The Long Scale Properties of Dense Electrolytes

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In this work, we combine phenomenological, numerical, and analytical approaches to explore the long scale statistical properties of dense electrolytes. In the first part, we present a phenomenological framework. We show that the potential of mean force (PMF) for an ion with charge $q$ inside a weak background of mean potential $\phi$ is nonlinear in $q$, and linear but nonlocal in $\phi$. From this, we derive all the long scale properties of the system, including the linear response theory of mean potential, the effective interaction between two ions, and the large scale structures of electric double layers, as well as the renormalized charge of a neutral particle. We also discuss the connection and difference between our theory and the Dressed Ion Theory developed by Kjellander and Mitchell in 1990’s. In the second part, we discuss the numerical method that is used to extract various renormalized quantities from Monte Carlo simulation data, as well as some numerical results that demonstrate the internal consistency of our theory. In the third part, we develop a systematic analytic formalism for the PMF of an ion in a weak background potential. We apply this formalism to study the primitive model, and calculate all renormalized parameters up to the second order of ion valences. These analytic results agree, both qualitatively and quantitatively, with our large scale MC simulations.

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I. INTRODUCTION

The properties of dense electrolytes remain an outstanding challenge in statistical physics [1,2]. The “standard model” for electrolytes is the so-called primitive model, where ions are modeled as point charges surrounded by hard spheres, whilst the solvent is treated as homogeneous and linear dielectric media. It is also assumed that the permittivity of solvent is identical to that of the ions, so image charge does not arise. From the experimental point of view, there is a serious issue whether this simple model captures all the important details of realistic electrolytes. For a review, see [3,5]. We shall however refrain from discussing this issue in the present work. From the theoretical point of view, correct accounting of ionic correlations in the primitive model is a challenging problem with fundamental importance. The techniques developed in field theory, which has been spectacularly successful in the study of critical phenomena, is not very useful for electrolytes, because of the difficulty in capturing the short scale structures of ions. Numerically, even though the primitive model is amenable for direct Monte Carlo studies, simulations are usually limited to rather small size, because of the intrinsic difficulties associated with the long range nature of Coulomb interaction.

In this work, we are primarily interested in the long scale properties of dense electrolytes, such as the far field structures of electric double layers (EDL in short, a quasi-two dimensional structure formed by a charged surface and the diffusive counter-ions and co-ions), the asymptotic form of effective interaction between two ions, the mean potential generated by a fixed ion, and more. We shall also avoid the other, complementary aspect of electrolyte physics, i.e. their thermodynamic properties [6,7]. Even though our formalism can be used to address the other aspect as well, limitation of space enforces us to leave it to a separate publication.

The classical Poisson-Boltzmann theory (PB) [8] treats all ion as point charges, and ignores all correlations between them. It provides the simplest mean field description to the primitive model. As early as 1930’s, Onsager [9] pointed out an internal inconsistency of nonlinear PB when applied to asymmetric electrolytes: it predicts an effective interaction between two ions that is asymmetric in two charges $q_1, q_2$. There is a general consensus that PB describes correctly the long scale structure of EDLs in sufficiently dilute electrolytes, but fails whenever the ion density becomes high. Many efforts have been attempted in the past decades to go beyond PB, but it turns out to be surprisingly difficult to capture simultaneously both ionic correlations and steric effects of hard spheres.

An alternative approach that is intermediate between PB and the primitive model is the integral equation method, which was proven very successful for neutral liquids. Though often giving quantitatively precise predictions, this method usually requires approximations, i.e. closure relations, whose physical meanings are often unclear. It is therefore usually not an ideal tool for elucidating conceptual questions, such as the structure of effective theory at long scales. There is one important exception, however. In a remarkable sequence of works, Kjellander and Mitchell [10,13] used the Ornstein-Zernike in-
tegral equation and analyzed the far field asymptotics of pair correlation functions of electrolytes without usage of any closure relation. Through some long and tortuous arguments, these authors show that the long scale properties of a dense electrolyte is still described by a theory that is similar to the linearized PB, but with ion valences, dielectric constant, and Debye length all renormalized. These results are summarized by an appealing physical picture: the part of charge distribution around a fixed ion that is beyond the description of linearized PB can be combined with the source charge to yield a quasiparticle, which is called a “dressed ion” by Kjellander and Mitchell, hence the term “Dressed Ion Theory” (DIT). More recently this method has been generalized by Guerrero-Garcia, González-Mozuelos and Olvera de la Cruz [14–17] to compute the effective interaction between charged colloids. We note that from the perspective of renormalization group theory, the emergence of an effective linear theory at long scale is not only natural but also inevitable, as long as the system is away from criticality.

In the setting of electrolyte physics, the concept of charge renormalization was first addressed by Alexander et. al. [18] in 1984, in an attempt to understand the far field asymptotics of effective interaction between charged colloids. The short scale details near the colloidal surfaces, such as nonlinearity and counter-ion condensation, are all wrapped into renormalization of colloidal charge. This method has been extensively used in colloidal physics, for a (not so recent) review, see [19, 20]. The bulk electrolytes are however always treated at the level of PB theory. Even earlier, there are works by Stell and Lebowitz [21], and by Mitchell and Ninham [22, 23], which calculated the correction to Debye length due to hard core and ionic correlations. It was however Kjellander and Mitchell who discovered the general form of the linear response theory of dense electrolytes.

The formalism of Kjellander and Mitchell is rather involved and difficult to follow (at least for us). Given the conceptual and practical importance of the topic, it is much worthy to re-derive their results using a more intuitive and accessible approach. What is even more important is, however, to construct a systematic analytic approach that allows controllable approximation of all renormalized quantities. For this purpose, one needs a suitable perturbation theory. Furthermore, to probe the dense regime, one must go beyond perturbation scheme. Finally, to test the validity of analytic theory, and to compute the renormalized quantities at high precision in an arbitrary density, large scale simulations using Monte Carlo (MC) or Molecular Dynamics (MD) are indispensable. We shall address all these issues in this work.

In the first part of this work (Sec. [1]), we develop a phenomenological formalism for the universal long scale physics of dense electrolytes. A key object is the potential of mean force (PMF) \( U(x, q; \phi) \) of a generic ion with variable charge \( q \) in a background of mean potential \( \phi \). The classical PB hinges on a simple (but incorrect) approximation that \( U(x, q; \phi) \) is the product of \( q \) and \( \phi(x) \). We shall replace it with a form that is nonlocal in \( \phi \) and nonlinear in \( q \), and show that it is asymptotically exact in the weak potential limit. From this PMF, we derive all long scale properties of dense electrolytes.

In the second part of this work (Sec. [III]), we present results of very large scale Monte Carlo (MC) simulation of dense electrolyte systems. Using both powerful graphic processing units (GPU) and efficient Oct-tree code algorithm [24], we simulate as many as a million ions and obtain all pair correlation functions of electrolytes up to high precision. From these data we directly compute all renormalized parameters, and verify the internal consistency of our phenomenological theory.

Finally, in the last part (Sec. [IV]), we first develop a systematic perturbation scheme for the PMF \( U(x, q; \phi) \), in terms of the charge \( q \). By identifying the source ion with one of the constituent ions and using the exact relation between \( U(x, q; \phi) \) and the renormalized valences, we self-consistently determine the PMF. We apply this scheme to study the primitive model, and calculate \( U(x, q; \phi) \) up to the order of \( q^2 \). For symmetric electrolyte, we find that steric effects of hard sphere ions induce substantial deviation from the classical PB in the dense regime, where Debye length is comparable with ion size. For asymmetric electrolytes, there are new effects due to loss of charge inversion symmetry and long range electrostatic correlations between ions. For both cases, we find nontrivial renormalization of ion valences, Debye length, and dielectric constant, as well as charge oscillation in the dense regime. The agreement between these analytic results and our numerical simulation is both qualitative and quantitative.

Combining all these results, we firmly establish the effective theory for the long scale properties of dense electrolytes. This theory shall be the foundation for future studies of the thermodynamic properties of these systems, and also of more complicated Coulomb many body systems where charged surfaces and interfaces are externally introduced.

