Charged plate in asymmetric electrolytes: One-loop renormalization of surface charge density and Debye length due to ionic correlations

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Self-consistent field theory (SCFT) is used to study the mean potential near a charged plate inside a $m\colon -n$ electrolyte. A perturbation series is developed in terms of $g = 4\pi\kappa b$, where b *and* $1/\kappa$ are Bjerrum length and *bare* Debye length, respectively. To the zeroth order, we obtain the nonlinear Poisson-Boltzmann theory. For asymmetric electrolytes ($m \neq n$), the first order (one-loop) correction to mean potential contains a *secular term*, which indicates the breakdown of the regular perturbation method. Using a renormalizaton group transformation, we remove the secular term and obtain a globally well-behaved one-loop approximation with *a renormalized Debye length* and *a renormalized surface charge density*. Furthermore, we find that if the counterions are multivalent, the surface charge density is renormalized substantially *downwards* and may undergo a change of sign, if the bare surface charge density is sufficiently large. Our results agrees with large MC simulation even when the density of electrolytes is relatively high.

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I. INTRODUCTION

There is a general consensus [1–4] that the Poisson-Boltzmann theory (PB) is inadequate in describing the statistical physics of strongly coupled electrolytes, where the electrostatic interaction between neighboring ions is large comparing with the thermal energy. This happens typically inside dense bulk electrolytes, or near strongly charged surfaces, or, more specifically, in tightly confined environments [5]. Failure of PB may also be caused by strong volume exclusion interactions between ions, if the ion sizes are sufficiently large and ion densities are sufficiently high. Last but not least, PB may also fail due to ion-specific interactions [6,7], which are manifestly beyond the primitive model. In the dilute limit, both correlations and ion-specific interactions become unimportant, and PB becomes asymptotically exact. Finally, it is often observed that PB fails for asymmetric electrolytes at much lower densities. The responsible mechanism, however, seems less clear. Because of the complexity of electrolyte systems, there does not exist a single theoretical framework capable of describing all non-PB aspects.

The present work is the third of a series that analyze the statistical physics of electric double layers (EDLs) with planar geometry inside asymmetric electrolytes. In Ref. [8] (which shall be referred to as Paper 1), M. Han and X. Xing solved the nonlinear Poisson-Boltzmann equation for a single strongly (and positively) charged plate inside a generic $m\colon -n$ electrolyte. Using the leading order far field asymptotics of the mean potential, one can define a renormalized (or effective) charge density for the strongly charged plate, which saturates to a finite value that depends on valences m,n, as well as the ion density. Note that this renormalization of surface charge density arises due to the nonlinearity inherent in the Poisson-Boltzmann equation, which is a *mean field theory*. There are also additional renormalization of charge density due to statistical fluctuations or correlations, which is completely ignored in PB. Subsequently, in Ref. [9] (which shall be referred to as Paper 2), two of us (B.S.L. and X.X.) calculated the *electrostatic* correlation energy of a test (point) ion near a strongly charged plate inside a $m\colon -n$ electrolyte, to the first order in g (a small parameter inverse proportional to the Debye length, as we will define later). It was found that for $m \neq n$, the correlation energy decays in the same fashion as the mean field potential in the far field. This correlation energy was used to calculate the first order correction to the mean potential, which was found to contain a *secular* term that dominates the zeroth order result in the far field, indicating the breakdown of regular perturbation method. In the present work, we shall use perturbation analyses and a renormalization group method to demonstrate that the physical origin of the secular term is the renormalization of Debye length due to *electrostatic correlations*. Additionally, we shall also obtain the renormalization of surface charge density due to the same correlations.

It is important to emphasize that the one-plate problem has been studied by many authors in the past, via both analytic and numerical methods. In particular, there is a large body of analytic results based on the strong-coupling theory and various generalizations; see references in Paper 1 and Paper 2. There are also a number of more recent relevant works [10–12]. For some analytic results using Ornstein-Zernike integral equation theory, see Ref. [13]. The same as our works, all these works are based on the *primitive model*, where ions are described as charged hard spheres. Our present work differs from all previous works in the sense that we provide analytic expressions for renormalized surface charge density and renormalized Debye length for generic (two-component) asymmetric electrolytes. These results, of course, are applicable only for relatively dilute systems.

The remaining of this paper is organized as follows. In Sec. II we discuss the framework of self-consistent field theory (SCFT) and formally derive the first order correction to the mean potential due to a (infinitely thick) charged plate inside electrolyte. In Sec. III we apply the method to the case of symmetric electrolytes and obtain the first order renormalized surface charge density. In Sec. IV we apply the theory to the

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(much harder) case of asymmetric electrolytes and find that the first order perturbation to the mean potential contains a secular term. As a result, the correction becomes larger than the mean field result in the far field, and the perturbation series becomes useless. We then apply a renormalization group transformation on the perturbation series and show that physical origin of the secular term is *renormalization of Debye length due to electrostatic correlations*. We obtain both renormalized Debye length and renormalized surface charge density up the first order. In Sec. V we present some Monte Carlo simulation results of a strongly charged surface inside a 2:−1 primitive model electrolyte. Comparison with analytical results shows that our renormalized theory works much better than the nonlinear PB. Finally in Sec. VI we summarize our work and discuss the implications of our results. In Appendix A we present some analytic details about 2: −1 and 1: −2 asymmetric electrolytes. The main results of this work are summarized by two equations (4.44) and (4.45).

II. FORMALISM

A. Self-consistent field theory (SCFT)

As in Paper 1 and Paper 2, we shall consider asymmetric electrolyte with *point-like* positive and negative ions carrying charges $+mq$ and $-nq$, respectively. The mean potential $\Phi(\boldsymbol{r})$ satisfies the exact Poisson equation:

$$-\,\epsilon\,\nabla^2\Phi(\boldsymbol{r}) = mq\,\rho_+^0\,e^{-\beta w_1(\boldsymbol{r},mq)} - nq\,\rho_-^0\,e^{-\beta w_1(\boldsymbol{r},-nq)}, \tag{2.1}$$

where $\rho_\pm^0$ are the average ion number densities in the bulk, $\beta = 1/k_BT, \epsilon$ is the dielectric constant of the electrolyte, and $q = 1.6 \times 10^{-19}C$ is the fundamental unit of electric charge. $w_1(\boldsymbol{r},mq), w_1(\boldsymbol{r},-nq)$ are the potentials of mean force (PMF) of positive and negative ions. As discussed in the first section of Paper 2, $w_1(\boldsymbol{r},kq)$ of a k-valence test ion can be formally expanded in terms of k:

$$w_1(\boldsymbol{r},kq) = kq\,\Phi(\boldsymbol{r}) + \tfrac{1}{2}k^2q\,\delta\Upsilon(\boldsymbol{r},\boldsymbol{r}) + O(k^3). \tag{2.2}$$

In this expansion, the first order term corresponds to the mean field theory, and higher order terms arise due to the correlation effects. $\delta\Upsilon(\boldsymbol{r},\boldsymbol{r})$ is defined as the correlation potential and is related to the electrostatic Green's function $\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')$ via

$$\delta\Upsilon(\boldsymbol{r},\boldsymbol{r}) = \lim_{\boldsymbol{r}'\to\boldsymbol{r}}\left[\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') - \lim_{\boldsymbol{r}''\to\infty}\mathcal{G}(\boldsymbol{r}+\boldsymbol{r}'',\boldsymbol{r}'+\boldsymbol{r}'')\right]. \tag{2.3a}$$

The Green's function is defined as incremental potential at $\boldsymbol{r}$ due to a monovalence test ion q inserted at $\boldsymbol{r}'$, in the presence of the background potential $\Phi(\boldsymbol{r})$. Substituting the preceding two equations back into (2.1) and neglecting terms of higher order in k, we arrive at a *modified Poisson-Boltzmann equation*:

$$\begin{aligned}-\,\epsilon\nabla^2\Phi(\boldsymbol{r}) &= mq\rho_+^0\,e^{-\beta mq\Phi(\boldsymbol{r})-\frac{1}{2}m^2\beta q\,\delta\Upsilon(\boldsymbol{r},\boldsymbol{r})}\\ &\quad - nq\rho_-^0\,e^{\beta nq\Phi(\boldsymbol{r})-\frac{1}{2}n^2\beta q\,\delta\Upsilon(\boldsymbol{r},\boldsymbol{r})}.\end{aligned} \tag{2.3b}$$

For details, see Sec. I of Paper 2.

To obtain a close system of equations, we need another equation for the Green's function $\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')$. A self-consistent treatment is to consider $\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')$ as a linear perturbation to the background $\Phi(\boldsymbol{r})$ in Eq. (2.3b) and linearize in terms of $\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')$. This leads to

$$\begin{aligned}-\,\epsilon\nabla^2\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') &= -\beta q^2\big[m^2\rho_+^0\,e^{-\beta mq\Phi(\boldsymbol{r})-\frac{1}{2}m^2\beta q\,\delta\Upsilon(\boldsymbol{r},\boldsymbol{r})}\\ &\quad + n^2\rho_-^0\,e^{\beta nq\Phi(\boldsymbol{r})-\frac{1}{2}n^2\beta q\,\delta\Upsilon(\boldsymbol{r},\boldsymbol{r})}\big]\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')\\ &\quad + q\,\delta(\boldsymbol{r}-\boldsymbol{r}').\end{aligned} \tag{2.3c}$$

Three equations (2.3) form the *self-consistent field theory* (SCFT) approximation and has been studied by various authors for symmetric case $m = n$ [14–16]. In these previous works, Eqs. (2.3) were derived using field-theoretic formalism and variational Gaussian approximation. The derivation presented in this work is more heuristic and provides an alternative viewpoint.

