Computing counterion densities at intermediate coupling

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By decomposing the Coulomb interaction into a long-distance component appropriate for mean-field theory, and a non-mean-field short distance component, we compute the counterion density near a charged surface for all values of the counterion coupling parameter. A modified strong-coupling expansion that is manifestly finite at all coupling strengths is used to treat the short-distance component. We find a nonperturbative correction related to the lateral counterion correlations that modifies the density at intermediate coupling.

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I. INTRODUCTION

The rise of biological physics has rekindled the long-standing interest in aqueous electrostatics [1]. Poisson-Boltzmann mean-field theory fails to describe a number of striking phenomena, such as charge inversion [2,3] and counterion-mediated attraction [4–14], that occur when strong correlations develop between multivalent counterions. Although there has been some success understanding aspects of counterion correlations using a variety of theoretical techniques [2–19] a physically transparent, quantitative theory spanning the entire range of counterion behavior is still lacking.

For quite some time, integral equations have provided a quantitative approach to computing charge densities near charge surfaces [4,5]. The drawback of these techniques, however, is their reliance on the summation of subclasses of cluster diagrams whose physical content is often unclear [20]. This has prompted a flurry of subsequent work based on a more direct physical understanding of counterion correlations [2,15], leading to approximations that are less quantitatively successful but seem to capture essential physics.

The introduction of field-theoretic methods to charged systems has led to the development of two systematic perturbation expansions valid in the limits of weak coupling (WC) [16,17], where mean-field theory is nearly valid, and strong coupling (SC) [18], where the ions are strongly associated with "fixed" macromolecular charge. For charged surfaces, the validity of each expansion is controlled by a single dimensionless coupling constant $\Gamma = l_B Q^2/\lambda$, where l_B is the Bjerrum length, $l_B Q^2$ is the distance at which two charges Qe interact with energy $k_B T$, and λ is the Gouy-Chapmann length, which represents the characteristic distance of the counterions from the surface.

While the WC expansion ($\Gamma \ll 1$) can be understood in terms of charge density fluctuations around solutions to the Poisson-Boltzmann equation, the SC expansion ($\Gamma \gg 1$) finds its success in perturbatively introducing counterion interactions through a Mayer cluster expansion [18]. Since the ions interact at long range, this expansion diverges term by term; however, in the case of the one-component plasma, the divergences can be subtracted by enforcing overall charge neutrality. Numerical simulations have demonstrated that this scheme not only correctly predicts the average counterion density in the strong-coupling limit, it also computes the form, *but not the magnitude*, of the corrections [22]. Finally, Burak *et al.* [19] have introduced a test-charge theory (TCT) which successfully reproduces both the long- and short-distance limits for the counterion density, though it fails to accurately capture the charge contact density at the surface, which is known exactly for a charged surface in a semi-infinite space.

This paper introduces an alternative method to compute the counterion density in the coupling regime where neither the SC nor WC expansion is valid. This is accomplished by decomposing the Coulomb interaction into long- and short-distance components in the spirit of the Weeks-Chandler-Andersen theory of simple fluids [21]. This decomposition seamlessly joins the perturbative weak-coupling [17] and strong-coupling [18,22] expansions, and provides a natural framework to understand how to develop simple continuum theories that, nevertheless, capture the essential physics of short-distance counterion correlations. Similar decomposition schemes have been introduced in the context of interacting electrons, allowing the combination of density functional theory at short distances with techniques valid only at long distances [23].

My method has the advantage of naturally allowing a more intuitive understanding of counterion correlations in order to make quantitative predictions in a range of physically relevant conditions. In contrast, the traditional SC expansion [18] is physically difficult to understand because it is formally a cluster expansion. One naively expects it to be invalid precisely when the counterions are strongly interacting since the density of ions near a charged surface in the strong-coupling limit will be quite large and the counterions will be strongly correlated laterally. I will also introduce a modified expansion that is manifestly finite but recovers the SC corrections in the appropriate limit. By rewriting the strong-coupling expansion as an expansion in a different parameter, I identify a nonperturbative correction to the density which is related to the short-distance correlations of the counterions [3]. This naturally leads to a physical interpreta-

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tion of the corrections to the SC expansion as an expansion in the density of counterions making excursions away from the surface. In the SC limit, these excursions are rare and the corrections to the SC limit are small even when the counterions near the surface are highly correlated. This approximation gives good quantitative agreement with simulations at large but intermediate coupling ($\Gamma \geqslant 10$).

In Sec. II, I introduce the decomposition by mapping the one-component plasma to a one-parameter family of field theories. In Sec. III, I discuss appropriate expansions for the short-distance part of the Coulomb interaction. I will make contact with the SC expansion, and introduce an alternative expansion which is manifestly finite as the coupling constant becomes large. In Sec. IV, I quantitatively explore the charge density near a charged surface and compare the results to simulations. Finally, in Sec. V, I summarize the results and discuss some outstanding issues.