II. PHENOMENOLOGICAL THEORY

Let us start with a brief recapitulation of the classical PB. Let an electrolyte consists of two species of ions, with bare charges \( q_+ = +e > 0 \), \( q_- = -n e < 0 \), and average number densities \( \rho_+ \), \( \rho_- \), respectively. Here \( m, n \) are the (bare) valences of positive and negative ions, and \( e \) is the fundamental unit of electric charge. Generalization to more complicated mixtures is immediate and does not bring qualitatively different physics. The system is overall neutral so we have:

\[
\rho_+ q_+ + \rho_- q_- = (m \rho_+ - n \rho_-) e = 0. \tag{1}
\]

Let there be a background of mean potential \( \phi(r) \), which vanishes in the bulk. We bring an ion with charge \( q \) to \( r \) from infinity far away, at the cost of a free energy penalty \( U(r, q; \phi) \). This free energy is called the potential
of mean force (PMF) of the test ion \( q \). By definition, then, \( U(r, q; \phi) \) vanishes as \( r \to \infty \). 

The local average number densities of constituent ions \( q_{\pm} \) are related to their PMFs via \( \phi \):

\[
\rho_{\pm}(r) = \rho_{\pm} e^{-\beta U_{\pm}(r)} = \rho_{\pm} e^{-\beta U(q_{\pm})}.
\]

(2)

The local average charge density \( \rho_q(r) \) at \( r \) is then

\[
\rho_q(r) = q_+ \rho_+ e^{-\beta U_+(r)} + q_- \rho_- e^{-\beta U_-(r)} + \rho_{q}^{ex}(r),
\]

(3)

where the last term \( \rho_{q}^{ex}(r) \) is the externally fixed charge density, i.e. charges other than the mobile ions. The local potential \( \phi(r) \) satisfies the exact Poisson Equation:

\[
- \epsilon \nabla^2 \phi(r) = \rho_q(r).
\]

(4)

The total potential of an ion on a single approximation:

\[
U(r, q; \phi) = q \phi(r).
\]

(5)

Substituting this back to Eqs. (3) and (4), we obtain the nonlinear Poisson-Boltzmann Equation (NLPBE):

\[
- \epsilon \nabla^2 \phi(r) = q_+ \rho_+ e^{-\beta q_+ \phi(r)} + q_- \rho_- e^{-\beta q_- \phi(r)} + \rho_{q}^{ex}(r).
\]

(6)

In the far field, \( \phi(r) \) is small, and Eq. (6) can be linearized. Using Eq. (1) we find the linearized PBE:

\[
- \nabla^2 \phi(r) + \kappa_0^2 \phi(r) = 0,
\]

(7)

The mean potential \( \phi(r) \) decays exponentially, with a characteristic length scale \( \ell_D^0 = 1/\kappa_0 \), defined as

\[
\kappa_0 = 1/\ell_D^0 = \sqrt{\beta (\rho_+ q_+^2 + \rho_- q_-^2) / \epsilon}.
\]

(8)

Eqs. (1) and (8) are the essential ingredients of the classical Poisson-Boltzmann Theory.

### A. Onsager’s Paradox

Consider now two test ions \( q_1, q_2 \), fixed at \( r_1, r_2 \) respectively, such that their distance is large comparing with the Debye length, and assume that there is no other fixed charges. The two-ions potential of mean force (PMF), i.e. the effective interaction between them, can be calculated in two ways. We can treat \( q_2 \) as a source charge that generates a mean potential \( \phi_2(r) \) in the absence of \( q_1 \). This potential acts on \( q_1 \) when the latter is brought to \( r_1 \) from the bulk. We can also swap the roles played by \( q_1 \) and \( q_2 \). According to the basic assumption of PB, the two-ions PMF can be written into two possible forms:

\[
U(1, 2) = q_1 \phi_2(r_1), \quad \text{or} \quad q_2 \phi_1(r_2). \quad (9)
\]

Consequently two forms of \( U_{12} \) in Eq. (9) would be consistent with each other, as it should be.

However, if the nonlinear PBE Eq. (6) is solved properly, we would find that the screened Coulomb potentials in Eq. (10) are applicable only in the far field, but not in the near field. Even in the far field, the coefficients would be different from \( q_2 \) and \( q_1 \). Consequently the two representations in Eq. (9) would become inequivalent with each other, since generically \( q_1 \phi_2(r_1) \neq q_2 \phi_1(r_2) \). Based on this reasoning, Onsager [9] concluded that nonlinear PB is self-inconsistent when applied to asymmetric electrolytes. However, since the ions \( q_1, q_2 \) need not to be the constituent ions of the electrolyte, the same argument also casts doubt on the consistency of nonlinear PB in symmetric electrolytes.

### B. Linear Response Theory of Dense Electrolytes

It is a very common misunderstanding that linearized PBE (7) should always be applicable in the far field, where \( \phi \) is sufficiently small. Simulations however have constantly shown that the Debye length predicted by PB, Eq. (8) is incorrect in the dense regime, and the discrepancy increases with density. In sufficiently high density, electrolytes exhibit charge oscillation, where the mean potential decays in an oscillatory manner.

As Eq. (5) is the only approximation underlying PB, it must be responsible for the failure. In fact, Eq. (5) would be valid if the test ion is infinitesimal and point-like, so that its insertion does not influence the distribution of mobile ions, as one have learned in elementary electromagnetism. In reality, however, ions have finite charges and sizes, so they always influence the distribution of mobile ions. As a consequence, the interaction between a test ion and a mean potential \( \phi \) is usually nonlinear in \( q \), and nonlocal in \( \phi(r) \). In the far field, where \( \phi \) is sufficiently weak, we can ignore the nonlinear effects of \( \phi \) and express \( U(x, q; \phi) \) as

\[
U(x, q; \phi) = \int K(x - y, q) \phi(y) dy + O(\phi^2). \quad (11)
\]

The form of convolution is demanded by translational symmetry. It is only for the case of infinitesimal point charge \( dq \) that the kernel \( K(x - y, q) \) reduces to \( dq \delta(x) \), and hence Eq. (11) reduces to Eq. (5).

Substituting Eq. (11) into Eqs. (3) and (4), leads to a non-local generalization of NLPBE (6):

\[
- \epsilon \nabla^2 \phi(r) = \sum \alpha q_{\alpha} \rho_{\alpha} e^{-\beta K_{\alpha} \phi(r)} + \rho_{q}^{ex}(r), \quad (12)
\]

where \( K_{\alpha} = K(r, q_{\alpha}) \), and \( * \) means convolution. This equation is an improvement over NLPBE (6), and includes the latter as a special case. It shall be the starting point of our analyses in Sec. [IV], and shall be referred to as the renormalized nonlinear Poisson-Boltzmann equation (RNLPBE).
In this section, we shall only be concerned with the far field asymptotics of Eq. (12). Expanding the RHS to the first order of \( \phi \), Eq. (12) can be rewritten into the following linear integro-differential equation:

\[
- \Delta \phi(r) = - \int dr' \alpha(r-r') \phi(r') + \epsilon^{-1} \rho_q^{ex}(r) \tag{13}
\]

where the kernel \( \alpha(r) \), defined as

\[
\alpha(r) = \epsilon^{-1} \beta \sum_{\alpha} \rho_{\alpha} q_{\alpha} K_{\alpha}(r, q_{\alpha})
\]

\[
= \epsilon^{-1} \beta \left[ \rho_+ q_+ K(r, q_+) + \rho_- q_- K(r, q_-) \right] \tag{14}
\]

completely characterizes the linear (but nonlocal) response properties of electrolytes.