Strictly speaking, two-component electrolytes with point-like ions are thermodynamically unstable because opposite ions can approach indefinitely close to each other, so that the energy does not have a lower bound. This pathology, however, does not show up in our theory, because the corresponding ultraviolet divergence is precisely canceled in the subtraction in Eq. (2.3). The same cancellation is also at work in the classical Debye-Huckle theory of bulk electrolytes.

Let us define the (bare) Debye length $1/\kappa$ and the Bjerrum length b via

$$1/\kappa \equiv \sqrt{\epsilon/\beta q^2(m^2\rho_+^0 + n^2\rho_-^0)}, \tag{2.4a}$$

$$b \equiv \beta q^2/4\pi\epsilon. \tag{2.4b}$$

We shall also define a dimensionless parameter$g$, small for a dilute electrolyte:

$$g = 4\pi\kappa b. \tag{2.4c}$$

The same as in Paper 2, we shall measure all lengths in units of $1/\kappa$, and define the dimensionless versions of mean potential Ψ and Green's function $G(\boldsymbol{r},\boldsymbol{r}')$ via

$$\boldsymbol{r} \to \boldsymbol{r}/\kappa, \tag{2.5a}$$

$$\Psi \equiv q\beta\Phi, \tag{2.5b}$$

$$G \equiv q\beta\mathcal{G}. \tag{2.5c}$$

For details, see Eqs. (2.3) of Paper 2. Equations (2.3b) and (2.3c) then reduce to the following dimensionless form:

$$-\frac{d^2\Psi(z)}{dz^2} + \frac{1}{m+n}\big[e^{n\Psi(z)-n^2\Delta\varepsilon(z)} - e^{-m\Psi(z)-m^2\Delta\varepsilon(z)}\big] = 0, \tag{2.6a}$$

$$\left[-\nabla^2 + \frac{1}{m+n}\left(me^{-m\Psi(z)-m^2\Delta\varepsilon(z)} + ne^{n\phi(z)-n^2\Delta\varepsilon(z)}\right)\right] \times G(\boldsymbol{r},\boldsymbol{r}') = g\,\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{2.6b}$$

where z is the distance to the charged plate, $\Delta\varepsilon(z)$ the correlation energy and is related to the electrostatic Green's function $G(\boldsymbol{r},\boldsymbol{r}')$ via

$$\Delta\varepsilon(z) = \tfrac{1}{2}\lim_{\boldsymbol{r}'\to\boldsymbol{r}}[G(\boldsymbol{r},\boldsymbol{r}') - \lim_{\boldsymbol{r}''\to\infty}G(\boldsymbol{r}+\boldsymbol{r}'',\boldsymbol{r}'+\boldsymbol{r}'')]. \tag{2.6c}$$

We shall solve Eqs. (2.6) perturbatively to the first order in g in this work. The leading order far field asymptotics of the mean potential has the following simple form:

$$\Psi(z) = \eta_R \, e^{-\alpha z}, \tag{2.7}$$

where η_R is the renormalized surface charge density, given by Eq. (4.45), while $\alpha = \kappa_R/\kappa$ is given by Eq. (4.44), with κ_R the renormalized inverse Debye length.

B. Perturbative expansion in g

We shall solve Eqs. (2.6) using perturbation method, in terms of the dimensionless parameter g. That means we expand $\Psi(z)$ and $G(\boldsymbol{r},\boldsymbol{r}')$ into asymptotic series of g and solve the coefficients order by order. Since the source on the RHS of Eq. (2.6b) is linear in g, whereas Eq. (2.6a) is formally independent of g, we expect that $\Psi(z)$ starts with 0th order, while $G(\boldsymbol{r},\boldsymbol{r}'), \Delta\varepsilon(z)$ start with first order:

$$\Psi(z) = \Psi_0(z) + g\,\Psi_1(z) + \cdots, \tag{2.8a}$$

$$G(\boldsymbol{r},\boldsymbol{r}') = 0 + g\,G_1(\boldsymbol{r},\boldsymbol{r}') + \cdots, \tag{2.8b}$$

$$\Delta\varepsilon(z) = 0 + g\,\Delta\varepsilon_1(z) + \cdots. \tag{2.8c}$$

This is equivalent to the well-known loop expansion in the field-theoretic formalism. Substituting these back into Eqs. (2.6), we find that, to the 0th order, $\Psi_0(z)$ satisfies the nonlinear Poisson-Boltzmann equation (PBE):

$$-\Psi_0''(z) + \frac{1}{m+n}\left(e^{n\Psi_0(z)} - e^{-m\Psi_0(z)}\right) = 0, \tag{2.9}$$

which, for the one-plate geometry, was solved for arbitrary integers m,n using the method of asymptotic matching discussed in Paper 1. To the order in g, the Green's function $G_1(\boldsymbol{r},\boldsymbol{r}')$ can be found in terms of $\Psi_0(z)$ by solving the following linear PDE:

$$\left[-\nabla^2 + \frac{1}{m+n}\left(n\,e^{-n\Psi_0(z)} + m\,e^{m\Psi_0(z)}\right)\right] G_1(\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{2.10}$$

From $G_1(\boldsymbol{r},\boldsymbol{r}')$ we can obtain the first order correlation energy $\Delta\varepsilon_1(z)$ using Eq. (2.6c). This problem has been solved in Paper 2, again for arbitrary m,n [17]. The first order correction to potential, $\Psi_1(z)$, satisfies the following inhomogeneous linear ODE:

$$-\Psi_1''(z) + \frac{1}{m+n}\left[n\,e^{n\Psi_0(z)} + m\,e^{-m\Psi_0(z)}\right]\Psi_1(z) = S(z), \tag{2.11}$$

where the source $S(z)$ is defined as

$$S(z) \equiv \frac{1}{m+n}\left(n^2 e^{n\Psi_0(z)} - m^2 e^{-m\Psi_0(z)}\right)\Delta\varepsilon_1(z) \tag{2.12}$$

and can be obtained in terms of $\Psi_0(z)$ and $\Delta\varepsilon_1(z)$. Here we shall try to find $\Psi_1(z)$, for arbitrary valences m,n.

As we have shown in Paper 1, the solution to Eq. (2.9) can be expressed in terms of a function $\Upsilon_{m,n}$ that depends on two integers m,n:

$$\Psi(z) = \Upsilon_{m,n}(z+z_0). \tag{2.13}$$

The parameter z_0 shall be determined by enforcing the boundary condition (2.14a).The function $\Upsilon(z)$ diverges logarithmically at $z=0$. As a consequence, the parameter z_0 goes to zero in the limit of infinite surface charge density. It therefore can be treated as a small parameter for a strongly charged surface.

C. The boundary conditions

Same as in Paper 1 and Paper 2, we shall take the convention that the plate is infinitely thick and *positively charged*, so that the negative ions (with charge $-ne$) are the counterions and the positive ions (with charge me) are the coions. In Paper 1 and Paper 2, the coordinate system was chosen such that the interface with dimensionless surface charge density η is located at $-z_0$, with z_0 chosen as a function of η, such that the potential $\Psi_0(z)$ is independent of the (dimensionless) surface charge density η and diverges at $z=0$. This choice substantially simplifies the analyses in Paper 1 and Paper 2. In the present work, we shall choose a different coordinate system, namely, we shall fix the interface at the origin $z=0$. It is then understood that all results in Paper 1 and Paper 2 need to be transformed via $z \to z+z_0$ before they can be used here.

Since the plate is infinitely thick, the mean potential is constant in the whole left space ($z<0$), which shall be conveniently chosen to be zero. The boundary conditions satisfied by the mean potential $\Psi(z)$ are given by (also in their dimensionless forms): The other derivative does not appear:

$$\Psi'(0) = -\eta, \quad \text{on the plate}, \tag{2.14a}$$

$$\Psi(\infty) = 0, \quad \text{in the bulk}, \tag{2.14b}$$

where

$$\eta = \frac{q\beta\sigma}{\epsilon\kappa} \equiv \frac{2}{\kappa\mu} \tag{2.15a}$$

is the dimensionless surface charge density, and μ the Guoy-Chapman length:

$$\mu = \frac{2\epsilon}{q\beta\sigma}. \tag{2.15b}$$

In writing Eqs. (2.14a), we have assumed that the potential is constant to the left of the interface.

What we need are, however, the boundary conditions for $\Psi_0(z)$ and $\Psi_1(z)$, respectively. It seems completely natural to require that both $\Psi_0(z)$ and $\Psi_1(z)$ vanishes as $z=\infty$. But their boundary conditions at $z=0$ are more subtle. Equation (2.14a) only fixes the boundary condition for the whole series. It is conventional (and indeed seems very appealing) to require that $\Psi_0, \Psi_1, \ldots$ are all *independent of* g, and to expand both sides of Eq. (2.14a):

$$\Psi_0'(0) + g\,\Psi_1'(0) + \cdots = -\eta + g \times 0 + \cdots. \tag{2.16}$$

We can then enforce equality to hold order by order, and obtain a inhomogeneous boundary conditions for $\Psi_0(z)$ and a homogeneous one for $\Psi_1(z)$:

$$\Psi_0'(0) = -\eta, \quad \Psi_0(\infty) = 0; \tag{2.17a}$$

$$\Psi_1'(0) = 0, \quad \Psi_1(\infty) = 0. \tag{2.17b}$$

We must remember, however, that Eq. (2.17a) is only one of infinite number of possible choices. In particular, the functions $\Psi_0(z), \Psi_1(z), \ldots$ need not be independent of g. In fact, we can freely add a part to $g\,\Psi_1(z)$ and subtract it from $\Psi_0(z)$, such that Eq. (2.16) is unaltered. This subtle point provides the key to understanding our renormalization group analysis below.