II. THE MODEL

Consider the primitive model for a charged surface neutralized by pointlike counterions of the opposite charge Qe in a dielectric medium with dielectric constant ϵ. We define the Bjerrum length $l_B = e^2/(\epsilon k_B T)$, and note that $l_B Q^2$ is the distance that two charges of valence Q interact with an energy $k_B T$. To proceed, introduce a length scale ℓ, and define $V_s(\mathbf{r}) = l_B Q^2 e^{-r/\ell}/r$ and $V_l(\mathbf{r}) = l_B Q^2 (1 - e^{-r/\ell})/r$. The length ℓ is currently arbitrary and will be chosen later to optimize the calculation. The Hamiltonian for ions of charge Qe centered at positions $\mathbf{R}_\alpha$ interacting with a surface of charge density $n_f(\mathbf{r}) = \sigma\delta(z)$ is given by

$$\mathcal{H} = \frac{1}{2}\int d^3r\, d^3r' N(\mathbf{r})[V_s(\mathbf{r}-\mathbf{r}') + V_l(\mathbf{r}-\mathbf{r}')]N(\mathbf{r}'), \quad (1)$$

where $N(\mathbf{r}) = n_f(\mathbf{r})/Q - \Sigma_\alpha \delta(\mathbf{r}-\mathbf{R}_\alpha)$. It is understood in this expression that ion self-interactions, which arise only from $V_s(\mathbf{r})$, are to be neglected.

The long-range interaction can be decoupled by introducing a continuous field ϕ through a Hubbard-Stratonovich transformation, resulting in the partition function for N ions of radius a,

$$Z_N \propto \int \mathcal{D}\phi \prod_{\alpha=1}^{N} \frac{d^3R_\alpha}{a^3} e^{-S'(\phi;\mathbf{R}_1,\ldots,\mathbf{R}_N)}$$

where $S' = S_s + S_l$,

$$S_s = \frac{1}{2}\int d^3r\, d^3r' \frac{n_f(\mathbf{r})}{Q} V_s(|\mathbf{r}-\mathbf{r}'|)\frac{n_f(\mathbf{r})}{Q} - \sum_\alpha \int d^3r\, n_f(\mathbf{r}) V_s(|\mathbf{r}-\mathbf{R}_\alpha|)/Q + \sum_{\alpha<\beta} V_s(|\mathbf{R}_\alpha - \mathbf{R}_\beta|), \quad (2)$$

and

$$S_l = \frac{1}{8\pi l_B Q^2}\int d^3r[(\nabla\phi)^2 + \ell^2(\nabla^2\phi)^2] + i\int d^3r \frac{N(\mathbf{r})\phi(\mathbf{r})}{Q}. \quad (3)$$

Since the first term of S_s plays no role in the counterion density, we will suppress it in the remainder of the paper. The counterion positions $\mathbf{R}_\alpha$ are implicitly restricted to be over the volume of space that can be occupied by the counterions. I impose the boundary condition that derivatives of ϕ vanish at infinity. From Eq. (3), the integral over the constant mode of ϕ leads to the condition that $\int d^3x\, n(\mathbf{x}) = 0$—only charge neutral configurations can occur.

To proceed, I will utilize the grand canonical ensemble $Z = \Sigma_N e^{\beta\mu} Z_N/N!$. Notice, however, that if I use Eq. (2) for Z_N, all terms of this sum vanish unless N is such that the entire system is charge neutral. This is a direct consequence of the boundary conditions on ϕ and Gauss' law—if the electric field vanishes at infinity, nonneutral configurations make no contribution.

As in the case of $\ell = 0$ [17], it is useful to retain the full sum over N in the grand partition function Z, now written as

$$Z \propto \sum_N \frac{1}{N!}\left(\frac{\kappa^2}{4\pi l_B Q^2}\right)^N \int \mathcal{D}\phi \prod_{\alpha=1}^{N} d^3R_\alpha \rho_0(\mathbf{r}_\alpha) e^{-S'}, \quad (4)$$

where the length κ^{-1} is defined by $\kappa^2/(4\pi l_B Q^2) = e^{\beta\mu}/a^3$, a is the de Broglie thermal wavelength of the ions, and μ is the chemical potential [17]. Now define the partial partition function with integrals only over the counterion positions,

$$Z_s = \sum_{N=0}^{\infty} \frac{1}{N!}\int \mathcal{D}\mathbf{R} \exp\left(-\sum_{\alpha<\beta} V_s(\mathbf{R}_\alpha - \mathbf{R}_\beta)\right), \quad (5)$$

where $\mathcal{D}\mathbf{R} = \Pi_\alpha d^3R_\alpha \rho_0(\mathbf{R}_\alpha)$,

$$\rho_0 = \frac{\kappa^2}{4\pi l_B Q^2} e^{F + i\phi}, \quad (6)$$

and

$$F(\mathbf{r}) = \int d^3r' V_s(|\mathbf{r}'-\mathbf{r}|) n_f(\mathbf{r}')/Q. \quad (7)$$