Let \( \phi^{ex}(r) \) be the potential due to \( \rho^{ex}_q(r) \) only:

\[
\phi^{ex}(r) = - \epsilon^{-1} \Delta^{-1} \rho^{ex}_q(r)
\]

\[
= - \int dr' \frac{1}{4\pi \epsilon |r-r'|} \rho^{ex}_q(r') \tag{15}
\]

Applying the inverse Laplacian on Eq. (13), and using Eq. (15) to express \( \rho^{ex}_q(r) \) in terms of \( \phi^{ex}(r) \), we find

\[
\phi^{ex}(r) = \int dr' \varepsilon(r-r') \phi(r'), \tag{16}
\]

where \( \varepsilon(r) \) is a relative dielectric function given by:

\[
\varepsilon(r) = 1 - \int dr' \frac{1}{4\pi |r-r'|} \alpha(r'). \tag{17a}
\]

As defined in Eq. (16), \( \varepsilon(r) \) gives the linear and nonlocal relation between \( \phi^{ex}(r) \) and \( \phi(r') \). In Fourier space, it is

\[
\hat{\varepsilon}(k) = 1 + \frac{1}{k^2} \hat{\alpha}(k). \tag{17b}
\]

We will see in Sec. IV that as \( k \to 0 \), \( \hat{\alpha}(k) \) remains finite and nonzero, hence \( \hat{\varepsilon}(k) \to 0 \). This implies that charges are completely screened inside electrolytes, i.e., electrolytes behave effectively as a metal at long scales.

Let us now consider a special case where the external charge distribution is an infinitesimal point charge at the origin. Eq. (13) then reduces to

\[
- \Delta \phi(r) + \alpha \ast \phi(r) = \epsilon^{-1} dq \delta(r), \tag{18a}
\]

which is readily solved via Fourier transformation:

\[
\phi(r) = \frac{dq}{\epsilon} \int_k \frac{e^{ik \cdot r}}{k^2 + \alpha(k)}. \tag{18b}
\]

Using standard techniques of contour integral, one can show that for large \( r \), the integral in the RHS of Eq. (18b) is controlled by the zero of the denominator \( k^2 + \alpha(k) \) in the upper complex plane (with \( k = |k| \) treated as a complex variable) that is nearest to the real axis [27]. Call it \( i\kappa_R \), where \( \kappa_R \) is naturally defined the renormalized inverse Debye length. We have:

\[
\kappa_R^2 = \hat{\alpha}(i\kappa_R). \tag{19}
\]

The far field asymptotics of \( \phi(r) \) is then given by the usual screened Coulomb potential, but with both Debye length and dielectric constant renormalized:

\[
\phi(r) \sim \frac{dq}{4\pi \epsilon \kappa_R} e^{-\kappa_R r}. \tag{20}
\]

The constant \( \epsilon_R \) in Eq. (20) is given by

\[
\epsilon_R = \epsilon \left[ 1 + \frac{1}{2k} \hat{\alpha}'(k) \right]_{k=i\kappa_R}. \tag{21}
\]

Kyellander and Mitchell (KM) called \( \epsilon_R \) the renormalized dielectric constant. It is important to note however, that \( \epsilon_R \) is relevant only if \( \rho^{ex}_q(r) \) is a localized charge distribution. In general, the dielectric properties of an electrolyte is nonlocal and is characterized by the whole function \( \varepsilon(r-r') \), rather than two parameters \( \epsilon_R \) and \( \kappa_R \).

Historically, KM first derived the linear integro-differential equation (13) using Ornstein-Zernike equation (OZ), and related the kernel \( \alpha(r) \) to the “short range part” of all pair correlation functions. KM’s derivation is rather involved and (at least to us) hard to follow. This is in strong contrast to our derivation, which takes one single step of linearization from Eq. (12) to (13).

There are two far field approximations we have used in this subsection. In the first approximation, the mean potential must be weak enough so that Eq. (12) can be linearized. In the second approximation, \( |r| \) must be large enough so that the integral in Eq. (18b) is dominated by the pole \( k = i\kappa_R \). Clearly, we can talk about the second approximation only if the first one is already justified. In general, there exists an intermediate regime of length scales where linearization is valid but the mean potential around an ion deviate from screened Coulomb Eq. (20). This point has to be kept in mind very carefully.

C. Resolution of Onsager’s Paradox

Let us go back to Eqs. (18), which describe the mean potential by an infinitesimal point charge. Now consider inserting an ion with charge \( q \) at the point \( \mathbf{x} \). According to Eq. (11), its effective interaction with the point charge \( dq \) is given by

\[
U(\mathbf{x}, dq, q) = K \ast \phi(\mathbf{x}) = \frac{dq}{\epsilon} \int_k \tilde{K}(k, q) e^{ik \cdot \mathbf{x}}. \tag{22}
\]

where in the second equality, we have used Eq. (18b) and have carried out the integral over \( r \).

On the other hand, the interaction Eq. (22) can be understood in a different way: we first insert the ion \( q \) at \( \mathbf{x} \), which generates a mean potential \( \phi(\mathbf{y} - \mathbf{x}, q) \) at
interaction between these two ions: Monte Carlo simulation to a remarkable precision. Comparing these two expressions, we easily obtain the potential at \( \mathbf{y} \) due to an ion with charge \( q \) at \( \mathbf{x} \):

\[
\phi(\mathbf{y} - \mathbf{x}, q) = \frac{1}{\epsilon} \int_k \frac{\dot{K}(k, q)}{k^2 + \alpha(k)} e^{ik(\mathbf{y} - \mathbf{x})}.
\]

Eq. \( (25) \) should be understood as far field asymptotics. More importantly, we emphasize that Eq. \( (25) \) is manifestly symmetric in two charges \( q_1, q_2 \), and hence Onsager’s paradox is already resolved. If the distance \( |\mathbf{x} - \mathbf{y}| \) is sufficiently large, so that the integrals over wave vector in Eqs. \( (24) \) and \( (25) \) are dominated by the pole \( k = i\kappa_R \) [28], these results reduce to

\[
\phi(r, q) = \frac{q_R(q)}{4\pi\epsilon_R r} e^{-\kappa_R r},
\]

\[
U(\mathbf{x} - \mathbf{y}, q, q') = \frac{q_R(q)q_R(q')}{4\pi\epsilon_R |\mathbf{x} - \mathbf{y}|} e^{-\kappa_R |\mathbf{x} - \mathbf{y}|},
\]

where \( q_R(q) \) is called the renormalized charge of an ion with bare charge \( q \), and is defined as

\[
q_R(q) = \dot{K}(i\kappa_R, q).
\]

Let us introduce the shorthand notations

\[
q_{R}^{\pm} = q_R(q^{\pm}) = \dot{K}(i\kappa_R, q^{\pm})
\]

for the renormalized charges of the constituent positive and negative ions. We combine these with Eqs. \( (19) \) and \( (14) \), and obtain an exact relation between \( \kappa_R \) and \( q_{R}^{\pm} \):

\[
\kappa_R^2 = \left( \frac{1}{\ell_{DB}^2} \right)^2 = e^{-1} \beta \left[ \rho_+ q_+ q_R^{+} + \rho_- q_- q_R^{-} \right].
\]

Dividing Eq. \( (30) \) by Eq. \( (8) \), we further obtain

\[
\frac{\kappa_R}{\kappa_0} = \frac{q_R^{+} - q_R^{-}}{q_+ - q_-}.
\]

As illustrated in Fig. \( 1(a) \), this is verified by our direct Monte Carlo simulation to a remarkable precision. Method that we use to extract \( q_R \) and \( \kappa_R \) from MC simulation data is discussed in Sec. \( \text{III} \)

D. Far Field Structures of EDLs

As is well-known, the statistical physics of strongly charged EDLs is very complicated in the near field. This is because the counter-ion density is very high near the surface, and the ionic correlations (together with other possible short range non-electrostatic details) impose serious difficulties. The large scale structure of EDLs, however, is markedly simpler, because it can be completely characterized by the kernel \( \alpha(r) \).