D. Formal solution to $\Psi_1(z)$

In order to solve Eq. (2.11), we need only to find the corresponding Green's function $H(z,z')$, defined as

$$-\frac{d^2}{dz^2}H(z,z') + \frac{1}{m+n}[n\,e^{n\Psi_0(z)} + m\,e^{-m\Psi_0(z)}]H(z,z') = \delta(z-z'), \tag{2.18}$$

together with homogeneous boundary conditions at $z = 0$ and at $z = \infty$. Note that $H(z,z')$ is a one-dimensional Green's function, while $G_1(\boldsymbol{r},\boldsymbol{r}')$ in Eq. (2.10) is a three-dimensional Green's function. As is well known, $H(z,z')$ can be constructed using the standard Liouville method [18]. For this purpose, we need two independent homogeneous solutions $\phi_L(z)$ and $\phi_R(z)$ to Eq. (2.18) [19]:

$$-\phi''_{L,R}(z) + \frac{1}{m+n}(ne^{n\Psi_0(z)} + me^{-m\Psi_0(z)})\phi_{L,R}(z) = 0, \tag{2.19}$$

subjected to the homogeneous boundary conditions

$$\phi'_L(0) = 0, \tag{2.20a}$$

$$\phi_R(\infty) = 0. \tag{2.20b}$$

Taking the derivative of the original PB equation (2.9) with respect to z, we find that $\Psi'_0(z)$ satisfies Eq. (2.19). Furthermore, since $\Psi_0(z)$ decays as e^{-z} for $z \gg 1$, so does its derivative. Therefore $-\Psi'_0(z)$ is precisely the homogeneous solution $\phi_R(z)$ that we are looking for:

$$\phi_R(z) \equiv -\Psi'_0(z). \tag{2.21}$$

The other solution $\phi_L(z)$ can be obtained by the method of variation of parameters. Let

$$\phi_L(z) = f(z)\phi_R(z), \tag{2.22}$$

and substituting it back into Eq. (2.19), we find $f(z)$ satisfies the following equation:

$$\phi_R(z)\frac{d^2 f(z)}{dz^2} + 2\frac{df(z)}{dz}\frac{d\phi_R(z)}{dz} = 0. \tag{2.23}$$

This equation can be readily solved:

$$f(z) = \int \frac{dz}{\phi_R(z)^2} + f_1. \tag{2.24}$$

Hence

$$\phi_L(z) = \phi_R(z)\left[\int \frac{dz}{\phi_R(z)^2} + f_1\right]. \tag{2.25}$$

The constant f_1 shall be determined by the boundary condition satisfied by ϕ_L at $z = 0$, Eq. (2.20a).

The Wronskian formed by two functions $g(z)$ and $h(z)$ is defined as

$$W(g,h;z) = g(z)h'(z) - h(z)g'(z). \tag{2.26}$$

Using Eq. (2.25), it can be easily shown that

$$W(\phi_L,\phi_R;z) = -1. \tag{2.27}$$

The Green's function $H(z,z')$ can now be obtained:

$$H(z,z') = \begin{cases} \phi_L(z)\phi_R(z'), & (z < z'), \\ \phi_L(z')\phi_R(z), & (z > z'). \end{cases} \tag{2.28}$$

The first order correction $\Psi_1(z)$ can be now expressed in terms of the Green's function as

$$\begin{aligned}\Psi_1(z) &= \int_0^\infty H(z,z')S(z')\,dz. \\ &= \phi_R(z)\int_0^z \phi_L(z')S(z')\,dz' \\ &\quad + \phi_L(z)\int_z^\infty \phi_R(z')S(z')\,dz'.\end{aligned} \tag{2.29a}$$

Constructed as such, $\Psi_1(z)$ naturally satisfies the homogeneous boundary conditions (2.17b) at both ends. In later sections, we shall use this general expression and previous results of $\Psi_0(z)$ and $\Delta\varepsilon_1(z)$ to calculate $\Psi_1(z)$ for the generic values of m,n.

E. Subtleties of the correlation energy

In Paper 2, it was shown that the first order correlation energy $\Delta\varepsilon(z)$ can be decomposed into two parts:

$$\Delta\varepsilon_1(z) = \Delta\varepsilon^\infty(z) + \delta\varepsilon(z). \tag{2.30}$$

Here $\Delta\varepsilon^\infty(z)$ scales as $-3g/16\pi(z+z_0)$ in the near field and decays exponentially in the far field. Furthermore, it is manifestly independent of the dielectric constant of the plate ϵ_1 in the region $z < 0$. By contrast, the second part $\delta\varepsilon(z)$ depends on the dielectric constant of the plate ϵ_1, and vanishes if $\epsilon_1 = \epsilon$, but is subdominant to $\Delta\varepsilon^\infty(z)$ except in a very thin region close to the plate $z \ll z_0 \sim \mu$, where μ is the Gouy-Chapman length. This regime is called the *extremely near field* in Paper 2. Evidently, $\delta\varepsilon(z)$ becomes important in this regime because of the image charge effects due to the discontinuity of dielectric constant on the interface. This effects is screened by the counterions once the test ion is a couple of μ away from the plate.

If the dielectric constant ϵ_1 of the plate is smaller than ϵ that of the solvent (as is the usual case of insulator plate inside aqueous solvent), $\delta\varepsilon(z)$ diverges to $+\infty$ as $z \to 0^+$, that is, as the test ion approaches the plate. The effect of this repulsive image charge is to push the test ion a few μ away from the plate. This effects can be largely ignored in our calculation of $\Psi_1(z)$, as long as $\kappa\mu \ll 1$. Actually we have performed a simulation to verify our inference, which is shown in Fig. 2.

In this work, we assume that $\epsilon_1 \ll \epsilon$, and hence the correction $\delta\varepsilon(z)$ can be safely ignored. This substantially simplifies our analyses below.

III. SYMMETRIC ELECTROLYTE

Let us apply the general formalism developed above to the simplest case of $1:-1$ symmetric electrolyte. The solution to the PBE (2.9) for the one-plate geometry is well known:

$$\Psi_0(z) = 2\log\coth\left(\frac{z+z_0}{2}\right). \tag{3.1}$$

Note that $\Psi_0(z)$ diverges logarithmically at $z=-z_0$, where the parameter z_0 is small for a strongly charged plate and remains undetermined at this stage. In the far field, $\Psi_0(z)$ scales as

$$\Psi_0(z) = 4\,e^{-(z+z_0)} + O(e^{-2z}), \quad z\to\infty. \tag{3.2}$$

Recall that we neglect the part of the correlation energy that explicitly depends on the dielectric constant of the plate ϵ_1. The remaining part $\Delta\varepsilon^\infty(z)$ is independent of ϵ_1 and is given by [9]

$$\Delta\varepsilon^\infty(z) = \frac{e^{-2(z+z_0)}}{16\pi(z+z_0)} - \frac{1}{16\pi}\mathrm{csch}^2(z+z_0)\{\log 4(z+z_0) + E_1(4[z+z_0]) + \gamma\},$$

where

$$E_1(z) = \int_1^\infty t^{-1}e^{-tz}\,dt \tag{3.3}$$

is one of the generalized exponential integral functions and γ is the Euler constant. The near field and far field asymptotic behaviors of the correlation energy are

$$\Delta\varepsilon^\infty(z) \sim \begin{cases} -\frac{3}{16\pi(z+z_0)}, & z\to 0;\\ -\frac{1}{4\pi}\left[\gamma + \log 4(z+z_0) - \frac{1}{4(z+z_0)}\right]e^{-2(z+z_0)}, & z\to\infty. \end{cases} \tag{3.4}$$

All near field asymptotics are valid only in the strongly charged regime where $z_0 \ll 1$. The asymptotic behaviors of the source term $S(z)$ [cf. Eq. (2.12), and with $\Delta\varepsilon(z)$ approximated by $\Delta\varepsilon^\infty(z)$] are given by

$$S(z) \sim \begin{cases} -\frac{3}{8\pi(z+z_0)^3}, & z\to 0;\\ -\frac{1}{4\pi}[\gamma + \log 4(z+z_0)]e^{-2(z+z_0)}, & z\to\infty. \end{cases} \tag{3.5}$$

Two homogeneous solutions $\phi_L(z),\phi_R(z)$ to Eq. (2.19) can also be easily found using Eqs. (2.21) and (2.25):

$$\phi_R(z) = -\frac{d\Psi_0(z)}{dz} = 2\,\mathrm{csch}(z+z_0), \tag{3.6}$$

$$\phi_L(z) = 2\,\mathrm{csch}(z+z_0)\left[-\frac{1}{8}(z+z_0) + \frac{1}{16}\sinh 2(z+z_0) + f_1(z_0)\right], \tag{3.7}$$

where the function $f_1(z_0)$ is fixed by the boundary condition (2.20a):

$$\begin{aligned} f_1(z_0) &= \frac{z_0}{8} + \frac{1}{16}\sinh(2z_0) - \frac{1}{4}\tanh(z_0)\\ &= \frac{z_0^3}{6} + O\left(z_0^5\right). \end{aligned} \tag{3.8}$$

The leading order near field asymptotics of ϕ_L,ϕ_R are

$$\phi_R(z) \sim \frac{2}{(z+z_0)}, \tag{3.9a}$$

$$\phi_L(z) \sim \frac{z_0^3}{3(z+z_0)} + \frac{(z+z_0)^2}{6}, \tag{3.9b}$$

while their far field asymptotics are

$$\phi_R(z) \sim 4\,e^{-(z+z_0)}, \tag{3.10a}$$

$$\phi_L(z) \sim \tfrac{1}{8}\,e^{z+z_0}. \tag{3.10b}$$

The first order correction to the mean potential $\Psi_1(z)$ is then given by Eq. (2.29a) with $\phi_{L,R}(z)$ and $S(z)$ given by the above results. Finally, the parameter z_0 can be expressed in terms of the dimensionless surface charge density using Eqs. (2.17) and (3.1):

$$\begin{aligned} z_0 &= \mathrm{ArcSinh}(2\,\eta^{-1})\\ &= 2\,\eta^{-1} + O(\eta^{-2}). \end{aligned} \tag{3.11}$$

For a strongly charged plate, z_0 is a small number.