This leaves $Z \propto \int \mathcal{D}\phi\, e^{-S}$, where

$$S = \frac{1}{4\pi l_B Q^2}\int d^3r\left(\frac{1}{2}(\nabla\phi)^2 + \frac{\ell^2}{2}(\nabla^2\phi)^2\right) - \ln Z_s[\rho_0(\mathbf{r})]. \quad (8)$$

It is also straightforward to derive an expression for the average counterion density, which turns out to be $\langle\rho(\mathbf{r})\rangle = \delta \ln Z_s/\delta F(\mathbf{r})$.

Equation (8) provides a one-parameter family of equivalent and exact field-theoretic formulations of the one-component plasma in an externally imposed field. When $\ell = 0$, this expression recovers the traditional mapping of the one-component plasma to a scalar field theory [17]. For finite ℓ, the additional higher-order gradient of ϕ "turns off" the

Coulomb interaction between ions mediated by the continuous field. The short-distance interaction is then encoded directly in the term $\ln Z_s[\rho_0]$.

Since this formulation is exact, the partition function is independent of the choice of ℓ. To proceed, make the following approximations: (1) use the mean-field approximation for the long-distance interaction (saddle point in ϕ), and (2) expand the effective potential $\ln Z_s[\rho_0]$ as described below. Making these approximations, the theory will lose its independence of the choice of ℓ, and there will be a "best" ℓ whose value gives the closest agreement with the full theory. In principle, its value should be determined by optimizing the error between a loop expansion on the long-distance interaction and perturbative corrections to the short-distance expansion. On physical grounds, however, I argue that $\ell \sim l_B Q^2$, or, in other words, ℓ is the distance over which fixed counterions interact with an energy of $k_B T$. Counterions at separations larger than this interact weakly, and mean-field theory is likely valid above this length scale. In addition, the distinction between short and long length scales should not depend on the geometry of the fixed charge distribution, and can therefore only depend on the Bjerrum length and counterion valence. For concreteness, I will choose $\ell = l_B Q^2$. This choice will be justified later by exploring the behavior of the counterion density in different asymptotic regimes.

The mean-field approximation, given by $\delta S/\delta\phi = 0$, results in the equation

$$\nabla^2\phi - \ell^2\nabla^4\phi + 4\pi l_B Q^2\langle\rho(\mathbf{r})\rangle = n_f(\mathbf{r})4\pi l_B Q. \tag{9}$$

I have performed the Wick rotation $\phi \to i\phi$ for convenience. This equation has a similar structure to the Poisson-Boltzmann (PB) equation: ϕ is the potential for the long-range interaction and is determined by solving a modified Poisson equation. While I will consider different approximations for the ion density $\langle\rho\rangle$, I will not attempt to go beyond the mean-field approximation for ϕ in this paper.

III. THE SHORT-DISTANCE INTERACTION

A. Recovering the SC expansion

It remains to find a suitable approximation for $\langle\rho(\mathbf{r})\rangle$. The SC expansion can be reproduced by expanding $\ln Z_s[\rho_0]$ in powers of $\rho_0(\mathbf{r})$, utilizing the Mayer cluster expansion [20]. In terms of $\langle\rho(\mathbf{r})\rangle$, this gives the formula

$$\langle\rho(\mathbf{r})\rangle = \rho_0(\mathbf{r})\left(1 + \int d^3r' v_2(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r}') + \cdots\right) \tag{10}$$

up to second order, where $v_2(\mathbf{x}) = 1 - e^{-V_s(\mathbf{x})}$.

It is instructive to consider this expansion in the limit that $\ell \to \infty$. Here, I will state without proof (it will be shown explicitly later) that ϕ becomes constant in this limit. This can be understood by considering that, in this limit, the short-distance potential $V_s(\mathbf{r})$ carries all of the counterion interactions and the continuous field corresponding to the long-distance interaction necessarily becomes unimportant.

For a charged surface with surface charge density σ, $n_f(\mathbf{r}) = \sigma\delta(z)/Q$, leading to

$$\rho_0(\mathbf{r}) = \frac{\kappa^2}{4\pi l_B Q^2} e^{F(\mathbf{r})} \sim \frac{\kappa^2}{4\pi l_B Q^2} e^{-z/\lambda}, \tag{11}$$

where $\lambda = 1/(2\pi l_B Q\sigma)$ is the Gouy-Chapmann length for the surface. Equation (11) comes directly from expanding $F(z)$ in powers of z and noting that terms of order $z^2/(l_B\ell)$ and higher are small in this limit. With this substitution, expansion (10) is then seen to reproduce the SC expansion. Notice that each term of this expansion diverges as the coupling constant $\Gamma = l_B Q^2/\lambda = 2\pi l_B^2 \sigma Q^3 \to \infty$, indicating that the counterion interactions are not small; this divergence can be absorbed by shifting κ^2 and utilizing overall charge neutrality [18].