The far field asymptotics of the mean potential satisfies Eq. \( (13) \) with \( \rho_q^\infty(r) = 0 \). For a flat interface, and if the distance to charged surface is large enough so that the integral Eq. \( (18) \) is dominated by the pole \( k = i\kappa_R \), we have the following asymptotic form:

\[
\phi(z) = \frac{\sigma_R}{\epsilon_R \kappa_R} e^{-\kappa_R z}.
\]

where \( \sigma_R \) is the only parameter characterizes the long scale structures of an EDL, and can be defined as the renormalized surface charge density. \( \sigma_R \) and \( \sigma_0 \) may have different signs (charge inversion). In asymmetric electrolytes, generically \( \sigma_R \) is non-vanishing even if the surface is uncharged, e.g. \( \sigma_0 = 0 \). That is, a neutral surface behaves effectively as charged.

Substituting Eq. \( (32) \) into Eq. \( (11) \) and performing the integral (and using the residue theorem), we find the effective interaction between a charged surface and an ion \( q \) in the far field is given by

\[
U_{q\sigma} = \frac{\sigma_R \kappa_R}{\epsilon_R \kappa_R} e^{-\kappa_R z} = q_R(q)\phi(r).
\]

The effective interaction per unit area between two parallel charged surfaces can be shown to be

\[
U_{\sigma_1\sigma_2} = \frac{\sigma_R(1)\sigma_R(2)}{\epsilon_R \kappa_R} e^{-\kappa_R L}.
\]

This implies that two identical surfaces always repel each other in the far field. Of course, the possibility of attraction between identical surfaces at short distance cannot be excluded. Finally the number densities \( \rho_{\pm}(z) \) of the positive/negative ions in the far field of an EDL are:

\[
\rho_{\pm}(z) = \rho_{\pm} e^{-\beta U_{\sigma_{\pm}}} \approx \rho_{\pm} - \beta \rho_{\pm} q_{R}^{\pm} \sigma_R e^{-\kappa_R z}.
\]

If the electrolyte is sufficiently dense, \( q_{R}^{\pm} \) (and \( \kappa_R, \sigma_R \)) as well become complex. This is the charge oscillation regime \([29,32]\), where physical quantities decay in an oscillatory fashion. This regime has been known to exist in dense electrolytes since 1936 \([29]\), and is usually deemed as a signature of a complete failure of classical PB. Nevertheless, it can be naturally described using the theory described in this work.

E. Non-neutrality of Renormalized Charges

In general, both non-electrostatic interactions and ion correlations renormalize charges in a complicated way.
As a consequence, the renormalized charges of the constituent ions are generically different, even if their bare values are identical. Therefore we expect that all electrolytes behave asymmetrically in one way or another. As a simple but interesting example, let us discuss the renormalized charge of a neutral hard sphere inside an asymmetric electrolyte.

The sum of bare charge density must vanish in the bulk of any electrolyte, see the charge neutrality Eq. (1). For electrolytes consisting of more than two species of ions, the relevant condition is \( \sum_\alpha \rho_\alpha q^\alpha = 0 \), where a sums over all ion species. Now generically the renormalized version of this neutrality condition is not valid: \( \sum_\alpha \rho_\alpha \tilde{q}^\alpha \neq 0 \). The LHS has the dimension of charge density and shall be called the excess renormalized charge density.

To appreciate the physical significance of the excess renormalized charge density, we consider a weak mean field theory [33] establishes the relation between the osmotic pressure acting on the sphere and the ion density at the surface of contact. (A detailed discussion of this theorem is presented in Sec. IV B.) Assuming that the inserted sphere is sufficiently small, so that the ion distribution outside the sphere is not perturbed by the insertion of the sphere. (This will be proved explicitly in Sec. IV B.) The osmotic pressure is:

\[
\delta P(r) = \rho_{\text{tot}}(r) k_B T = - \sum_\alpha \rho_\alpha K_\alpha \phi(r).
\]

Integrating this over the volume, we obtain the PMF of the neutral hard sphere (due to electrostatic interaction).

Comparing the result with Eq. (11), we obtain the kernel \( K(r, q = 0) \) for a small neutral hard sphere:

\[
K(r, q = 0) = - v \sum_\alpha \rho_\alpha K(r, q_\alpha).
\]

Combining this with Eqs. (28) and (29), we finally find the renormalized charge of the neutral particle:

\[
q_R(0) = - v \sum_\alpha \rho_\alpha \tilde{q}_\alpha^R.
\]

Therefore the excess renormalized charge density can be understood as the renormalized charge of a small neutral hard sphere per unit volume. A more precise calculation of the renormalized charge of a neutral sphere inside an asymmetric electrolyte is given in Sec. IV B. Loosely speaking, the deficit of total renormalized charge is transferred to the solvent, which carries no bare charge.

III. DIRECT VERIFICATION OF THEORY USING MONTE CARLO SIMULATIONS

In this section, we test the validity of our phenomenological theory using pair correlation functions, obtained from large scale Monte Carlo (MC) simulations. We perform two different MC simulations 1) large scale simulation (containing 7,000 ions) using efficient Oct-tree code algorithm on CPU systems [24]; and 2) very large scale simulation (containing 10^6 ions) using GPU systems. As a consequence, sufficient data are generated within a few days that allow us to compute very precisely all pair correlation functions. Detailed description of our GPU simulation techniques will be reported in a separate publication. Here we shall discuss how to compute all renormalized parameters \( \kappa_R, \epsilon_R, q^R_\pm \) from tails of pair correlation functions.

Let us fix a positive ion \( q_+ \) at the origin in the bulk electrolyte. The densities of positive and negative ions \( \rho_{\pm}(r) \) are related to the pair correlation functions \( g_{\pm}(r) \) and two-ion PMFs \( U_{\pm}(r) \) via:

\[
\rho_{\pm}(r) = \rho_+ g_+(r) + \rho_- g_-(r) = \rho_{\pm} e^{-\beta U_{\pm}(r)},
\]

where \( \rho_{\pm} \) are the average ion densities in the bulk. The total charge density around the fixed ion \( q_+ \) is

\[
\rho_0^R(r) = \rho_+(r) q_+ + \rho_-(r) q_-.
\]

Using the above two equations, we can calculate \( U_{\pm}(r) \) and \( \rho_0^R(r) \) using \( g_{\pm}(r) \). Since \( U_{\pm}(r) \) and \( \rho_0^R(r) \) all decay in the form of screened Coulomb \( e^{-\kappa_R r}/r \) in the far field, we can use the tails of these functions to extract the renormalized inverse Debye length \( \kappa_R \).

The mean potential \( \phi_+(r) \) is related to \( \rho_0^R(r) \) via the exact Poisson equation:

\[
- \epsilon \nabla^2 \phi_+(r) = \rho_0^R(r).
\]

On the other hand, since in the far field \( \phi_+(r) \) is given by Eq. (26), it satisfies the linearized PBE:

\[
- \epsilon \nabla^2 \phi_+(r) = - \epsilon \kappa_R^2 \phi_+(r).
\]

Combining Eqs. (41) and (42) we find that \( \phi_+(r) \) can be expressed in terms of \( \rho_+(r) \) and \( \kappa_R \):

\[
\phi_+(r) = - \frac{\rho_0^R(r)}{\epsilon \kappa_R^2}.
\]

Also, using both Eq. (26) and Eq. (27) we have:

\[
U_{\pm}(r) = \frac{q_R^R}{\rho_0^R(r)} \phi_+(r).
\]

Combining Eqs. (43) and (44), we can express the renormalized charges \( q_\pm^R \) in terms of known quantities:

\[
q_\pm^R = - \epsilon \kappa_R^2 \frac{U_{\pm}(r)}{\rho_0^R(r)}.
\]
In fact we can carry out the steps Eqs. (41)-(45) for the other case where a negative ion $q_-$ is fixed at the origin. Combining, we find

$$q_+ = -\epsilon R \frac{U_{++}(r)}{\rho^+_{\kappa R}(r)} = -\epsilon R \frac{U_{++}(r)}{\rho^+_{\kappa R}(r)}, \quad (46a)$$
$$q_- = -\epsilon R \frac{U_{+-}(r)}{\rho^-_{\kappa R}(r)} = -\epsilon R \frac{U_{+-}(r)}{\rho^-_{\kappa R}(r)}. \quad (46b)$$

With $\kappa R, q_{R\pm}$ determined, we can extract the renormalized dielectric constant $\epsilon_R$ using Eqs. (26) and (43):

$$\phi_{\pm}(r) = \frac{q_{R\pm}}{4\pi \epsilon_R r} e^{-\kappa R r}, \quad \epsilon_R = \frac{q_{R+}^2}{4\pi \lambda^2 \phi_{\pm}(r)} e^{-\kappa R r}. \quad (47)$$

Note that Eqs. (42)-(47) are valid only as the far field asymptotics. Hence we have two independent ways to compute the renormalized charges and renormalized dielectric constant. As shown in Fig. 1, they give the same renormalized charges and renormalized dielectric constant within computational error. We can also use the computed $\kappa_R$ and $q_{R\pm}$ to test the validity of the relation Eq. (31). The results are displayed in Fig. 1(a). All these numerical tests show unambiguously the internal consistency of our theory.