Near field and far field behaviors of the mean potential

Using the following identity in Eq. (2.29a):

$$\int_0^z dz' = \int_0^\infty dz' - \int_z^\infty dz', \tag{3.12}$$

we can rewrite the first order perturbation solution to $\Psi(z)$ in the following form:

$$\begin{aligned} \Psi(z) &= \Psi_0(z) + g\,\Psi_1(z)\\ &= \Psi_0(z) + g\,\phi_R(z)\int_0^\infty \phi_L(z')S(z')\,dz'\\ &\quad + g\left[\phi_L(z)\int_z^\infty \phi_R(z')S(z')\,dz' - \phi_R(z)\int_z^\infty \phi_L(z')S(z')\,dz'\right]. \end{aligned} \tag{3.13}$$

Using the far field asymptotics (3.5) and (3.10), we easy see that each of three integrals in Eq. (3.13) converges separately. Furthermore, it is easy to see that the last two terms (inside the bracket) scale as $\log(z)\,e^{-2z}$ for large z and therefore do not contribute to the leading order far field asymptotics of $\Psi(z)$. Using Eqs. (3.2) and (3.10) in (3.13), we obtain the following leading order far field asymptotics of $\Psi(z)$:

$$\begin{aligned} \Psi(z) = &\left\{4\,e^{-z_0}\left[1 + g\int_0^\infty \phi_L(z')S(z')\,dz'\right]\right\}e^{-z}\\ &+ O[g\,\log(z)\,e^{-2z}]. \end{aligned} \tag{3.14}$$

The quantity inside the square bracket then can be identified as the dimensionless *renormalized surface charge density*.

We still need to calculate the integral in Eq. (3.14). To simplify the problem, let us analyze the near field asymptotics of the integrand. Using Eqs. (3.5) and (3.9), we find that for $z, z_0 \ll 1$:

$$\phi_L(z) S(z) = -\frac{1}{16\pi(z+z_0)} - \frac{z_0^3}{8\pi(z+z_0)^4} + O(1). \quad (3.15)$$

As $z_0 \to 0$, integration (from 0 to ∞) of the first term gives $(16\pi)^{-1} \log z_0$, whereas that of the second term gives a finite number. Therefore the following limit exists:

$$C_s \equiv \lim_{z_0 \to 0} \left[\int_0^\infty \phi_L(z') S(z')\, dz' - \frac{1}{16\pi} \log z_0 \right]. \quad (3.16)$$

Numerical integration using Wolfram Mathematica gives

$$C_s \approx 0.005\,673. \quad (3.17)$$

Now we can use this result to reexpress the integral in Eq. (3.14) in the following form:

$$\int_0^\infty \phi_L(z') S(z')\, dz' = \frac{1}{16\pi} \log z_0 + C_s.$$

Further using Eq. (3.11) to trade z_0 in for η, we finally obtain the leading order far field asymptotics of $\Psi(z)$ (in the strongly charged limit):

$$\Psi(z) = 4\left[1 - \frac{g}{16\pi} \log\left(\frac{\eta}{2}\right) + g\, C_s + O(\eta^{-1})\right] e^{-z} + O[g \log(z)\, e^{-2z}]. \quad (3.18)$$

The coefficient of e^{-z} defines the *renormalized surface charge density* $\eta_R(\eta, g)$ of a highly charged surface, calculated to the leading orders in g and in η:

$$\eta_R(\eta, g) = 4 - 4\, g\left[\frac{1}{16\pi} \log\left(\frac{\eta}{2}\right) - C_s\right] + O(\eta^{-1}) + O(g^2). \quad (3.19)$$

In the dilute and strongly charged limit, $g \to 0, \eta \to \infty$, and $\eta_R \to 4$, which is what we obtained in Paper 1.

Lau [20] studied the one-loop correction to surface charge density of an infinitely thin charged plate inside an $1\!:\!-1$ electrolyte. We note that boundary conditions used by Lau are different from ours.

IV. $m\!:\!-n$ ASYMMETRIC ELECTROLYTE

For the generic case of an $m\!:\!-n$ electrolyte, there is no closed form for the 0th order solution $\Psi_0(z)$ (except for the cases of $2\!:\!-1$ and $1\!:\!-2$). Nevertheless, we can find both near field and far field expansions up to arbitrary orders. As is shown in Eqs. (22) and (30) of Paper 1 [21], the leading order near field and far field asymptotics of $\Psi_0(z)$ are given by

$$\Psi_0(z) = \Upsilon_{m,n}(z+z_0) \sim \begin{cases} \frac{1}{n} \log \frac{2(m+n)}{n(z+z_0)^2}, & z \to 0; \\ c_1^{m,n}\, e^{-(z+z_0)}, & z \to \infty, \end{cases} \quad (4.1)$$

where $\Upsilon_{m,n}(w)$ is a universal function that only depends on two integers m, n. Note that the near field asymptotics is valid only for strongly charged plates, for which $z_0 \ll 1$. The numerical values of $c_1^{m,n}$ were calculated and tabulated for many cases in Paper 1. Unlike the case of symmetric electrolytes, however, here we shall *not* impose the boundary conditions (2.17). Instead, we shall first obtain a globally well-behaved approximation for the mean potential $\Psi(z)$, and then determine the value of z_0 by imposing Eq. (2.14).

The near and far field asymptotics of the correlation energy are given by Eqs. (5.14a) and (5.26) in Paper 1:

$$\Delta\varepsilon_1(z) \sim \begin{cases} -\frac{3}{16\pi(z+z_0)}, & z \to 0; \\ \frac{(\log 3)(m-n) c_1^{m,n}}{16\pi}\, e^{-(z+z_0)}, & z \to \infty. \end{cases} \quad (4.2)$$

The function $S(z)$ is related to $\Psi_0(z)$ and $\Delta\varepsilon_1(z)$ via Eq. (2.12). Its far field and near field asymptotics are

$$S(z) \equiv \mathcal{S}(z+z_0) \sim \begin{cases} -\frac{3n}{8\pi(z+z_0)^3}, & z \to 0; \\ -s_{m,n}\, c_1^{m,n}\, e^{-(z+z_0)}, & z \to \infty, \end{cases} \quad (4.3)$$

where

$$s_{m,n} \equiv \frac{\log 3}{16\,\pi} (m-n)^2. \quad (4.4)$$

For symmetric electrolyte, $s_{m,n} = 0$, and $S(z)$ scales as e^{-2z} in the far field.

Two homogeneous solutions ϕ_R, ϕ_L to Eq. (2.19) were already formally constructed in Eqs. (2.21) and (2.25). The factor f_1 in Eq. (2.25) depends on the parameter z_0, and can be found by imposing the boundary condition Eq. (2.17b). Using Eqs. (4.1), (2.21), and (2.25), we determine the leading order near field asymptotics of $\phi_{L,R}(z)$:

$$\phi_R(z) \sim \frac{2}{n(z+z_0)} + O(z+z_0), \quad (4.5a)$$

$$\phi_L(z) \sim \frac{2 f_1(z_0)}{n(z+z_0)} + \frac{n}{6}(z+z_0)^2. \quad (4.5b)$$

Now imposing the boundary condition Eq. (2.20a) on Eq. (4.5b), we find [cf. Eq. (3.8) for the $1\!:\!-1$ case]

$$f_1(z_0) \sim \frac{n^2}{6} z_0^3 + O\big(z_0^5\big). \quad (4.6)$$

We can also obtain the far field asymptotics of $\phi_R(z)$:

$$\phi_R(z) = -\Psi_0'(z) \sim c_1^{m,n}\, e^{-(z+z_0)}. \quad (4.7a)$$

Combining this with Eq. (2.27), we obtain the leading order far field asymptotics of $\phi_L(z)$:

$$\phi_L(z) \sim \frac{1}{2 c_1^{m,n}}\, e^{(z+z_0)}. \quad (4.7b)$$

Note that the part $f_1(z_0)$ in Eq. (2.25) does not contribute to the leading order far field asymptotics of $\phi_L(z)$.

