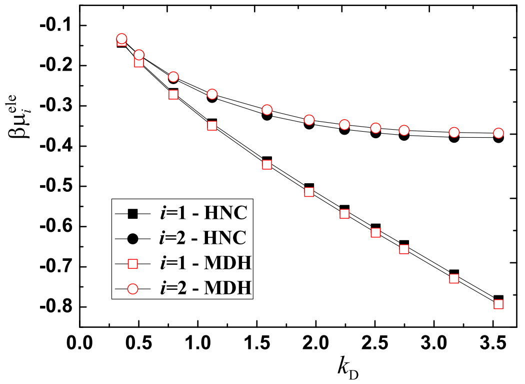


(b)Excess electrostatic chemical potentials $\beta\mu_i^{ele}$

FIG. 2. Excess thermodynamic properties of a binary size asymmetric electrolyte with $\sigma_{1,2} = 1, 0.5$. The results from MSA are denoted by filled symbol, while our MDH theory is denoted by hollow symbol. The lines are guides to the eyes.



(a)Excess internal energies βu_i^{ex}



(b)Excess electrostatic chemical potentials $\beta\mu_i^{ele}$

FIG. 3. Excess thermodynamic properties of a binary size asymmetric electrolyte with $\sigma_{1,2} = 1, 0.7$. The results from HNC are denoted by filled symbol, while our MDH theory is denoted by hollow symbol. The lines are guides to the eyes.

for a partially charged ion with charge ξq_j can be determined from HNC theory, which is further used to calculate $\beta\mu_j^{ele}$ according to the first part of Eq. (22). Our numerical calculation shows that the typical relative difference between these two routes is about 1 percent, so one can conclude that those two routes are in very good agreement with each other. In the following part of this subsection, $\beta\mu_j^{ele}$ from the first route will be used as our benchmark.

The parameters used for a binary electrolyte solvent are $q_s = 1$, $\epsilon_s = 1$, $\beta = 1$, and $\sigma_{1,2} = 1, 0.7$. We take the total particle number density n as the control parameter, with which the Debye parameter is evaluated as $k_D = \sqrt{\frac{4\pi\beta n q_s^2}{\epsilon_s}}$. The excess internal energies βu_i^{ex} and excess electrostatic chemical potential $\beta\mu_i^{ele}$ are shown in Fig. 3. Again, good agreement between our MDH theory and HNC theory is found. MDH theory differs by HNC up to 4 percent for solvent species $i = 1, 2$, while DH theory overestimate the excess internal energy by about 38 percent and 5 percent for solvent ions $i = 1, 2$ at $k_D = 3.54$.

C. Application to the solvation processes in electrolyte solutions

In Subsections III A and III B, we show that the MDH theory is very accurate in evaluating the thermodynamics of pure solvents. In this section, we show that the MDH theory can also be used to study the solvation problem. The central ion j is the solute. As presented in Section II, as long as we know $\{k_n\}$ and $\{C_{jn}^{a,s}\}$, we will be able to evaluate the electrostatic contribution to the excess chemical potential. In general, one can expect that $\{C_{jn}^{a,s}\}$ depends both on the solute size and the solute charge. We would like to show that $\{C_{jn}^{a,s}\}$ is not sensitive to the ion charge q_j, and hence $\{C_{jn}^{a,s}\}$ for a pair of test ions with $q_{3,4} = \pm 1$ can be used to predict the thermodynamics of other ions with the same size but different charges. We use $\rho_{3,4}(k)$ for a pair of test ions with $q_{j=3,4} = \pm 1$ as an input to get $\{C_{3n}\}$ and $\{C_{4n}\}$, which can be further used to determine $\{C_{jn}^{a,s}\}$, i.e.,

$$\begin{aligned}(q_3 + q_3^{hs})C_{3n} &= q_3 C_{jn}^{a} + q_3^{hs} C_{jn}^{s},\\ (q_4 + q_4^{hs})C_{4n} &= q_4 C_{jn}^{a} + q_4^{hs} C_{jn}^{s}.\end{aligned} \tag{26}$$

Then the sets of $\{C_{jn}^{a,s}\}$ are used to evaluate the excess chemical potentials $\beta\mu_j^{ele}$ of ions with the same size but different charges according to Eq. (22).