**IV. ANALYTIC APPROACH**

In Sec. II, we have shown that the long scale properties of dense electrolytes are completely characterized by the kernel $K(r, q)$, defined in Eq. (11). In this section, we shall analytically calculate this kernel for a test ion with charge $q$, in the framework of the primitive model. The basic strategy is to calculate the PMF $U(r, q; \phi)$ up to the order of $q^2$, in terms of renormalized parameters, and then let $q = q_o$ and use Eqs. (14), (19), and (28) to determine $\alpha(r)$ and $K(r, q)$ self-consistently. Our method is similar in spirit to the variational Gaussian approximation [34], but is taylor-designed to tackle the physics of hard core repulsion.

From now on we shall use $\phi^{b,g}(r)$ to denote the mean potential in the absence of the test ion $q$, which is assumed to satisfy Eq. (12). The subscript “b.g.” refers to “background”. Assuming $\phi^{b,g}(r)$ is sufficiently weak, so that Eq. (12) can be linearized to yield Eq. (13). Furthermore, we shall only need to consider the case where both $\phi^{b,g}(r)$ and $\rho^{e,g}(r)$ are plane waves:

$$\phi^{b,g}(r) = \phi_0 e^{ik \cdot r}, \quad \rho^{e,g}(r) = \rho_0 e^{ik \cdot r}. \quad (48)$$

Via Eq. (13), we get a linear relation between $\phi_0$ and $\rho_0$:

$$\rho_0 = \epsilon \left( k^2 + \hat{\alpha}(k) \right) \phi_0. \quad (49)$$

Note that $\phi^{b,g}(r)$ is due to both the external charge distribution $\rho^{e,g}(r)$ and all mobile ions in the electrolyte. Substituting Eqs. (48) into Eq. (11), we find that $U(0, q; \phi^{b,g})$ is directly proportional to $K(r, q)$:

$$U(r, q; \phi^{b,g}) = \hat{K}(k, q) \phi_0 e^{ik \cdot r}. \quad (50)$$

Let $\psi(r, q)$ be the potential acting on an ion with charge $q$ inserted at $r$. The following relation between $\psi(r, q)$ and $U(r, q; \phi^{b,g})$ is well known [35]:

$$\frac{\partial U(r, q; \phi^{b,g})}{\partial q} = \psi(r, q) - \lim_{\phi^{b,g} \to 0} \psi(r, q) \equiv \delta \psi(r, q). \quad (51)$$
By definition, \( \delta \psi(r, q) \) is the part of \( \psi(r, q) \) that arises due to \( \phi^{b-s}_r \), and vanishes with \( \phi^{b-s}_r \). Integrating over the charge \( q \) once, we find:

\[
U(r, q; \phi^{b-s}_r) = \int_0^q dq \, \delta \psi(r, q) + U(r, 0; \phi^{b-s}_r). 
\]

(52)

where \( U(r, 0; \phi^{b-s}_r) \) is the PMF of a neutral particle. This is the famous Debye charging method. Our problem is therefore reduced to the calculation of \( U(r, 0; \phi^{b-s}_r) \) and \( \psi(r, q) \). Below we calculate \( \psi(r, q) \), and leave \( U(r, 0; \phi^{b-s}_r) \) for Sec. IV B.

Insertion of the test ion modifies the distributions of all mobile ions in two ways: 1) All ions are excluded from a sphere with radius \( d \), 2) Ions outside also redistribute in order to minimize the free energy. By strong contrast, because the external charge density \( \rho_b^{ex}(r) \) serves no purpose other than generating the background potential \( \phi^{b-s}_b(r) \), it is not changed by the insertion of test ion. Now, to obtain \( \phi^{h-c}(r) \) the part due to the test ion itself, and take the diagonal limit \( r \to 0 \):

\[
\psi(0, q) = \lim_{r \to 0} \left( \phi(r) - \frac{q}{4 \pi e r} \right).
\]

(54)

To obtain \( \delta \psi(0, q) \), we further subtract from \( \psi(0, q) \) the part that is independent of \( \phi^{b-s}_r \).

Recall that we want to calculate \( U(r, q; \phi^{b-s}_r) \) to the first order in \( \phi^{b-s}_r(r) \), and to the second order in \( q \). Hence we only need to calculate \( \phi(r) \) to the first order, both in \( \phi^{b-s}_r(r) \) and in \( q \). Let us decompose \( \phi(r) \) into four parts:

\[
\phi(r) = \phi^{b-s}_b(r) + \phi^{h-c}_b(r) + q G_0(r, 0) + q \phi^c(r) + O(q^2) + O(\phi^c_0) \]

(55)

We demand that \( \phi^{h-c}_b(r) \) is linear in \( \phi^{b-s}_r(r) \) but independent of \( q \), \( G_0(r, 0) \) is linear in \( q \) but independent of the background potential \( \phi^{b-s}_b \). Finally \( q \phi^c(r) \) is bilinear in \( q \) and \( \phi^{b-s}_r(r) \). All higher order terms are ignored.

Subtracting Eq. (12) from Eq. (53) (with \( \phi(r) \) replaced by \( \phi^{b-s}_b(r) + \phi^{h-c}_b(r) \) and \( q \) set to zero in the latter), and expanding the resulting equation to the first order in \( \phi^{b-s}_b(r) \) (note that \( \phi^{h-c}_b(r) \) is proportional to \( \phi^{b-s}_b(r) \)), we find that \( \phi^{h-c}_b(r) \) satisfies the following linearized PDE:

\[
- \Delta \phi^{h-c}_b(r) = \begin{cases} 
- \alpha q \phi^{h-c}_b(r), & r > d; \\
\alpha q \phi^{b-s}_b(r), & r < d.
\end{cases}
\]

(56)

This equation is hard to solve because of its integral nature. To simplify the analyses, we make the following simple approximations on the kernels \( \hat{\alpha}(k) \) and \( \hat{K}_\alpha(k) \): \( \hat{\alpha}(k) \approx \hat{\alpha}(ik_\ell) = k^2_\ell, \hat{K}_\alpha(k) \approx \hat{K}_\alpha(ik_\ell) = q^{R}_\alpha \). (57a)

In real space, they correspond to local approximations:

\[
\alpha(r) \approx k^2_\ell \delta(r), \quad K_\alpha(r) \approx q^{R}_\alpha \delta(r). \quad (57b)
\]

Note that the relation Eq. (14) between \( \alpha \) and \( K \) is preserved by the approximations. Eq. (56) then reduces to:

\[
- \Delta \phi^{h-c}_b(r) = \begin{cases} 
- k^2_\ell \phi^{h-c}_b(r), & r > d; \\
k^2_\ell \phi^{b-s}_b(r), & r < d.
\end{cases}
\]

(58)