A. First order correction and secular term

The first order correction Eq. (2.29a) is repeated here:

$$\Psi_1(z) = \phi_R(z)\int_0^z \phi_L(z')S(z')\,dz' + \phi_L(z)\int_z^\infty \phi_R(z')S(z')\,dz'. \tag{4.8}$$

In the far field, $z \gg 1$, all functions in the second term can be replaced by their leading order far field asymptotics, Eqs. (4.7) and Eq. (4.3). The integral then becomes trivial:

$$\phi_L(z)\int_z^\infty \phi_R(z')S(z')\,dz' \sim -\frac{1}{4}c_1^{m,n}\,s_{m,n}\,e^{-(z+z_0)}. \tag{4.9}$$

By the same token, we can also replace $\phi_R(z)$ in front of the first integral in Eq. (4.8) by its far field asymptotics. This leads to the following asymptotics for $\Psi(z)$ (up to the order of g) in the far field regime:

$$\Psi(z) = \Psi_0(z) + g\,\Psi_1(z) \sim \left[1 - \frac{1}{4}g\,s_{m,n} + g\int_0^z \phi_L(z')S(z')\,dz'\right]c_1^{m,n}\,e^{-(z+z_0)}. \tag{4.10}$$

Inside the bracket, the first term (independent of g) comes from the nonlinear PB theory, whereas the other two terms (both linear in g) come from the electrostatic correlations.

We still need to calculate the remaining integral in Eq. (4.10). Let us first introduce a sufficiently large number z^* so that for $z' > z^*$, we can use far field asymptotics for $\phi_L(z')$ and $S(z')$, Eqs. (4.7) and (4.3). The portion of integral from z^* to z can then be approximately calculated:

$$g\int_{z^*}^z \phi_L(z')S(z')\,dz' \sim -\frac{1}{2}g\,s_{m,n}\,(z - z^*). \tag{4.11}$$

The integral therefore *grows linearly with z without bound* as $z \to \infty$. Substituting this back into Eq. (4.10), we see that the correction due to electrostatic correlations becomes much larger than $\Psi_0(z)$, the mean field potential predicted by PB, for sufficiently large z. Such a perturbative correction is usually called a *secular term* and indicates the breakdown of regular perturbation method, in the regime $g\,s_{m,n}\,z \geqslant 1$. A perturbation problem with secular term is called a *singular perturbation problem.*

B. Renormalization group (RG) method

There are many kinds of singular perturbation problems, and there seems to be no existing universal method capable of dealing with all problems. Heuristically speaking, the reason underlying this unsatisfactory *status quo* is that regular perturbation method may break down in many different ways, and discovery of the most relevant method is necessarily led by an intuitive understanding of the particular problem being studied. For the case of perturbation series containing a secular term, the most efficient method is the renormalization group transformation [22].

In Eqs. (2.29a) and (2.28), we constructed the Green's function $H(z,z')$ and $\Psi_1(z)$ such that they satisfy the homogeneous boundary condition at $z = 0$, Eq. (2.17b). We shall now relax these boundary conditions and add to $\Psi_1(z)$ an arbitrary homogeneous solution $C\,\phi_R(z)$ [23]. The resulting function still satisfies the ODE Eq. (2.11). The total mean potential $\Psi(z)$ can then be written as

$$\begin{aligned}\Psi(z,z_0,C) &\equiv \Psi_0(z,z_0) + g[\Psi_1(z,z_0) + C\,\phi_R(z,z_0)]\\ &= \Psi_0(z,z_0) + g\,\phi_L(z,z_0)\int_z^\infty \phi_R(z',z_0)S(z',z_0)\,dz'\\ &\quad + g\,\phi_R(z,z_0)\left[C + \int_0^z \phi_L(z',z_0)S(z',z_0)\,dz'\right].\end{aligned} \tag{4.12}$$

Note that we have explicitly shown the dependence of various functions on the parameter z_0 as well. Among these, ϕ_R and S depend on z and z_0 only through the sum $z + z_0$, whereas ϕ_L depends on two variables in a nonadditive way; see Eqs. (2.25) and (4.6).

The perturbative solution Eq. (4.12) automatically satisfies the boundary condition at $z = \infty$ [Eq. (2.14b)], and we still need to impose the other BC, Eq. (2.14a), at $z = 0$. On the other hand, Eq. (4.12) contains two arbitrary parameters z_0, C. Therefore these two parameters cannot be truly independent of each other. In another word, if we tune C, there must be a corresponding way to tune z_0, such that the solution Eq. (4.12) remains invariant [24]. This consideration establishes the existence of the renormalization group transformation.

Let us vary C and z_0 simultaneously such that the mean potential Eq. (4.12) is invariant up to the order of g:

$$\begin{aligned}O(g^2) = d\Psi(z,z_0,C) &= \frac{\partial\Psi}{\partial z_0}dz_0 + \frac{\partial\Psi}{\partial C}dC\\ &= \phi_R(z,z_0)(-dz_0 + g\,dC) + g\left(\frac{\partial\Psi_1}{\partial z_0} + C\,\frac{\partial\phi_R}{\partial z_0}\right)dz_0,\end{aligned} \tag{4.13}$$

where we have used the following identities:

$$\frac{\partial\Psi_0}{\partial z_0} = \frac{\partial\Psi_0}{\partial z} = \frac{\partial\Psi}{\partial C} = -\phi_R(z,z_0). \tag{4.14}$$

Applying the argument of dominant balance to Eq. (4.13), we easily see that $dz_0 \sim g\,dC$, and hence the bracket in Eq. (4.13), being linear in $g\,dz_0$, is of higher order in g and therefore can be neglected, since we only keep terms of order g. Consequently we find the following first order *renormalization group equation*:

$$dz_0 = g\,dC. \tag{4.15}$$

Integrating once, we find the relation between z_0 and C:

$$z_0(C) = g\,C + \bar{z}_0, \tag{4.16}$$

where $\bar{z}_0$ is a constant to be determined later by boundary condition. Therefore, replacing z_0 by $z_0(C)$ in Eq. (4.12), we are guaranteed to obtain a one-parameter family of solutions (parameterized by C) that are equivalent to each other up to the order of g:

$$\begin{aligned}\Psi(z,z_0(C),C) &= \Psi_0(z,z_0(C)) + g\,\Psi_1(z,z_0(C)) + g\,C\phi_R(z,z_0(C))\\ &= \Upsilon[z+z_0(C)] + g\,\phi_L(z,z_0(C))\int_z^{\infty}\Upsilon'[z'+z_0(C)]\mathcal{S}[z'+z_0(C)]\,dz',\\ &\quad - g\,\Upsilon'[z+z_0(C)]\left\{C + \int_0^z \phi_L(z',z_0(C))\mathcal{S}[z'+z_0(C)]\,dz'\right\}.\end{aligned} \tag{4.17}$$

Now comes the most crucial step of the RG transformation. We shall bootstrap the parameter C to be a *function* of z, $C(z)$, such that the approximate solution Eq. (4.17) is free of the secular term. Comparing with Eq. (4.11) we easily see that the choice

$$C(z) = \tfrac{1}{2}s_{m,n}\,z \tag{4.18}$$

fulfills this purpose. Let us check this explicitly. Upon the aforementioned replacement, the integral inside the bracket in Eq. (4.17) becomes

$$\int_0^z \phi_L(z',g\,s_{m,n}\,z'/2+\bar{z}_0)S(z',g\,s_{m,n}\,z'/2+\bar{z}_0)\,dz'. \tag{4.19}$$

We can use the far field asymptotics for two functions, Eq. (4.7b) and (4.3), in the integrand:

$$\phi_L(z',g\,s_{m,n}\,z'/2+\bar{z}_0) \sim \frac{1}{2\,c_1}e^{\alpha z'+\bar{z}_0}, \tag{4.20}$$

$$S(z',g\,s_{m,n}\,z'/2+\bar{z}_0) \sim -s_{m,n}c_1^{m,n}\,e^{-(\alpha z'+\bar{z}_0)}, \tag{4.21}$$

where

$$\alpha = 1 + g\,s_{m,n}/2. \tag{4.22}$$

Using these in the integral Eq. (4.19), we find that it contains the following secular term:

$$\text{Integral} = -\tfrac{1}{2}\,s_{m,n}\,z + \text{finite}, \tag{4.23}$$

which is exactly canceled by our choice of $C(z)$, Eq. (4.18). In other words, we have proved that the following limit exists:

$$h_{m,n}(\bar{z}_0) \equiv \lim_{z\to\infty}\left[\frac{1}{2}\,s_{m,n}\,z \right. \tag{4.24}$$

$$\left. + \int_0^z \phi_L(z',g\,s_{m,n}z/2+\bar{z}_0)S(\alpha z'+\bar{z}_0)\,dz'\right]. \tag{4.25}$$

Note that Eq. (4.18) is not the only way to remove the secular term. In fact, there are an infinite number of choices that are equally good, characterized by one arbitrary constant C_0: $C(z) = \frac{1}{2}s_{m,n}\,z + C_0$. We shall see below why the particular choice $C_0 = 0$ is the most convenient one.