Consider the solvation of a pair of dilute conjugate ions $j = 3, 4$ that immersed in a binary primitive electrolyte. The parameters of the pure solvent are $\beta = 1, \epsilon_s = 1, q_{1,2} = \pm 1, \sigma_{1,2} = 1, 0.7, n = 1.0$. The ion diameter is $\sigma_{3,4} = \sigma_o$ and the ion charge is $q_{3,4} = \pm q_o$. In this case, the electrolyte is in the high electrostatic coupling case, where $k_D \simeq 3.54$. The dielectric response function $\chi(k)$ from HNC is fitted to the empirical function, from which the first four decay parameters are $k_{1,2} = 2.573 \pm 3.493i$ and $k_{3,4} = 6.703 \pm 16.333i$. The hard sphere correlation function $h_{ij}^{hs}(k)$ is evaluated with the

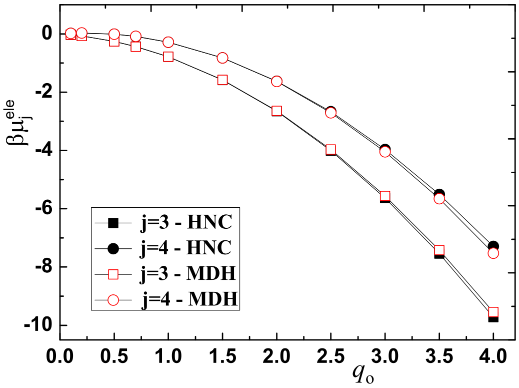


FIG. 4. Excess electrostatic chemical potentials $\beta\mu_j^{ele}$ for the solute $j = 3, 4$ as a function of the solute charge q_o, where the solute size is $\sigma_o = 1$. The results from HNC are denoted by filled symbol, while our MDH theory is denoted by hollow symbol. The lines are guides to the eyes.

PY theory, which is used to evaluate the two parameters Q_j^{hs} and ψ_j^{hs}.

As the first case, the central ion size is fixed to be $\sigma_o = 1$. The MDH theory is applied to a pair of test ions with $q_o = 1$, where the linear coefficients are found to be $C^a_{j1,2} = 0.270 \mp 0.293i$, $C^a_{j3,4} = 0.230 \pm 0.038i$, $C^s_{j1,2} = 0.659 \pm 0.027i$, and $C^s_{j3,4} = -0.159 \mp 0.321i$. Excess chemical potential $\beta\mu_j^{ele}$ as a function of the ion charge q_o is shown in Fig. 4. As one can see, the accuracy of MDH theory decreases a little bit as the ion charge q_o increases, which implies that nonlinear response could play a role for ions with high charges. Nevertheless, the MDH theory still leads to very accurate solvation energies, e.g., the relative excess chemical potential difference between MDH theory and HNC theory is no more than 5 percent even for $q_o = 4$.

As the second test case, the central ion size is fixed to be $\sigma_o = 3$. When applied to a pair of test ions with $q_o = 1$, the MDH theory leads to parameters as $C^a_{j1,2} = 0.231 \mp 0.281i$, $C^a_{j3,4} = 0.269 \mp 0.008i$, $C^s_{j1,2} = 0.602 \mp 0.354i$, and $C^s_{j3,4} = -0.102 \mp 0.195i$. For fixed ion size $\sigma_o = 3$, excess chemical potential $\beta\mu_j^{ele}$ as a function of the ion charge q_o is shown in Fig. 5. Again very good agreement between the MDH theory and the HNC theory is found, i.e., the energy difference between MDH theory and HNC theory is less than 3 percent in the range of $0 < q_o < 4$.

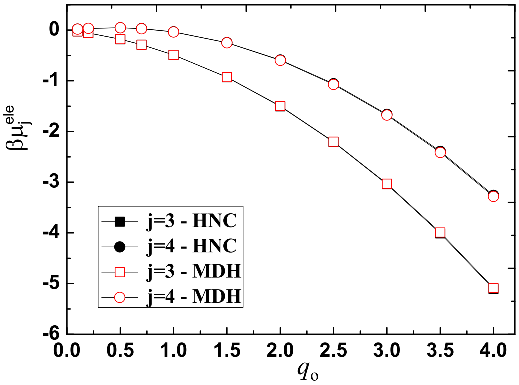


FIG. 5. Excess electrostatic chemical potentials $\beta\mu_j^{ele}$ for the solute $j = 3, 4$ as a function of the solute charge q_o, where the solute size is $\sigma_o = 3$. The results from HNC are denoted by filled symbol, while our MDH theory is denoted by hollow symbol. The lines are guides to the eyes.