Eq. (58) can be easily solved by expanding in terms of spherical harmonics, and using the standard Liouville method [36]. As the interface conditions, both \( \phi^{h-c}_b(r) \) and its normal derivative are continuous across the interface \( r = d \). Instead of presenting the full results, here we only give the value of \( \phi^{h-c}_b(r) \) at the origin:

\[
\phi^{h-c}_b(0) = \phi_0 \xi(k_\ell, k^2_\ell), \quad \xi(x, y) = \frac{y^2 [y(x - \sin x) + x (1 - \cos x)]}{x^3(y + 1)}, \quad (59b)
\]

To obtain the equations satisfied by \( G_0(r, 0) \), we set \( \rho^{ex}_b, \phi^{b-s}_b, \phi^{h-c}_b \) all to zero in Eqs. (53) and (55):

\[
- \Delta G_0(r, 0) + \theta(r - d) \int_{r'} \alpha(r - r') G_0(r', 0) = \frac{1}{\epsilon} \delta(r). \quad (60)
\]

Making the same local approximation Eq. (57), we can easily solve this equation and find

\[
G_0(r, 0) = \begin{cases} 
\frac{e^{-\eta_0(r-d)}}{4\pi \epsilon r(1 + \eta_0 d)}, & r > d; \\
\frac{1}{4\pi \epsilon} \psi_0, & r < d.
\end{cases}
\]

(61)

Note that \( G_0(r, 0) \) is independent of \( \phi_0 \) and hence makes no contribution to \( \psi(0, q) \). Finally to find the equation satisfied by \( \phi^c(r) \), we need to extract the part of Eq. (53) that is bilinear in \( q \) and \( \phi^{b-s}_r \):

\[
- \Delta \phi^c(r) + \theta(r - d) \phi^c(r) = \frac{\theta(r - d)}{\epsilon} \sum_q \rho_q K^{q}_\alpha \phi^{b-s}_b + \phi^{h-c}_b \times K^{q}_\alpha G_0(r, 0). \quad \]

(62)

It will be solved, separately, for the cases of electrolytes and asymmetric electrolytes, in Sec. IV A and Sec. IV C.
Finally, using Eqs. (65) and (61), as well as the fact that Eq. (61) is independent of \( \phi^{d,k} \), we now see:

\[
\delta \psi(0) = \phi^{b,k}(0) + \phi^{b,c}(0) + q \phi^{c}(0),
\]

which vanishes linearly with \( \phi^{b,g} \).

### A. Symmetric Electrolyte with Hardcores

For symmetric electrolyte consisting of \( \pm q \) ions with same hardcore diameter \( d \), we have \( \rho_+ = \rho_- \) and \( q^R = -q^R \), and \( K_- = -K_+ \), which follow naturally from the symmetry of charge inversion. Therefore the RHS of Eq. (62) vanishes identically, and \( \phi^c = 0 \). Using Eqs. (64) and (59a), we find:

\[
\delta \psi(0, q) = \phi^{b,g}(0) + \phi^{b,c}(0).
\]

Finally, to carry out the Debye charging process Eq. (52), we still need the constant of integration \( U(r,0; \phi^{b,g}) \). This is just the PMF of a neutral hard sphere in the presence of a background potential \( \phi^{b,g} \), expanded to the first order in \( \phi^{b,g} \). Again the symmetry of charge inversion guarantees that it vanishes identically for symmetric electrolytes. Substituting Eq. (64) into Eq. (52) and using Eqs. (50) and (59a), we obtain

\[
\hat{K}(k,q) = q \left[ 1 + \xi(kd, \kappa_R d) \right],
\]

with \( \xi(kd, \kappa_R d) \) defined in Eq. (59b). It becomes now clear that \( \hat{K}(k,q) \) has no pole as a function of \( k \) (treated as a complex variable), as we have assumed in Sec. II C. The fact that there is no quadratic \( q^2 \) term in the kernel \( \hat{K}(k,q) \) is enforced by the charge-inversion symmetry of the model. In the point ion limit, \( d \to 0 \), and \( \xi(kd, \kappa_R d) \to 0 \) (c.f. Eq. (59b)), and \( \hat{K}(k,q) \to q, \hat{K}(r,q) \to q \delta(r) \). This is just the fundamental assumption of PB.

We can now use Eqs. (14), (19), (28), and (21) to calculate the kernel \( \alpha \), and all renormalized parameters:

\[
\hat{\alpha}(k) = \kappa_0^2 \left[ 1 + \xi(kd, \kappa_R d) \right], \tag{66a}
\]

\[
\left( \frac{\kappa_R}{\kappa_0} \right)^2 = q_R(q) = \frac{e^{\kappa_R d}}{1 + \kappa_R d}, \tag{66b}
\]

\[
\frac{\epsilon_R}{\epsilon} = 2 - \frac{\kappa_R d}{2} - e^{-\kappa_R d} \left[ 1 + \kappa_R d - \frac{\sinh \kappa_R d}{2} \right]. \tag{66c}
\]

Kyellander [27] obtained Eq. (66b) some time ago using a different method. No previous analytic result has been found for the renormalized dielectric constant.

Careful analysis of Eq. (66b) indicates that there is a critical value \( \kappa_0^* \) defined by

\[
\kappa_0^* d = \sqrt{2} \left( 2 + \sqrt{3} \right) e^{-\frac{3}{2}} \approx 1.3465, \tag{67}
\]

such that for \( \kappa_0 > \kappa_0^* \), all renormalized parameters become complex, and the system exhibits charge oscillation. The corresponding \( \kappa_R^* \) and \( \epsilon_R^* \) at the threshold are

\[
\kappa_R^* d = 1 + \sqrt{3} \approx 2.732, \tag{68a}
\]

\[
\epsilon_R^*/\epsilon \approx 0.640. \tag{68b}
\]

We simulated \( 1 : -1 \) electrolytes with three different ion sizes: \( d = 5\AA, 7.5\AA, 10\AA \) respectively, and determine all renormalized parameters using the method discussed in Sec. III. As shown in Fig. 2, our MC results agree with Eqs. (66) remarkably well, and compare favorably with all previous results obtained by other groups.

### B. The PMF of a Neutral Hard Sphere

Consider a system of \( N \) interacting particles with hard-cores diameter \( d \), and insert a neutral hard sphere with
radius $a$ at the origin. The center-of-mass of all ions are therefore excluded from a spherical region with radius $R_c = a + d/2$. The boundary of this excluded region is defined as the surface of contact. See Fig. 3 for illustration of the geometry. The canonical partition function of $N$ mobile particles and the associated free energy both depend on the radius $R_c$ of the contact surface:

$$Z(R_c) = \prod_{i=1}^{N} \int_{|\mathbf{x}_i| > R_c} d^3 \mathbf{x}_i e^{-\beta H[\mathbf{x}]},$$

(69a)

$$F(R_c) = -k_B T \log Z(R_c),$$

(69b)

where the concrete form of the Hamiltonian is irrelevant to our present discussion, as long as it does not depend on the radius $R_c$.

Now taking the derivative of $F(R_c)$ with respect to $R_c$, we obtain the pressure (or the normal force) acting on the surface of contact, integrated over the surface:

$$\frac{dF(R_c)}{dR_c} = 4\pi R_c^2 \bar{p}(R_c).$$

(70)

Here and below, the over-line means average over the surface of contact. Also using Eqs. (69) we can show

$$\frac{dF(R_c)}{dR_c} = -\frac{\partial}{\partial R_c} k_B T \log Z(R_c)$$

(71)

$$= \sum_i \int_S d\hat{A}_i \frac{k_B T}{Z(R_c)} \int_{j \neq i} \int d^3 \mathbf{x}_j e^{-\beta H[\mathbf{x}]_{|\mathbf{x}_i| = R_c}},$$

where the first integral refers to $i$-th coordinate $\mathbf{x}_i$ integrated over the surface of contact $|\mathbf{x}_i| = R_c$. But the RHS is the particle density integrated over the same surface, multiplied by $k_B T$. Combining Eqs (70) and (71), and dividing them by $4\pi R_c^2$, we have the following exact relation between the mean pressure $\bar{p}$ and the mean particle density, both evaluated on the surface of contact:

$$\bar{p}(R_c) = \frac{k_B T}{4\pi R_c^2} \int_S d\hat{A} \rho(r) = k_B T \bar{p}(R_c).$$

(72)

This is a variant of the famous contact value theorem.