B. The counterion-hole expansion

For a charged surface, it will prove more useful to consider the variable $\delta\rho_0(\mathbf{r}) = \rho_0(\mathbf{r}) - \delta(z)/(2\pi l_B Q^2\lambda)$ rather than $\rho_0(z)$. This has the property that $\int dz\, \delta\rho_0(z) = 0$ due to overall charge neutrality, and yields

$$Z_s = \sum_n \frac{1}{n!}\int \prod_{\alpha=1}^{n} d^2r_\alpha dz_\alpha \prod_\alpha \delta\tilde{\rho}_0(\mathbf{r}_\alpha, z_\alpha) \times \exp\left(-\sum_{\alpha<\beta} V_s(\mathbf{r}_\alpha - \mathbf{r}_\beta; z_\alpha - z_\beta)\right) Z_p, \tag{12}$$

where $\mathbf{r}_\alpha$ indicates the position of a counterion projected to the surface, z_α its distance from the surface, and $\delta\tilde{\rho}_0(\mathbf{r}_\alpha, z_\alpha) = \langle\exp[-\Sigma_i V_s(\mathbf{r}_\alpha - \mathbf{r}_i, z_\alpha)]\rangle_p \delta\rho_0(\mathbf{r}_\alpha, z_\alpha)$. Here, $\langle\cdots\rangle_p$ is the average taken with respect to the partition function

$$Z_p = \sum_m \frac{1}{m!}\left(\frac{2}{4\pi l_B Q^2\lambda}\right)^m \int \prod_{i=1}^{m} d^2r_i \exp\left(-\sum_{i<j} V_s(\mathbf{r}_i - \mathbf{r}_j; 0)\right). \tag{13}$$

The expression $\langle\exp[-\Sigma_i V_s(\mathbf{r}_\alpha - \mathbf{r}_i; z_\alpha)]\rangle_p$ represents the interaction of a charge at coordinates $(\mathbf{r}_\alpha, z_\alpha)$ with a layer of counterions at positions $(\mathbf{r}_i, z_i = 0)$. In deriving Eq. (12), I have assumed

$$\left\langle \prod_\alpha \exp\left(-\sum_i V_s(\mathbf{r}_\alpha - \mathbf{r}_i; z_\alpha)\right)\right\rangle_p \approx \prod_\alpha \left\langle \exp\left(-\sum_i V_s(\mathbf{r}_\alpha - \mathbf{r}_i; z_\alpha)\right)\right\rangle_p.$$

This assumption has the physical content that counterions making excursions away from the surface ($z > 0$) are uncorrelated with each other. This will be valid as long as counterions that are far from the surface interact weakly, something that is manifestly true in the WC limit and also accurate if most of the ions are close to the surface (so that very few ions make large excursions) as they are in the SC limit.

Performing a cluster expansion with respect to $\delta\tilde{\rho}_0$ yields

$$\ln Z_s[\phi] = \int d^3r\, \delta\tilde{\rho}_0(\mathbf{r})\left(1 + \frac{1}{2}\int d^3r' v_2(\mathbf{r}-\mathbf{r}')\delta\tilde{\rho}_0(\mathbf{r}') + \cdots\right). \quad (14)$$

Terms higher than zeroth order vanish in the limit $\Gamma \to \infty$ as the density becomes δ-function-like and $\delta\tilde{\rho}_0 \to 0$. As $\Gamma \to 0$, these corrections also vanish because $\ell^3 \delta\tilde{\rho}_0 \to 0$, and the interactions become predominantly long ranged.

It is useful to define

$$\tilde{\rho}_0 = \frac{\kappa^2}{4\pi l_B Q^2} e^{\zeta(z)-\phi(z)} \quad (15)$$

with

$$\exp[\zeta(\mathbf{r},z)] \equiv \left\langle \exp\left(F(z) - \sum_i V_s(\mathbf{r}-\mathbf{r}_i;0)\right)\right\rangle. \quad (16)$$

The function $\zeta(z)$ can be interpreted as the short-distance interaction potential of a charge at height z with the charged surface and with a layer of counterions at $z=0$. Therefore, it encodes the response of the counterions at $z=0$ to the presence of a charge at $z>0$, and is reminiscent of the TCT [19]. One difference between $\zeta(z)$ and the TCT, however, is that $\zeta(z)$ also depends, at least in principle, on the short-range structure of the counterions induced by the short-range interaction.