Substituting Eq. (4.18) back into Eq. (4.17) we find the *renormalized* average potential:

$$\begin{aligned}\Psi^R(z,\bar{z}_0) &= \Psi(z,z_0[C(z)],C(z))\\ &= \Psi_0(z,z_0[C(z)]) + g\,\Psi_1(z,z_0[C(z)]) + g\,C(z)\phi_R(z,z_0[C(z)])\\ &= \Upsilon(\alpha z+\bar{z}_0) + g\,\phi_L(z,(\alpha-1)z+\bar{z}_0)\int_z^{\infty}\phi_R(\alpha z'+\bar{z}_0)S(\alpha z'+\bar{z}_0)\,dz'\\ &\quad + g\,\phi_R(\alpha z'+\bar{z}_0)\left[\frac{1}{2}\,s_{m,n}\,z + \int_0^z \phi_L(z',g\,s_{m,n}z/2+\bar{z}_0)S(\alpha z'+\bar{z}_0)\,dz'\right].\end{aligned} \tag{4.26}$$

C. Renormalized potential solves modified PBE

It remains to be shown that the renormalized potential Eq. (4.26) is still an approximate solution to Eq. (2.6a) up to order of g. [Of course, with the correlation energy given by its first order approximation $\Delta\varepsilon_1(z)$.] This can be easily done as follows. Firstly, let us note that the perturbation solution $\Psi(z,z_0[C],C)$, whose first order expression was shown in Eq. (4.17), satisfies Eq. (2.6a), for arbitrary *given* constants $C,\bar{z}_0$. Note that the same equation would also hold if we replace the parameters $C,z_0(C)$ by functions of $C(z)$, and $z_0(C(z))$ *after the derivatives have been taken*. Let us further define "partial derivatives":

$$\frac{\partial\Psi^R}{\partial z} \equiv \frac{\partial\Psi}{\partial z}(z,C,z_0)\bigg|_{C=C(z),z_0=z_0(C(z))}, \tag{4.27a}$$

$$\frac{\partial^2\Psi^R}{\partial z^2} \equiv \frac{\partial^2\Psi}{\partial z^2}(z,C,z_0)\bigg|_{C=C(z),z_0=z_0(C(z))}. \tag{4.27b}$$

Our discussion above then shows that

$$\begin{aligned}&-\frac{\partial^2\Psi^R}{\partial z^2} + \frac{1}{m+n}\left[e^{n\Psi^R(z)-n^2\Delta\varepsilon(z)} - e^{-m\Psi^R(z)-m^2\Delta\varepsilon(z)}\right]\\ &= O(g^2).\end{aligned} \tag{4.28}$$

Therefore the renormalized potential Ψ^R would solve the modified PB if the following identity holds:

$$\frac{d^2\Psi^R}{dz^2} = \frac{\partial^2\Psi^R}{\partial z^2} + O(g^2). \tag{4.29}$$

Now, let us calculate the first order full derivative of the renormalized potential $\Psi^R(z,\bar{z}_0)$ w.r.t. z, using Eq. (4.26) and the chain rule:

$$\frac{d\Psi^R}{dz} = \frac{\partial\Psi}{\partial z} + \frac{dC}{dz}\left(\frac{\partial\Psi}{\partial C} + \frac{dz_0}{dC}\frac{\partial\Psi}{\partial z_0}\right). \tag{4.30}$$

[Here and below C and z_0 are treated as functions of z via Eqs. (4.16) and (4.18).] But the sum inside the bracket in Eq. (4.30) vanishing is precisely the content of the renormalization group equation Eq. (4.13). Hence we have

$$\frac{d\Psi^R}{dz} = \frac{\partial\Psi}{\partial z} + O(g^2). \tag{4.31}$$

Obviously, if we work out the perturbation series up to infinite order, Eq. (4.31) would become an exact result, valid up to arbitrary order of g.

Let us take one more derivative with respect to z:

$$\begin{aligned}\frac{d^2\Psi^R}{dz^2} &= \frac{d}{dz}\left[\frac{\partial\Psi}{\partial z} + O(g^2)\right]\\ &= \frac{\partial^2\Psi}{\partial z^2} + \frac{dC}{dz}\left(\frac{\partial}{\partial C} + \frac{dz_0}{dC}\frac{\partial}{\partial z_0}\right)\frac{\partial\Psi}{\partial z} + O(g^2)\\ &= \frac{\partial^2\Psi}{\partial z^2} + \frac{dC}{dz}\frac{\partial}{\partial z}\left(\frac{\partial\Psi}{\partial C} + \frac{dz_0}{dC}\frac{\partial\Psi}{\partial z_0}\right) + O(g^2)\\ &= \frac{\partial^2\Psi}{\partial z^2} + O(g^2),\end{aligned} \tag{4.32}$$

where in the third line we have exchanged the order of partial derivatives and have used the identity

$$\frac{\partial}{\partial z}\frac{dz_0}{dC} = 0. \tag{4.33}$$

This is because dz_0/dC is considered as a function of C and does not explicitly contain z. In the fourth line, we have used again the renormalization group equation (4.13). Thus the renormalized potential indeed satisfies the modified PBE up to the order of g.

D. Renormalized surface charge density and renormalized Debye length

The renormalized potential Eq. (4.26) contains one undetermined parameter $\bar{z}_0$, which must be fixed by enforcing the boundary condition at $z = 0$:

$$\left.\frac{d\Psi^R}{dz}\right|_{z=0} = -\eta. \tag{4.34}$$

Using Eq. (4.31) and (4.17), we have (with z always set to zero after taking the derivative)

$$\begin{aligned}\frac{d\Psi^R}{dz} &= \frac{\partial\Psi^R}{\partial z} = \frac{\partial}{\partial z}(\Psi_0 + g\,\Psi_1 + g\,C\,\phi_R)\\ &= \left.\frac{\partial\Psi_0}{\partial z}\right|_0 + g\left.\frac{\partial\Psi_1}{\partial z}\right|_0 + g\,C(z=0)\left.\frac{\partial\phi_R}{\partial z}\right|_0.\end{aligned} \tag{4.35}$$

Now the second term vanishes because it is constructed in this way [see Eqs. (2.17b) and (4.8)], whereas the third term vanishes because $C(z)$ does so [see Eq. (4.18)]. Therefore the physical boundary condition is transformed into the following simple form:

$$\left.\frac{\partial\Psi_0}{\partial z}\right|_{z=0} = -\eta. \tag{4.36}$$

Interestingly enough, this is identical to the boundary condition Eq. (2.17a) we used previously for $\Psi_0(z)$. Now using the near field asymptotics of $\Psi_0(z)$, Eq. (4.1), we find that to the order of $O(g^0)$:

$$\bar{z}_0 = \frac{2}{n\eta} + O(\eta^{-2}). \tag{4.37}$$

Let us now analyze the leading order far field asymptotics of the renormalized potential (4.26). The far field asymptotics of the first term can be directly written using Eq. (4.1):

$$\text{1st term} \sim c_1^{m,n}\, e^{-\alpha z - \bar{z}_0}. \tag{4.38a}$$

To obtain the asymptotics of the second term, we use Eqs. (4.7) and Eq. (4.3):

$$\text{2nd term} \sim -\frac{1}{4\,\alpha} c_1^{m,n} g\, s_{m,n} e^{-\alpha z - \bar{z}_0}. \tag{4.38b}$$

Since we are calculating quantities only up to the order of g, we can replace α in the denominator in Eq. (4.38b) by *unity* and rewrite the equation as

$$\text{2nd term} \sim -\tfrac{1}{4} c_1 g\, s_{m,n} e^{-\alpha z - \bar{z}_0} + O(g^2). \tag{4.38c}$$

Finally the third term goes asymptotically as

$$\text{3rd term} \sim g\, c_1^{m,n}\, h_{m,n}(z_0)\, e^{-\alpha z - \bar{z}_0}, \tag{4.38d}$$

where the function $h_{m,n}(z_0)$ is defined in Eq. (4.25). Note that all three terms Eqs. (4.38a), (4.38b), and (4.38d) are free of secular term and decay with the same length scale $1/\alpha$, which shall be identified with the renormalized Debye length (up to the first order of g).

We still need to calculate the function $h_{m,n}(z_0)$ in order to fully determine the far field asymptotics of the renormalized potential. Since this function appears together with g, and since we are only calculating quantities up to the order of g, we are allowed to set $g = 0$ inside the definition of $h_{m,n}(z_0)$, Eq. (4.25). This leads to

$$\begin{aligned}h_{m,n}(\bar{z}_0) &= \lim_{z\to\infty}\left[\frac{1}{2}\, s_{m,n}\, z + \int_0^z \phi_L(z',\bar{z}_0) S(z' + \bar{z}_0)\, dz'\right]\\ &\equiv h^0_{m,n}(\bar{z}_0).\end{aligned} \tag{4.39}$$

Note that the large z (IR) divergence in the above integral has already been canceled by our renormalization procedure. On the other hand, the integral also exhibits logarithmic divergence as $z_0 \to 0$ (UV divergence). Using the near field asymptotics of $\phi_L(z)$ and $S(z)$ in the integral, we see that for small z_0, it scales as

$$\begin{aligned}&\int_0^{z_*}\left(-\frac{3n}{8\pi}\right)\frac{1}{(z' + \bar{z}_0)^3}\,\frac{n}{6}(z' + \bar{z}_0)^2\, dz'\\ &\sim \frac{n^2}{16\pi}\log\left(\frac{\bar{z}_0}{z_*}\right),\end{aligned} \tag{4.40}$$

where z_* is an undetermined small number such that near field asymptotics can be used in the regime (z_0, z_*). Consequently we expect that the following double limit exists:

$$C_s^{m,n} = \lim_{\bar{z}_0 \to 0} \lim_{z \to \infty} \left\{ -\frac{n^2}{16\pi} \log \bar{z}_0, \right. \\ \left. + \int_0^z \left[\phi_L(z') S(z') + s_{m,n}/2 \right] dz' \right\}, \tag{4.41}$$

and Eq. (4.38d) can be rewritten as

$$\text{3rd term} \sim g\, c_1^{m,n} \left[\frac{n^2}{16\pi} \log \bar{z}_0 + C_s^{m,n} \right] e^{-\alpha z - \bar{z}_0} + O(g^2). \tag{4.42}$$

Summing up Eqs. (4.38a), (4.38c), and (4.42), we finally obtain the leading order far field asymptotics of the renormalized average potential:

$$\Psi^R(z) \sim c_1^{m,n} \left[1 + g \left(\frac{n^2}{16\pi} \log \bar{z}_0 + C_s^{m,n} - \frac{1}{4} s_{m,n} \right) \right] e^{-\alpha z - \bar{z}_0}. \tag{4.43a}$$

$$\equiv \eta_R\, e^{-\alpha z}. \tag{4.43b}$$

The coefficient α therefore is the inverse length scale over which the average electrostatic potential decays in the far field (recall we are using dimensionless units in this work). It is therefore *the ratio between the non-renormalized Debye length and the renormalized one*:

$$\alpha = \frac{\kappa^R}{\kappa} = 1 + \frac{1}{2} g\, s_{m,n} + O(g^2), \tag{4.44}$$

where $s_{m,n}$ is defined in Eq. (4.4).