We have also test our MDH theory for binary electrolytes with different parameters. As long as the reduced temperature β and size ratio σ_1/σ_2 are not too large, MDH theory leads to very satisfactory results compared with the HNC theory and the results are not shown here.

IV. CONCLUDING REMARKS

In conclusion, a molecular Debye-Hückel theory for electrolytes with size asymmetry is developed, where the dielectric response of an electrolyte solution is described by a linear combination of Debye-Hückel-like response modes with decay parameters $\{k_n\}$. As the size asymmetry of electrolytes leads to a charge imbalanced border zone around a central ion, an ion j is characterized by two types of charge sources, i.e., a bare solute charge q_j and a hard sphere contribution to the induced charge density $\rho_j^{hs}(k)$. These two kinds of charge sources are screened by the surrounding ions differently, from which the multi-Yukawa electric potential as well as the electrostatic contributions to thermodynamic properties are obtained. Therefore, our model could discriminate the solvation energy of an ion with positive or negative charges and is successfully applied to binary as well as multi-component primitive models of electrolyte solutions.

ACKNOWLEDGMENTS

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APPENDIX: THERMODYNAMIC PROPERTIES OF A PRIMITIVE ELECTROLYTE MODEL FROM THE MEAN SPHERICAL APPROXIMATION

For the convenience of the readers, we summarize some of the key results from the mean spherical approximation (MSA) of a primitive electrolyte model,[33,42] which are closely related to the MDH approach presented in our report.

Consider a primitive model of electrolyte solutions. For species i, σ_i, q_i, and n_i are the hard sphere diameter, the point charge, and the particle number density, respectively. The dielectric constant of the background is ϵ_s. The total particle number density is $n = \sum_i n_i$, and the mole fraction of the i-th species is $x_i = n_i/n$. T is the temperature, k_B is the Boltzmann constant. Then the reduced temperature is $\beta = \frac{1}{k_B T}$, the Debye parameter is $k_D = \sqrt{\frac{4\pi\beta\sum_i n_i q_i^2}{\epsilon_s}}$.

The main feature of MSA theory is that the thermodynamic properties of an electrolyte can be expressed as a function of an energy parameter Γ. The parameter Γ can be determined numerically by solving the following equation:[33]

$$4\Gamma^2 = k_D^2 \sum_i n_i (q_i - \frac{\pi\sigma_i^2 P_n}{2\Delta})^2 / [(1+\sigma_i\Gamma)^2 \sum_k n_k q_k^2], \quad \text{(A1)}$$

where the functions are defined as

$$\begin{aligned} \Delta &= 1 - \frac{\pi}{6}\sum_k n_k \sigma_k^3, \\ \Omega &= 1 + \frac{\pi}{2\Delta}\sum_k \frac{n_k\sigma_k^3}{1+\sigma_k\Gamma}, \\ P_n &= \frac{1}{\Omega}\sum_k \frac{\sigma_k n_k q_k}{1+\sigma_k\Gamma}. \end{aligned} \quad \text{(A2)}$$

The excess internal energy per particle from MSA is[33]

$$\beta u_i^{ex} = \frac{q_i B_i}{\epsilon_s} = \frac{q_i}{\epsilon_s}(-\frac{q_i\Gamma}{1+\sigma_i\Gamma} + B_i^0). \quad \text{(A3)}$$

where the parameters are defined as

$$\begin{aligned} \chi_2 &= \sum_k \rho_k q_k \sigma_k^2, \\ N_i &= -\frac{q_i\Gamma}{1+\sigma_i\Gamma} - \frac{\pi P_n}{2\Delta}\frac{\sigma_i\Gamma}{1+\sigma_i\Gamma}, \\ \Lambda &= \Delta\sum_k n_k\sigma_k^3 N_k - \frac{\pi\chi_2}{4}\sum_k n_k\sigma_k^3, \\ B_i &= N_i - \frac{\pi}{4\Delta}(\chi_2 + \frac{2}{3}\Lambda), \\ B_i^0 &= lim_{q_i\to 0} B_i = -\frac{\pi P_n}{2\Delta}\frac{\sigma_i\Gamma}{1+\sigma_i\Gamma} - \frac{\pi}{4\Delta}(\chi_2 + \frac{2}{3}\Lambda). \end{aligned} \quad \text{(A4)}$$