If we multiply Eq. (72) by $4\pi R_c^2$ and integrate over the radius $R_c$, we obtain the free energy cost of creating a spherical void (excluded volume) with radius $R_c$:

$$U = k_B T \int_0^{R_c} \rho(R_c) 4\pi R_c^2 dR_c.$$  

(73)

For an electrolyte, $\rho(R_c)$ in RHS is the total particle density, summed over all species of ions. Using Eqs. (47) and (11), linearizing, and further using the local approximation Eq. (57) we find:

$$\rho(R_c) = \sum_\alpha \rho_\alpha e^{-\beta \kappa_\alpha \Phi_\alpha(r)} \approx \sum_\alpha \rho_\alpha - \beta \sum_\alpha \rho_\alpha q_\alpha^R \bar{\Phi}(R_c).$$

(74)

Substituting this back into Eq. (73) and take only the part that is linear in $\phi$, we obtain the PMF of a neutral hard sphere at $r = 0$ (c.f. Eq. 52):

$$U(0, 0; \Phi^{b,c}) = -\sum_\alpha \rho_\alpha q_\alpha^R \int_0^\pi \bar{\Phi}(R_c) 4\pi R_c^2 dR_c.$$  

(75)

To average Eq. (74) over the spherical surface of contact we only need to take the isotropic component with $l = 0$. Now according to Eq. (55), since the inserted sphere is neutral, $\phi = \phi^{b,c} + \phi^{h,c}$, where $\phi^{h,c}$ satisfies Eq. (68), with the radius of excluded region $d$ replaced by $R_c$. Solving this equation we find:

$$\bar{\phi} = \phi_0 \left[ \sin k R_c + \eta(k R_c, \kappa_R R_c) e^{-\kappa_R R_c} \right] \frac{k R_c}{\kappa_R R_c},$$

(76a)

$$\eta(x, y) = \frac{y^3 e^y (\sin x - x \cos x)}{x^3(y + 1)}.$$  

(76b)

Substituting this into Eq. (75), we find the PMF of a neutral hard sphere inside the electrolyte, in the presence of a back ground mean potential Eq. (48):

$$U(0, 0; \Phi^{b,c}) = -4\pi l_0 d^3 \Psi_0(kd, \kappa_R d) \sum_\alpha \rho_\alpha q_\alpha^R.$$  

(77)

where the function $\Psi_0(kd, \kappa_R d)$ is defined as

$$\Psi_0(x, y) = \int_0^1 \left[ \frac{1}{x} \sin xt + \frac{1}{y} \eta(xt, yt) e^{-yt} \right] t dt.$$  

(78)

Comparing this with Eq. (50), we find:

$$\tilde{K}(k, 0) = -4\pi d^3 \left( \sum_\alpha \rho_\alpha q_\alpha^R \right) \Psi_0(kd, \kappa_R d).$$

(79)

For infinitesimally small particle, $d \to 0$, and we find $\Psi_0(0, 0) = 1/3$, and hence

$$\tilde{K}(k, 0) = -\frac{4\pi}{3} d^3 \sum_\alpha \rho_\alpha q_\alpha^R.$$  

(80)
which is what we derived heuristically for a small neutral particle, see Eq. (38).

Using Eqs. (1) and (8), one can prove an identity (with \(e\) the fundamental unit of electric charge, and \(m, -n\) are the bare valences of ions):

\[
\kappa_0^2 = \epsilon^{-1} \beta e^2 \rho_+ m(m + n).
\]  

(81)

Using this, we can rewrite Eq. (79) into:

\[
\frac{1}{e} \hat{K}(k, 0) = -\frac{\kappa_0^2}{\kappa_R} (\kappa_R b)^3 \frac{(m_R n - n_R m)}{mn(m + n)} \Psi_0(kd, \kappa_R d),
\]  

(82)

C. Asymmetric Electrolytes with Hardcores

For asymmetric electrolyte, the RHS of Eq. (62) no longer vanishes. Again we only need the isotropic (\(l = 0\)) component of \(\phi^e(r)\). The isotropic component of RHS of Eq. (62) can be easily shown as

\[
\frac{\phi_0 q}{e} \delta(r - d)(m_R - n_R)(\kappa_R b) \frac{e^{\kappa_R d}}{1 + \kappa_R d} e^{-\kappa_R r} \left[ \sin kr \frac{kr}{r} + \eta(kd, \kappa_R d) e^{-\kappa_R r} \right].
\]  

(83)

Substituting this back into Eq. (62), \(\phi^e(r)\) can be found using standard Liouville method. We find:

\[
\phi^e(0) = \frac{2 \phi_0 q}{e} (m_R - n_R)(\kappa_R b) \Psi_2(kd, \kappa_R d),
\]  

\[
\Psi_2(x, y) = -\frac{e^{2y}}{4(1 + y)^2} \left[ 2\eta(x, y) Ei(-3y) + \frac{y}{x} Ei(-iy - 2y) - Ei(2y) \right],
\]  

(84)

with \(\eta(x, y)\) defined in Eq. (76b) and \(Ei(y)\) the exponential integral function, defined as:

\[
\expint(y) = -\int_{-y}^\infty t e^{-t} dt.
\]  

(85)

Substituting this and Eqs. (59a), (48) back into Eq. (63), we find the potential acting on the charge \(q\):

\[
\delta \psi = \phi_0 \left[ 1 + \xi(kd, \kappa_R d) + \frac{2q}{e} (m_R - n_R)(\kappa_R b) \Psi_2(kd, \kappa_R d) \right].
\]  

(86)

Now using Eqs. (62) and (82) to carry out the Debye charging process:

\[
\hat{K}(k, q) = -\frac{e^{\kappa_0^2}}{\kappa_R} (\kappa_R b)^3 \frac{(m_R n - n_R m)}{mn(m + n)} \Psi_0(kd, \kappa_R d) + q \left[ 1 + \xi(kd, \kappa_R d) \right] + \frac{q^2}{e} (m_R - n_R)(\kappa_R b) \Psi_2(kd, \kappa_R d),
\]  

(87)

Again one can check that \(\hat{K}(k, q)\) has no role as a function of the complex variable \(k\). Substituting this into Eq. (14), we find the linear response kernel \(\hat{\alpha}(k)\):

\[
\hat{\alpha}(k) = \kappa_0^2 \left[ 1 + \xi(kd, \kappa_R d) + (m - n)(m_R - n_R)(\kappa_R b) \Psi_2(kd, \kappa_R d) \right].
\]  

(88)

Setting \(k = \kappa_R b\) in Eq. (87), and using Eq. (28), we find the renormalized charge of a hard sphere ion as a function of the bare charge (where \(s = \kappa_R b\)):

\[
\frac{q_R(q)}{e} = \frac{\kappa_0^2}{\kappa_R} (m_R n - n_R m) \frac{F_0(\kappa_R d)}{s} + \left( \frac{q}{e} \right) F_1(\kappa_R d) + \left( \frac{q}{e} \right)^2 (m_R - n_R) s F_2(\kappa_R d),
\]  

(89)
where functions $F_0(y), F_1(y), F_2(y)$ are defined as

$$F_0(y) = -\Psi_0(iy, y) = -\frac{1}{y^2} \left[ \frac{1}{e} Ei(y + 1) - \frac{1}{e} Ei(1) + e^y(y - 2) + 2 \right],$$

$$F_1(y) = 1 + \xi(iy, y) = \frac{e^y}{1 + y},$$

$$F_2(y) = \Psi_2(iy, y) = \frac{e^{2y}}{4(1 + y)^3} \left[ (1 - y) e^{2y} Ei(-3y) - (1 + y) Ei(-y) \right].$$

Eq. [89] should be understood as a power series in terms of the bare valence of the inserted ion $q/e$.