In the strongly charged regime, $\bar{z}_0$ is a small number and can be neglected in the exponent of Eq. (4.43). We can further use Eq. (4.37) to express $\bar{z}_0$ inside the logarithm in terms of the bare surface charge density η, and use Eq. (4.4) to replace $s_{m,n}$. We finally obtain the following result for the *one-loop renormalized surface charge density* for a strongly charged plate:

$$\eta_R^{m,n}(\eta, g) = c_1^{m,n} \left[1 - g \left(\frac{n^2}{16\pi} \log \left(\frac{n\,\eta}{2} \right) \right. \right. \\ \left. \left. - C_s^{m,n} + \frac{\log 3}{64\pi} (m-n)^2 \right) \right] + O(g^2, \eta^{-1}). \tag{4.45}$$

We can check explicitly that Eq. (4.45) reduces to Eq. (3.19) for the case $m = n = 1$ (noticing that $c_1^{1,1} = 4$).

Except for the some special cases, we are not able to calculate the constant $C_s^{m,n}$ analytically. For the cases of $1\!:-1$, $2\!:-1$, and $1\!:-2$, all parts in Eq. (4.41) are known explicitly, and we can calculate $C_s^{m,n}$ numerically:

$$C_s^{1,1} \approx 0.005\,673, \tag{4.46}$$

$$C_s^{2,1} \approx 0.053\,428, \tag{4.47}$$

$$C_s^{1,2} \approx 0.018\,332. \tag{4.48}$$

In general, this coefficient seems to be rather small and increases with valences of counterions as well as coions. Finally let us also quote the corresponding exact results for $c_1^{m,n}$ from Paper 1:

$$c_1^{1,1} = 4, \tag{4.49}$$

$$c_1^{2,1} = 6, \tag{4.50}$$

$$c_1^{1,2} = 6(2 - \sqrt{3}). \tag{4.51}$$

The results for case $1\!:-1$ have of course already been shown in Eqs. (3.19) and (3.17).

V. COMPARISON WITH SIMULATIONS

In this section, we shall compare our analytic results with Monte Carlo simulation of a strongly charged surface inside a $1\!:-2$ electrolyte. For this purpose, we first need to represent various theoretical results in physical units.

A. Charge density in the far field regime

The dimensionless mean potential as predicted by PB is given by Eq. (A6). In the far field limit, it reduces to

$$\Psi(z) \sim 6(2 - \sqrt{3})\, e^{-\kappa(z + z_0)}, \tag{5.1}$$

with z_0 related to the Gouy-Chapman length via Eqs. (2.15a) and (4.37). Now the corresponding physical charge density is given by [using Eq. (2.5b)]

$$\rho_q^{PB}(z) = -\epsilon \Phi_0''(z) = -\frac{\epsilon}{\beta q} \Psi_0''(z) \\ \sim q\, \zeta^{PB} e^{-\kappa z}, \tag{5.2}$$

where

$$\zeta^{PB} \equiv -6(2 - \sqrt{3}) \frac{\kappa^2}{4\pi b} e^{-\kappa\mu/2}. \tag{5.3}$$

Similarly, the far field charge density predicted by SCFT [Eq. (4.43)] is

$$\rho_q^{SC}(z) = -\frac{\epsilon (\Psi^R)''(z)}{\beta q} \sim q\, \zeta^{SC} e^{-\alpha\kappa z}, \tag{5.4}$$

where

$$\zeta^{SC} \equiv \eta_R^{1,2} \frac{(\alpha\kappa)^2}{4\pi b}. \tag{5.5}$$

and η_R is given in Eq. (4.45) and α in Eq. (4.44), with $m = 1, n = 2$. Equations (5.2) and (5.4) shall be used to compare with Monte Carlo simulations. Note that both ζ^{PB} and ζ^{SC} have unit of $[length]^{-3}$.

B. Simulation methodology

We use the recently developed Brush Metropolis GPU code [25] to carry out MC simulations of $1\!:-2$ asymmetric primitive model electrolytes. In each simulation the system contains in total 65 536 ions with radii $r = 3.75$ Å. The geometry of the simulation domain is a spherical shell formed by two concentric spheres, with the inner surface uniformly charged. The radius of the inner surface is no less than 700 Å,

TABLE I. Renormalized surface charge densities η_R in logarithmic scales. Column 1: system label; column 2, bare Debye length (in Å); column 3, Gouy-Chapman length (in Å); column 4, simulation results of $\log \zeta$, obtained using Eq. (5.8), together with error bars; columns 5 and 6: the corresponding values predicted by our theory and PB as shown in Eqs. (5.3) and (5.5). Data fitting is performed using OringinLab Origin9.

Label	$1/\kappa$	μ	$\log(\zeta^N \text{Å}^3)$	$\log(\zeta^{SC} \text{Å}^3)$	$\log(\zeta^{PB} \text{Å}^3)$
1	59.09	19.00	-12.32 ± 0.09	-12.36	-12.18
2	42.59	6.90	-11.90 ± 0.24	-11.97	-11.52
3	34.53	19.00	-11.36 ± 0.09	-11.30	-11.11
4	25.11	19.00	-10.73 ± 0.15	-10.62	-10.48
5	20.18	12.00	-10.32 ± 0.04	-10.35	-10.04
6	18.01	9.18	-10.16 ± 0.24	-10.29	-9.81

which is at least 10 times larger than the Debye length. Consequently, the curvature effects can be neglected, and the inner surface behaves approximately as a *charged plate*. The distance between inner and outer surfaces is taken to be 8 to 15 Debye lengths, to ensure that there is a sufficiently large region where the influence of the outer surface is negligible. Finally, in all simulations, the temperature is set to 300 K and the relative dielectric constant of the solvent is chosen to be that of water $\epsilon = 78.3$, thus the Bjerrum length $b = 7.117$ Å. For the chosen parameters, the Debye length κ is substantially larger than b (see Table I) so that the expansion in the parameter g is expected to be valid. The simulation lengths are 5×10^5 MC steps for system 5 and 5×10^4 steps for the other systems; see Table I.

Using the simulation data, we measure the three-dimensional local charge density $\rho_q^N(z)$ as a function of distance z to the charged surface. Here the superscript N means *numerical*. One particular example is shown as the red curve in Fig. 1. The plot range is chosen to be in the far field regime of the inner surface, while the influences of the outer surface is negligible, so that our analytic results are applicable. It can be seen there that SCFT gives a much more precise result than the classical PB.

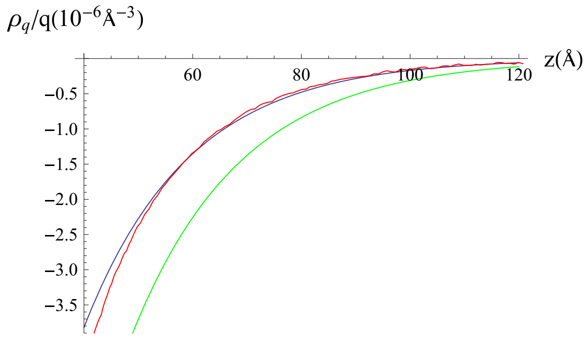

FIG. 1. Comparison of total charge density profile between simulation (red line), SCFT far field [Eq. (5.4), blue line] and PBE far field [Eq. (5.2), green line] in the far field. The Debye length is 20.18 Å and the Gouy-Chapman length is 12.00 Å (System 5 in Table I).

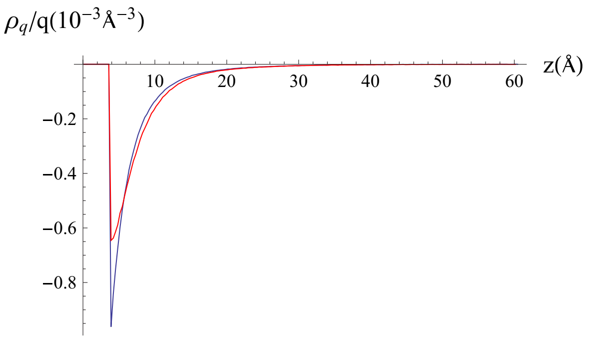

FIG. 2. Total charge density profiles for simulations with no image charge effect (red) and with image charge effect (blue). The Debye length and Gouy-Chapman are, respectively, 11.30 Å and 6.75 Å. This plot verifies that image charge effects are indeed negligible as long as the far field asymptotic is concerned. These data are not shown in Table I.