In order to complete the analysis of this expansion, it remains to generate a model for $\zeta(z)$. Here, I will develop a simple approximation leading to reasonable quantitative answers by putting in the correlation hole structure "by hand." Though this will not constitute a systematic approximation to $\zeta(z)$, my approach has the advantage of physical clarity leading to quantitative results. A more sophisticated analysis is, of course, possible but beyond the scope of this paper.

I assume that each counterion at $z>0$ interacts with a uniform distribution of charge at $z=0$ containing an induced circular correlation hole of radius $r_0 = \sqrt{Q/\sigma}$. This approximates the size of a vacancy in a locally ordered lattice of counterions at the surface, which should be valid when Γ is large. Thus,

$$\zeta(z) = (\ell/\lambda)(e^{-z/\ell} - e^{-\sqrt{r_0^2+z^2}/\ell}). \quad (17)$$

It is interesting that, for $z \ll \ell$, $\zeta(z) \approx \Gamma(1-e^{-r_0/\ell}) - z/\lambda$ is dominated by the interaction of the counterions with the bare surface and not the $z=0$ layer of counterions whose contribution is of order $\sim z^2/(\lambda\ell) \ll z/\lambda$. While one could develop more sophisticated and systematic approximations, this will turn out to be suitable for understanding the ion density for sufficiently large Γ.

IV. SOLUTIONS OF THE MEAN-FIELD EQUATION

To lowest order in the counterion-hole expansion, $\langle\rho\rangle \approx \tilde{\rho}_0 = \kappa^2\Theta(z)e^{\zeta(z)-\phi(z)}$, and the mean-field equation for a charged surface now reads

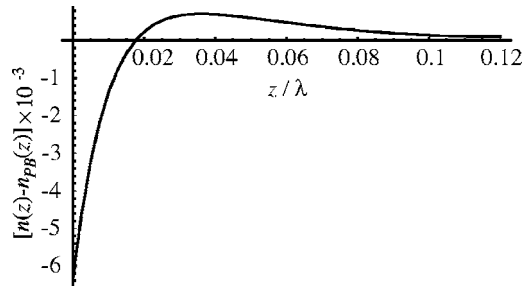

FIG. 1. The normalized density difference $n(z)-n_{PB}(z)$ as a function of z/λ for $\Gamma=0.01$ for ions in a box of size $L=12l_BQ^2$.

$$\partial_z^2\phi - \ell^2\partial_z^4\phi + \kappa^2\Theta(z)e^{\zeta(z)-\phi(z)} = 4\pi l_B Q\sigma\delta(z). \quad (18)$$

For small z, $\zeta(z)-F(z)$ is analytic and can be expanded as a power series in $(z/\ell)^2$. On the other hand, $F(z)$ is nonanalytic at $z=0$ and contributes to the boundary conditions. This additional contribution can be disentangled by defining $\Phi \equiv \phi - F$. In terms of Φ, $\zeta(z)$ is replaced with $\zeta(z)-F(z)$ and there is an additional source term on the right of Eq. (18) of the form $-4\pi l_B Q\sigma\ell^2\partial_z^2\delta(z)$. This equation encodes two boundary conditions:

$$\lim_{z\to 0+}\partial_z\Phi(z) - \lim_{z\to 0-}\partial_z\Phi = \partial_z\Phi|_{0-}^{0+} = 4\pi l_B Q\sigma,$$

$$\partial_z\Phi|_{0-}^{0+} - \ell^2\partial_z^3\Phi|_{0-}^{0+} = 4\pi l_B Q\sigma. \quad (19)$$

In terms of the original ϕ, the boundary conditions are

$$\partial_z\phi|_{0-}^{0+} = 0,$$

$$-\ell^2\partial_z^3\phi|_{0-}^{0+} = 4\pi l_B Q\sigma. \quad (20)$$

Charge neutrality, $\int dz\, \kappa^2\exp[\zeta(z)-\phi(z)] = 4\pi l_B Q\sigma$, is ensured for any solution to Eq. (18), as can be seen readily by integrating both sides of the equation.