The induced electric potential $\psi_i \equiv \lim_{r\to 0}[\Phi_i(r) - \frac{q_i}{\epsilon_s r}]$ for the ion i can be evaluated with B_i as[33]

$$\psi_i = \frac{2B_i}{\epsilon_s} = -\frac{2q_i}{\epsilon_s}\frac{\Gamma}{1+\sigma_i\Gamma} + \frac{2B_i^0}{\epsilon_s}. \quad \text{(A5)}$$

For a neutral solute with $q_i = 0$, the induced potential $\frac{2B_i^0}{\epsilon_s}$ is nonzero, which is due to the size asymmetry of the charged solvent particles. Such a property measures the charge density $\rho_j^{hs}(r)$ purely due to the size asymmetry of the electrolyte ions and is coincided with our Eq. (8) presented in Sec. II. The excess internal energy of the system is[33]

$$\beta U^{ex} = \sum_i n_i \beta u_i^{ex} = -\frac{\beta}{\epsilon_s}(\sum_i \frac{q_i^2 n_i \Gamma}{1+\sigma_i\Gamma} + \frac{\pi\Omega P_n^2}{2\Delta}). \quad \text{(A6)}$$

The electrostatic contribution to the excess Helmholtz free energy βA^{ele} can be evaluated as[33]

$$\beta A^{ele} = \int_0^\beta U^{ex}(\beta) d\beta = \beta U^{ex} + \frac{\Gamma^3}{3\pi}. \quad \text{(A7)}$$

The electrostatic contribution to the excess osmotic coefficient ϕ is found to be[33]

$$\phi = n\frac{\partial(\beta A^{ele}/n)}{\partial n}|_{\Gamma=\text{const}} = -\frac{\Gamma^3}{3\pi n} - \frac{1}{8n}(\frac{\alpha P_n}{\Delta})^2, \quad \text{(A8)}$$

with $\alpha^2 = \frac{4\pi\beta}{\epsilon_s}$, and then the mean activity coefficients $\ln\gamma_m$ can be evaluated as[33]

$$\ln\gamma_m = \frac{\beta A^{ele}}{n} + \phi = \frac{\beta U^{ex}}{n} - \frac{1}{8n}(\frac{\alpha P_n}{\Delta})^2. \quad \text{(A9)}$$

The excess chemical potential can evaluated from two routes. For the first route, one can evaluate the excess chemical potential based on $\beta\mu_j^{ex} = \frac{\partial\beta A^{ex}}{\partial n_i}$, where the result is found to be[42]

$$\begin{aligned} \beta\mu_i^{ele} &= \frac{\partial\beta A^{ele}}{\partial n_i}|_{\Gamma=\text{const}} = \frac{\beta q_i}{\epsilon_s}[-\frac{q_i\Gamma}{1+\sigma_i\Gamma} \\ &\quad + 2B_i^0 + (\frac{\pi P_n}{2\Delta})^2(\frac{\sigma_i^3}{3} - \frac{\sigma_i^3}{1+\Gamma\sigma_i})]. \end{aligned} \quad \text{(A10)}$$

For the second route, one can use the Kirkwood charging process as shown in Sec. II to evaluate the excess chemical potential as

$$\begin{aligned} \beta\mu_i^{ele} &= \beta n\sum_i x_i \int_0^1 d\xi \int d\mathbf{r}\, u_{ij}^{ele}(r) g_{ij}(r;\xi) \\ &= \beta\int_0^1 d\xi q_j \psi_j(\xi q_j) = \frac{\beta q_i}{\epsilon_s}(-\frac{q_i\Gamma}{1+\sigma_i\Gamma} + 2B_i^0). \end{aligned} \quad \text{(A11)}$$

One may note that Eqs. (A10) and (A11) differ by a term of $\frac{\beta q_i}{\epsilon_s}(\frac{\pi P_n}{2\Delta})^2(\frac{\sigma_i^3}{3} - \frac{\sigma_i^3}{1+\Gamma\sigma_i})$, which is due to the thermodynamic inconsistency of the MSA theory, but the presence of the $2B_i^0$ term reflects the size asymmetry effect in both routes which motivates our two types of charges response strategy developed in Sec. II. On the other hand, numerical results indicate that the results of Eqs. (A10) and (A11) are in good agreement with each other, where the typical relative difference is about one percent.

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