Finally, setting $q = m e, -n e$ in Eq. [89], the LHS reduces to the renormalized valences $m_R, -n_R$ respectively. Solving for $m_R, n_R$ we find:

$$m_R = \frac{F_1(\kappa_{RD}) m [F_0(\kappa_{RD}) \kappa_0^2 / \kappa_R^2 + mns(F_2(\kappa_{RD})sn(m + n) - 1)]}{mns [F_2(\kappa_{RD})s(m^2 + n^2) - 1] - [F_2(\kappa_{RD})s(m - n)^2 - 1] F_0(\kappa_{RD}) \kappa_0^2 / \kappa_R^2},$$

$$n_R = \frac{F_1(\kappa_{RD}) n [F_0(\kappa_{RD}) \kappa_0^2 / \kappa_R^2 + mns(F_2(\kappa_{RD})sm(m + n) - 1)]}{mns [F_2(\kappa_{RD})s(m^2 + n^2) - 1] - [F_2(\kappa_{RD})s(m - n)^2 - 1] F_0(\kappa_{RD}) \kappa_0^2 / \kappa_R^2}. $$

Plugging these back into Eq. [31], we find the following self-consistent equation for $\kappa_R$:

$$\left( \frac{\kappa_R}{\kappa_0} \right)^2 = \frac{F_1(\kappa_{RD}) \left[ F_0(\kappa_{RD}) \left( \frac{\kappa_0}{\kappa_R} \right)^2 + mns \left[ 2F_2(\kappa_{RD})mns - 1 \right] \right]}{mns [F_2(\kappa_{RD})s(m^2 + n^2) - 1] - [F_2(\kappa_{RD})s(m - n)^2 - 1] F_0(\kappa_{RD}) \left( \frac{\kappa_0}{\kappa_R} \right)^2}. $$

This defines the renormalized inverse Debye length $\kappa_R$ as an implicit function of the bare one $\kappa_0$. Finally the
renormalized dielectric constant can also be obtained using Eq. (21) (with shorthand $y = \kappa_R d$ below):

$$\frac{\epsilon_R}{\epsilon} - 1 = -\frac{1}{24(y + 1)^3} \left(\frac{\kappa_0}{\kappa_R}\right)^2 \left\{ 12(y + 1)^2 \left[ 2 + 2y - 3e^y + y \sinh y + (y + 1) \cos y \right] + se^{-y}(m - n)(m_R - n_R)\left[ (y + 1) \left[ 3e^y Ei(-y) + 3e^{2y} + 1 \right] - 3e^y Ei(-3y) \left( 2e^y (y^2 + 3) \sinh y - 6e^y \cos y + y + 1 \right) \right] \right\}. \tag{91d}$$

In Fig. 4 we show the comparison between the analytic results Eqs. (91) and large scale MC simulation.

Let us check two special cases:

**Symmetric electrolytes** $m = n, m_R = n_R$. All results reduce to those in Sec. [IV.A]. In particular, Eqs. (91a) and (91b) reduce to Eq. (66b), and Eq. (91c) reduces to Eq. (66b), and Eq. (91d) reduces to Eq. (66c).

**Asymmetric electrolyte with point ions:** $d \to 0$, hence $F_0 \to 0, F_1 \to 1, F_2 \to \frac{1}{2} \log 3$, Eqs. (91a) and (91b) reduce to

$$\frac{m_R}{m} = \frac{4 - ns(m + n) \log(3)}{4 - s(m^2 + n^2) \log(3)}, \tag{92}$$

$$\frac{n_R}{n} = \frac{4 - ns(m + n) \log(3)}{4 - s(m^2 + n^2) \log(3)}. \tag{93}$$

and Eq. (91c) reduces to

$$\frac{\kappa_R^2}{\kappa_0^2} = \frac{4 - 2(\kappa_R b)mn \log(3)}{4 - (\kappa_R b)(m^2 + n^2) \log(3)}. \tag{94}$$

and finally Eq. (91d) reduces to

$$\frac{\epsilon_R}{\epsilon} = 1 - \frac{s(4 - 3 \log 3)(m - n)^2}{12(2 - mn \log 3)}. \tag{95}$$

Strictly speaking, a two-component plasma model with point-like ions is not well-defined because of the instability towards annihilation of opposite charges. For small but finite ion sizes, this instability is manifested as formation of bound pairs of ions, or even larger clusters. This instability does not show up at the level of our approximation, just as in the classical Debye-Hückel theory. Linearization, which is adopted in both theories, is responsible for the suppression of this instability at short scales. As a logical consequence, whenever bound ion clusters can not be ignored, linearization breaks down, and the short scale properties derived in our theory (similar to those of Debye-Hückel theory) can not be trusted. This happens, for example, for dense electrolytes with small ions where the electrostatic energy between neighboring ions becomes much larger than the thermal energy $k_B T$. Indeed, we have also simulated 3 : 1 electrolyte with $d = 7.5\,\text{Å}$. The largest interaction energy between two ions (in close contact) is then approximately $3k_B T$, which makes linearization a bad approximation in the dense regime. As expected, we found that substantial disagreement between theory and simulation.

### V. CONCLUSIONS AND OUTLOOK

The effective linear theory that describes the long scale properties of dense electrolytes can be summarized as follows: 1) Both steric interactions and ionic correlations lead to nonlocal effects in the PMF of ions, Eq. (11). 2) The linear response theory of dense electrolyte is characterized by a nonlocal integro-differential equation, Eq. (13). This implies renormalization of Debye length, ion valences, as well as dielectric constant, and eventually leads to charge oscillation if the ion density is sufficiently high. 3) The far field structure of electric double layers should be described by a renormalized Poisson-Boltzmann theory (Sec. [IV.D]). 4) Generically, a neutral object behaves effectively as charged in dense electrolytes. It is as if some fraction of charges of the ions are transferred to the solvent, due to the ionic correlations.

Taking advantage of the power of GPU and perturbation analyses, we have computed, both numerically and analytically, all the generalized quantities of dense electrolytes. For systems with negligible effects of Bjerrum association, these two approaches give results that are remarkably consistent with each other, without using any adjustable parameter. This firmly establish the validity of both approaches, and also of the general phenomenological theory as well.

There are several directions that we shall pursue in the immediate future. Firstly, we can numerically compute the whole linear response kernel $\alpha(r)$ using the intelligent method of umbrella sampling. This shall constitute a more stringent test of our analytic formalism. Secondly, we will generalize the analytic formalism to include the effects of Bjerrum association, and to explore the thermodynamic properties of dense electrolytes. Thirdly, we will explore the effects of various non-electrostatic interactions that are beyond the primitive model. Finally, we shall try to understand the effects of ionic correlations and steric effects in the dynamics of electrolyte systems. For example, what is the role of charge renormalization in transport processes, such as electrophoresis?

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[24] Note that $\phi(r)$ is the mean potential at $r$ in the absence of the test ion. Note also that $\phi(r)$ is not the total mean potential acting on the test ion. The easiest way to see this is to consider a test ion in the bulk, where the mean potential $\phi(r)$ vanishes. The local potential acting on the test ion is of course nonzero, due to the correlation between ions. Also, in the framework of primitive model, there is no non-electrostatic potential energy acting on the electrolytes. Therefore the PMF $U(r,q;\phi)$ only depends on the mean potential $\phi$.
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[26] Here we are assuming that there is no branch cut or essential singularity. Otherwise, the argument below would not be valid. Our analytic calculation in Sec. shows that this assumption is indeed valid.
[27] Here we need to assume that $K(k,q)$ has no pole on the upper half-plane that is closer to the real axis than $k = i\pi q$. This is equivalent to the assumption that $K(r,q)$ in real space decays faster than $e^{-\kappa R}$, which is quite
reasonable, because $\kappa R$ sets the longest relevant length scale in electrolytes. This assumption will be shown to be satisfied by our explicit calculations in Sec. IV A and Sec. IV C.

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[38] Clearly, this is no longer true if the inserted sphere has a different dielectric constant than that of the solvent.