Similar to Eq. (5.4), the simulation result of charge density decays exponentially in the far field:

$$\rho_q^N(z) \sim q\, \zeta^N\, e^{-\alpha^N \kappa z}, \tag{5.6}$$

where

$$\zeta^N \equiv \eta_R^N \frac{(\alpha^N \kappa)^2}{4\pi b}. \tag{5.7}$$

Taking the logarithm, we find

$$\log\left(\rho_q^N(z)/q\right) = \log \zeta^N - \alpha^N \kappa z. \tag{5.8}$$

By linear fitting the logarithm of charge density, therefore, we can extract the values of ζ^N and α^N for each MC simulation. The results for ζ^N are shown in the fourth column of Table I. For all simulations, we find α^N [the ratio between bare Debye length and the renormalized Debye length; see Eq. (4.44)] is very close to unity, so we do not shown them. Comparison of ζ^N with the corresponding theoretical values (columns five and six of Table I, respectively) demonstrates that our one-loop SCFT results agree with numerical simulations within error, whereas results of classical PB almost always fall outside the range.

Finally, in Fig. 2 we plot the total charge density as a function of z for two simulations that only differ in the dielectric constant ϵ_1 of the plate. The black and red curves correspond to the cases where $\epsilon_1 = 0{,}78.3$, respectively. The corresponding difference in correlation energy is just $\delta\epsilon(z)$ in Eq. (2.30). As we can see, there is almost no difference as soon as z is a few μ away from the plate, suggesting that the dielectric constant of plate is indeed unimportant as long as one is interested in the far field regime. Consequently, it is legitimate to neglect the part of correlation energy due to image charge effects, $\delta\epsilon(z)$ in Eq. (2.30), at the very beginning, as we have done in Sec. II E.

It is important to note that in our theory, all ions are pointlike, while in simulations ions must have finite size. The agreement between theory and simulations therefore must depend on the choice of ion sizes. If ion diameters are much smaller than Bjerrum length, ions form bound pairs and clusters. If ion diameters are too large, steric interactions can no longer be ignored near the charged surface. In either case, approximation of pointlike ions is no longer valid, and our theory breaks down. A self-consistent field theory treatment of electrolytes with ion size taken into account is much more difficult and is beyond the scope of the present work.

VI. CONCLUSION AND ACKNOWLEDGEMENT

Equations (4.45) and (4.44) are the main results of this work. First order renormalization of Debye length by electrostatic correlation in asymmetric electrolytes was studied originally by Mitchell and Ninham [26] long ago, and our result Eq. (4.44) agrees with theirs. In a more recent work [27], we have also obtained an (approximate) analytic result for the renormalized Debye length of the primitive model of asymmetric electrolytes [28], where ions are charged hard spheres, and the density is not necessarily low. In the limit of low density and zero ion size, this result reduces to Eq. (4.44).

Equation (4.45) is more interesting because it demonstrates certain general features about the renormalization of surface charge density due to electrostatic correlations. The leading order renormalization is linear in $g = 4\pi\kappa b$. Comparison with simulation, however, demonstrates that Eq. (4.45) is quantitatively good as long as $1/\kappa$ is moderately larger than the Bjerrum length b and the Gouy-Chapman length μ. In the dilute and strongly charged $g \to 0, \eta \to \infty$, and Eq. (4.45) reduces to $c_1^{m,n}$, which is the prediction of nonlinear PB theory studied in Paper 1. For nonvanishing g, the one-loop renormalization contains a negative term logarithmic in η. Such a singular term can not be obtained by simple calculations. Furthermore, the magnitude of this term is proportional to n^2 and therefore increases strongly with the valence of counter ions. Therefore high-valence counterions can strongly renormalize the surface charge density downwards, as also seen in simulation, and can drive charge inversion if the bare surface charge density is sufficiently large. By contrast, the valence of coions only appear in the last two terms of Eq. (4.45), which are independent of the bare surface charge density. The valence of coions therefore plays a less important role in the renormalization of surface charge density, which is, of course, rather natural. Finally, let us emphasize again that all our results break down if counterions and coions form bound pairs, which happens if, for example, both species of ions are multivalent, and their densities are sufficiently high.

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APPENDIX: DETAILS OF THE TWO SPECIAL CASES: 2:−1 AND 1:−2 ASYMMETRIC ELECTROLYTES

In this appendix we give some results for 2: −1 and 1: −2 electrolytes. For these two special case we have closed form of $\Psi_0(z)$, $\phi_L(z)$ and $\phi_R(z)$.

For the case of 2: −1 electrolyte, the solution to PBE is

$$\Psi_0(z) = \log\left[\frac{1 + 4\,e^{-(z+z_0)} + e^{-2(z+z_0)}}{(1 - e^{-(z+z_0)})^2}\right]. \tag{A1}$$

Expanding to obtain the far field asympytotics according to Eq. (4.1), we get the coefficient $c_1^{2,1} = 6$. The full expression for the correlation energy $\delta\varepsilon(z) = g\,\delta\hat{\varepsilon}(z)$ is very complicated. We refer the readers to Ref. [9] for details. Here we only display its leading order near field and far field asymptotic behaviors:

$$\delta\hat{\varepsilon}(z) \sim \begin{cases} -\frac{3}{16\pi(z+z_0)}, & z \to 0; \\ \frac{3\log 3}{8\pi}\, e^{-z}, & z \to \infty. \end{cases} \tag{A2}$$

The function $S(z)$ is related to $\phi_0(z)$ and $\delta\hat{\epsilon}(z)$ via Eq. (2.12). Its far field and near field asymptotics are

$$S(z) \sim \begin{cases} -\frac{3}{8\pi(z+z_0)^3}, & z \to 0; \\ -\frac{3\log 3}{8\pi}\, e^{-z}, & z \to \infty. \end{cases} \tag{A3}$$

Two homogeneous solutions to Eq. (2.19) can also be found:

$$\phi_R(z) = -\phi_0'(z) = \frac{3\ \coth[(z+z_0)/2]}{2 + \cosh(z+z_0)}, \tag{A4a}$$

$$\begin{aligned}\phi_L(z) = {}& \frac{1}{12[2+\cosh(z+z_0)]} \\ & \times \{1 + 10\coth(z+z_0) + \cosh[2(z+z_0)] \\ & - 6(z+z_0)\coth[(z+z_0)/2]\} + f_1(z_0)\,\phi_R(z).\end{aligned} \tag{A4b}$$

The constant $f_1(z_0)$ is again determined by the boundary condition Eq. (2.17b):

$$\begin{aligned} f_1(z_0) &= \frac{1}{6}\,z_0 + \frac{1}{9}\left[1 - \frac{18}{3 + 2\cosh(z_0) + \cosh(2z_0)}\right] \\ &\quad \times \sinh(z_0) + \frac{1}{36}\sinh(2z_0) \\ &= \frac{1}{6}\,z_0^3 + O\left(z_0^4\right). \end{aligned} \tag{A5}$$

For the 1: −2 electrolyte, the mean potential is

$$\Psi_0(z) = \log\left[\frac{(1 + u e^{-(z+z_0)})^2}{1 - 4u e^{-(z+z_0)} + u^2 e^{-2(z+z_0)}}\right], \tag{A6}$$

where $u = 2 - \sqrt{3}$. Hence $c_1^{1,2} = 6u = 6(2 - \sqrt{3})$.

The leading order near field and far field asymptotic behaviors of the correlations energy are

$$\delta\hat{\varepsilon}(z) \sim \begin{cases} -\frac{3}{16\pi(z+z_0)}, & z \to 0; \\ -\frac{3u\log 3}{8\pi}\, e^{-z}, & z \to \infty. \end{cases} \tag{A7}$$

The function $S(z)$ is related to $\phi_0(z)$ and $\delta\hat{\epsilon}(z)$ via Eq. (2.12). Its far field and near field asymptotics are

$$S(z) \sim \begin{cases} -\frac{3}{4\pi(z+z_0)^3}, & z \to 0; \\ -\frac{3u\log 3}{8\pi}\, e^{-z}, & z \to \infty. \end{cases} \tag{A8}$$

The two homogeneous solutions are

$$\phi_R(z) = \frac{\phi_{Ld}(z)}{12u(u+e^{z+z_0})(u^2-4ue^{z+z_0}+e^{2(z+z_0)})} + f_1(z_0)\phi_R(z), \tag{A9a}$$

with

$$\begin{aligned}\phi_{Ld}(z) = {}& e^{-(z+z_0)}(u^5 - 9u^4e^{z+z_0} - 4u^3e^{2(z+z_0)}(-3z-3z_0+6\sqrt{3}+2) + 4u^2e^{3(z+z_0)}(-3z-3z_0\\ &+6\sqrt{3}-2) - 9ue^{4(z+z_0)} + e^{5(z+z_0)})\end{aligned} \tag{A10}$$

and

$$f_1(z_0) = \frac{1}{72}\left[\frac{e^{2z_0}}{u^2} - \frac{4e^{z_0}}{u} + 4ue^{-z_0} - u^2e^{-2z_0} + 12(-2\sqrt{3}+z_0)\right] + \frac{2ue^{z_0}(e^{2z_0}-u^2)}{(e^{4z_0}-2ue^{3z_0}+6u^2e^{2z_0}-2u^3e^{z_0}+u^4)}. \tag{A11}$$

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