Equation (18) is difficult to solve analytically. Therefore, I will consider approximate solutions in both the WC and SC limits. In the WC limit, I assume the solution will decay with characteristic length λ, with $\lambda \gg \ell = l_B Q^2$. The fourth-order derivative is negligible and, since $\zeta(\mathbf{r}) \ll 1$, ϕ takes the Poisson-Boltzmann form

$$\phi(z>0) = 2\ln(1 + \kappa z/\sqrt{2}). \quad (21)$$

The boundary conditions are satisfied by choosing

$$\phi(z<0) = 2(\ell/\lambda)A(e^{z/\ell} - 1), \quad (22)$$

where $\ell^2A^3/\lambda^2 - A = 1$. This requires $\kappa\lambda/2 = A$. The approximate nature of this solution is apparent, as it does not respect charge neutrality. However, as $\Gamma \to 0$, $\phi(z<0) \to 0$, and Eq. (21) becomes exact. To verify this prediction, I have solved Eq. (18) for $\Gamma=0.01$ in a box of size $L=12l_BQ^2$, with the boundary condition that ϕ and its first three derivatives are continuous across $z=L$. In Figure 1, I have plotted the difference between the solution of Eq. (18) and the numerical solution to the Poisson-Boltzmann equation in a box and found that they agree very well. For convenience, I have plotted $n(z)-n_{PB}(z)$, where $n(z) = 2\pi l_B Q^2\lambda^2\langle\rho(z)\rangle$ and

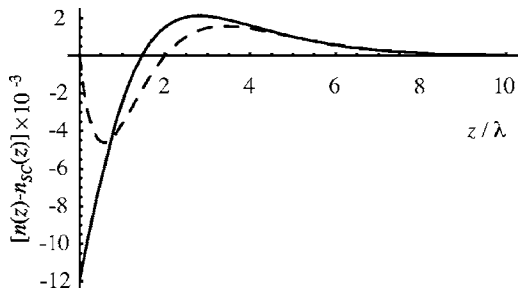

FIG. 2. Normalized density difference $n(z)-n_{SC}(z)$ as a function of z/λ for $\Gamma=1000$. The solid curve gives the result from solving Eq. (18) while the dashed curve is the *renormalized* first-order correction derived from the SC expansion (it has been multiplied by a factor of 20, as is needed to agree with simulations for this coupling constant [22]).

$n_{PB}(z)=2\pi l_B Q^2\lambda^2\rho_{PB}(z)$ is the normalized Poisson-Boltzmann density [in a semi-infinite system, $n_{PB}(z)=1/(1+z)^2$]. Thus, $n(z)$ is normalized so that $n(0)=1$ if the system exactly obeys the contact value theorem.

In the SC limit, the fourth-order term dominates over the second-order term near the surface. I make the additional assumption that $\phi \ll 1$, and solve

$$\ell^2 \partial_z^4 \phi = \kappa^2 e^{\zeta(z)} \approx \kappa^2 e^{\zeta(0)-z/\lambda}, \tag{23}$$

which has the solution

$$\phi(z>0) = \frac{\kappa^2\lambda^4}{\ell^2} e^{\zeta(0)}(e^{-z/\lambda}-1). \tag{24}$$

Applying the boundary conditions, I find that

$$\phi(z<0) = -\frac{2\lambda}{\ell(1-\lambda^2/\ell^2)}[\exp(z/\ell)-1], \tag{25}$$

$$\kappa^2 = \frac{2}{\lambda^2(1-\lambda^2/\ell^2)} \exp[-\zeta(0)]. \tag{26}$$

The counterion density is given by $\langle\rho\rangle \approx \kappa^2 e^{\zeta(z)-\phi(z)}$. For large Γ, we have $\langle\rho\rangle \approx (2/\lambda^2)e^{-z/\lambda}$ and the exponential SC density is recovered for large Γ. This solution also becomes exact as $\Gamma\to\infty$, and can be verified by plotting the exact numerical solution for very large Γ. This also verifies the statement in Sec. III that ϕ becomes constant and unimportant in the limit of $\ell\to\infty$.

I plot the difference between the density at $\Gamma=10^3$ and the exact SC density in Fig. 2. It is known from numerical simulations that the first-order SC correction has the wrong magnitude [22]. The analytical first-order SC correction has, therefore, been multiplied by 20 to find the dashed curve in Fig. 2, as is needed to find agreement between the SC theory and numerical simulation. Here, we see that Eq. (18) does not predict the correct form for this difference (especially because of a small deviation of the contact density at $z=0$), but does naturally predict the correct magnitude for this difference.

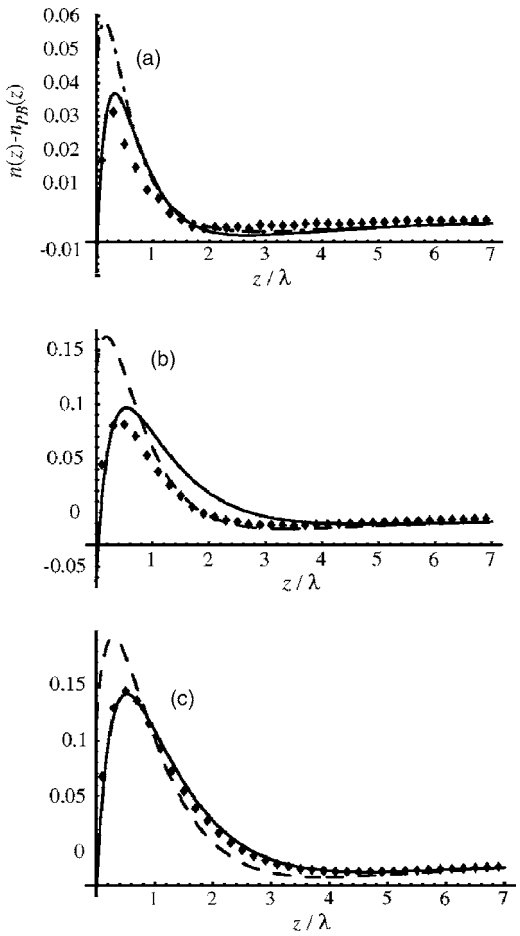

FIG. 3. Normalized density difference $n(z)-n_{PB}(z)$ as a function of z/λ for $\Gamma=$ (a) 1, (b) 10, and (c) 100. Solutions to Eq. (18) (solid line) are compared to numerical simulations from Ref. [22] (diamonds) and the TCT from Ref. [19] (dashed line).

For $z\gg\ell$, $\zeta(z)\ll 1$ even in the SC limit. The solution to Eq. (18) must therefore transition to that given by Eq. (21). The fourth-order derivative can be neglected in this limit because κ is exponentially suppressed by $\zeta(0)$ being large. Therefore, the density at large distances is PB-like and is controlled by a renormalized Gouy-Chapman length, $\lambda_{ren}=\sqrt{2}/\kappa=\lambda\exp[\zeta(0)]$. This is in agreement with the arguments of Burak *et al.* [19], which also exhibit a crossover to a slow decay far from the surface. Using $\zeta(z)$, I obtain the estimate

$$\ln(\lambda_{ren}/\lambda) = \Gamma(1-e^{-\sqrt{2\pi l_B Q^2/(\ell\Gamma)}}). \tag{27}$$

I have also solved Eq. (18) numerically for $\Gamma=1$, 10, and 100 in Fig. 3. These numerical solutions are compared to actual simulation data from Ref. [22] (courtesy of A. Moreira) and show quite good agreement. Furthermore, Eq. (18) outperforms the TCT (shown as dashed lines using data provided by Y. Burak from Ref. [19]). The nonperturbative function $\zeta(z)$ is an important component of this numerical agreement; when the original cluster expansion in powers of ρ_0 is used to compute $\ln Z_s$ [equivalent to setting $\zeta(z)=F(z)$ at lowest order], the agreement with the simulation data is only

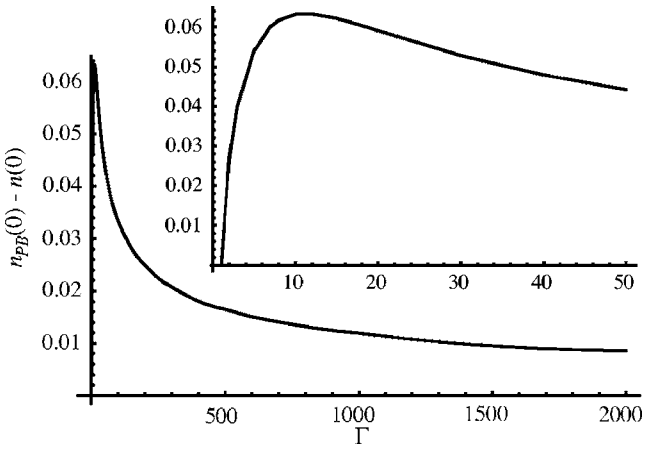

FIG. 4. The difference in normalized contact density from the exact contact density in an infinite box [given by $n(0)=1$] as a function of coupling constant Γ. The inset shows the normalized contact density for $\Gamma<50$.

slightly better than the TCT and not nearly as good as Fig. 3. To be clear, the value for r_0 used in Fig. 3 is simply an estimate of the real correlation hole size, which may differ up to a factor of order 1 depending on the model used. Though there is still good agreement for other *reasonable* values of r_0, $r_0=\sqrt{Q/\sigma}$ seems to give the best agreement with simulations.

It is important to realize, however, that for $\Gamma=10$, the TCT agrees with the simulation data better in the intermediate-distance region. A possible reason for this is clear: at these distances, the approximation of a counterion interacting with a correlation hole used to compute $\zeta(z)$ begins to fail because the average correlation hole size will decrease. This is something the TCT evidentally captures in the $\Gamma=10$ case. A more careful evaluation of $\zeta(z)$ is likely to improve the quantitative agreement in this distance regime. I also note here it is the failure of the TCT to agree with the exact contact density that leads to its disagreement with simulations. In Fig. 4 I plot the error $n(0)-n_{PB}(0)$ between the contact value found by solving Eq. (18) and its exactly known value $1/(2\pi l_B Q^2\lambda^2)$ in an infinite half space. From this figure, it is seen that the contact values approach their exact result as Γ increases, but that deviations for $10<\Gamma<100$ are still quite small.

V. DISCUSSION

Notice that the crossover in Eq. (18) is governed by ℓ/λ rather than $\Gamma=l_B Q^2/\lambda$. This further corroborates choosing $\ell=l_B Q^2$. Changes in ℓ merely shift the crossover between strong and weak coupling, and the predicted counterion densities do not depend too sensitively as long as ℓ changes by a factor of order 1.

The SC expansion can be reconstructed in this framework as an asymptotic expansion around the $\ell\to\infty$ limit by considering the higher-order terms in $\delta\tilde{\rho}_0$ for $\ln Z_s$. This is seen by substituting the asymptotically exact result $\tilde{\rho}_0=e^{-z/\lambda}/(2\pi l_B Q^2\lambda^2)$ into $\langle\rho\rangle=\tilde{\rho}_0(1+\Delta_1+\cdots)$. The first-order correction Δ_1 gives a contribution

$$\Delta_1=\int d^3r' v_2(\mathbf{r}-\mathbf{r}')\left(\tilde{\rho}_0(z')-\frac{1}{2\pi l_B Q^2\lambda}\delta(z')\right). \quad (28)$$

Using the identity $\lambda e^{-z'/\lambda}=\partial(e^{-z'/\lambda})/\partial z'$, it is possible to extract the divergences from the first term in Eq. (28). I integrate z' in the first term by parts, then utilize the replacement $z'\to -z$, resulting in

$$\Delta_1=\int d^2r' \partial_z v_2(\mathbf{r}_\perp-\mathbf{r}'_\perp;z-z')/\lambda\tilde{\rho}_0(z'). \quad (29)$$

In the limit $\ell\to\infty$, the boundary term in the integration by parts diverges. Yet this divergence is regularized by finite ℓ, and cancels exactly with the δ function in Eq. (28). The part that remains yields exactly the finite part of the first-order SC correction in the limit of $\ell\to\infty$ [18]. I conjecture that the higher-order corrections also agree with the finite part of the strong-coupling expansion. The full solution to Eq. (18) must lead to an effective resummation of the SC expansion, yielding numerical corrections that are the right magnitude. A more systematic accounting of these corrections, as well as the loop corrections, is left for future work [24].

The counterion-hole expansion suggests a physical picture for the SC corrections: these corrections arise from the interactions between only those counterions that have made excursions away from the wall, as measured by $\delta\tilde{\rho}_0$. It is clear that the density of these excited counterions becomes small for large Γ, as the SC limit becomes exact. The function $\zeta(z)$ encodes the interaction of these excitations with their $z=0$ correlation holes, and becomes important at intermediate coupling, once counterions get far enough from the surface. The effect of the correlation holes on the counterion density is a fundamental component of the strongly coupled Coulomb fluid picture [3]; here, as in the TCT, it emerges naturally. However, in Eq. (18) the behavior of the correlation hole is put in by hand. Though this leads to reasonable quantitative agreement, a more complete theory for the correlation holes should lead to even better quantitative agreement with simulations.

It is also interesting to note here that, since $\partial(\ln Z)/\partial\ell=0$, one can derive a hierarchy of identities relating averages of ϕ to derivatives of the short-distance partition function Z_s. These relations resemble the Ward-Takahashi identities in quantum field theory arising from the existence of symmetries [25]. Whether these identities can be exploited to understand further the interplay between short and long length scales in charged systems is unknown to me. One possibility is to set ℓ quantitatively by enforcing one or more of these identities after evaluating the terms within the framework of some approximation scheme.

The decomposition between short- and long-distance interactions also provides a natural framework to compute the counterion free energy at intermediate coupling. This is given by $F=S(i\phi)-\mu N/(k_B T)$, where N is the number of counterions, ϕ is the mean-field long-range potential, and the chemical potential is related to κ^2 by $\mu=k_B T\ln[\kappa^2 a^3/(4\pi l_B Q^2)]$. Since κ^2 depends exponentially on

$\zeta(0)$, nonperturbative correlations also play a role in the free energy, and subsequently in the interaction between two surfaces at separations where the SC expansion cannot be applied. This will be explored in a future publication.

To summarize, I have computed the counterion density around a charged surface using a scheme to decompose the Coulomb interaction into short- and long-distance components. Each is treated with different approximations. For large Γ, we recover the SC results and for small Γ we recover the WC Poisson-Boltzmann density. At intermediate coupling, the model agrees reasonably well with the simulation data, though it depends on a nonperturbative correlation correction whose form we have only estimated. These correlations also play a role in determining the renormalized Gouy-Chapman length when the densities recovers its Poisson-Boltzmann form far from the surface.

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