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Charge fluctuations and counterion condensation

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We predict a condensation phenomenon in an overall neutral system, consisting of a single charged plate and its oppositely charged counterions. Based on the ‘‘two-fluid’’ model, in which the counterions are divided into a ‘‘free’’ and a ‘‘condensed’’ fraction, we argue that for high surface charge, fluctuations can lead to a phase transition in which a large fraction of counterions is condensed. Furthermore, we show that depending on the valence, the condensation is either a first-order or a smooth transition.

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I. INTRODUCTION

Electrostatic interactions control the structure, phase behavior, and function of macroions in aqueous solutions [1]. The macroions may be charged membranes, stiff polyelectrolytes such as DNA, or charged colloidal particles. The fundamental description of these charged systems has been the Poisson-Boltzmann (PB) theory. However, it ignores fluctuations and correlations, which are important for the cases of low temperatures, highly charged surfaces, or multivalent counterions. These fluctuation and correlation effects, which have been the focus of recent theoretical efforts, may drastically alter the mean-field picture of PB theory [2–5]. For example, one surprising effect [5] is the *attraction* between two highly charged macroions, as observed in experiments [6] and in simulations [7]. In this paper, we argue that correlation effects may lead to condensation of counterions onto an oppositely charged plate, whose surface charge becomes effectively renormalized. In particular, the counterion valence plays an interesting role: for $Z>Z_c\sim 1.62$ for typical system parameters (see below), we find a first-order phase transition in which a large fraction of the counterions is *condensed*, while for $Z<Z_c$ the condensation proceeds smoothly, implying that monovalent and divalent counterions exhibit qualitatively distinct behavior. This is in contrast with more familiar theories of counterion condensation [8], e.g., Manning condensation for charged rods, where the effective charge is continuously modified by the valence.

Recall that for a single plate of charge density $\sigma(\mathbf{x}) = \sigma_0 \delta(z)$ immersed in an aqueous solution of dielectric constant ϵ, containing pointlike counterions of charge $-Ze$ on both sides of the plate, PB theory predicts that the counterion density [1]

$$c(z)=\frac{1}{2\pi Z^2 l_B(|z|+\lambda)^2}, \tag{1}$$

decays to zero algebraically with a characteristic length $\lambda \equiv e/(\pi l_B Z\sigma_0)$, where $l_B \equiv e^2/\epsilon k_B T \approx 7$ Å is the Bjerrum length in water at room temperature, k_B is the Boltzmann constant, and T is the temperature. This Gouy-Chapman (GC) length λ defines a sheath near the charged surface within which most of the counterions are confined. Typically, it is of the order of few Angstroms for $\sigma_0 \sim e/100$ Å^{-2}. Note that Eq. (1) implies that at *zero* temperature all of the counterions would collapse onto the charged plane. However, for high surface charge (or low temperature) $Z^2 l_B \gg \lambda$, fluctuation and correlation corrections can become so large that the solution Eq. (1) to the PB equation is no longer valid [3]. Therefore, we might expect a quantitative deviation from the conclusion above. Indeed, as pointed out by Netz and Orland [3], a perturbative expansion about the PB solution breaks down in this regime, as indicated by an unphysical (negative) counterion density in the one-loop approximation. Motivated by these observations, we propose a *two-fluid* model in which the counterions are divided into a *free* and a condensate fraction. The *free* counterions have the usual three-dimensional (3D) spatial distribution, while the *condensed* counterions are confined to the two-dimensional charged plane, with a mean (2D) density n_c. We treat the fraction of 2D condensed counterions $\tau \equiv Zen_c/\sigma_0$ as a variational parameter, which is determined self-consistently by minimizing the total free energy of the system.

It may be useful to illustrate the essential physics first by a simple picture. In the spirit of the two-fluid model, the 2D condensed counterions partially neutralize the charged plate, effectively reducing the surface charge density from σ_0 to $en_R = \sigma_0 - Zen_c$, where n_c is their surface (2D) density. The free counterions can be modeled as a 3D ideal gas confined to a slab of thickness $\lambda_R \equiv 1/(\pi l_B Z n_R)$. At the Debye-Hückel level, the free energy per unit area for the condensed counterions $f_{2D}(n_c)$ can be written as [9]

$$\beta f_{2D}(n_c)=n_c\{\ln[n_c a^2]-1\}+\frac{1}{2}\int \frac{d^2\mathbf{q}}{(2\pi)^2} \times\left\{\ln\left[1+\frac{1}{q\lambda_D}\right]-\frac{1}{q\lambda_D}\right\}, \tag{2}$$

where $\beta^{-1}=k_B T$ and $\lambda_D = 1/(2\pi l_B Z^2 n_c)$ is the 2D screening length. The first term in Eq. (2) is the entropy and the second term arises from the 2D fluctuations. Note that the latter term is logarithmically divergent, which may be regularized by a microscopic cut-off $q_c \sim 2\pi/a$, yielding $\beta\Delta f_{2D}(n_c) \simeq -(1/8\pi\lambda_D^2)\ln(2\pi\lambda_D/a)$. The free energy of the free counterions $f_{3D}(n_c)$ consists of the entropy of a confined 3D ideal gas and the fluctuation free energy. The latter term may be estimated by using the fluctuation contribution to the free energy density from the 3D Debye-Hückel theory [10] and multiplying it by the thickness of the slab λ_R

$$\beta f_{3D}(n_c) \approx c\,\lambda_R\{\ln[c\,a^3]-1\} - \frac{\kappa_s^3}{12\pi}\lambda_R, \tag{3}$$

where $c = n_R/(Z\lambda_R)$ average (3D) concentration of the free counterions and $\kappa_s^2 \equiv 4\pi Z^2 l_B c$ is the $3D$ screening length. Note that the second term scales as $\sim -\lambda_R^{-2}$. This simple picture to estimate $f_{3D}(n_c)$ contains all the qualitative physics [11], which follow from the more precise analysis presented below. The total free energy in the two-fluid model is $f(\tau) = f_{2D}(\tau) + f_{3D}(\tau)$. Minimizing $f(n_c)$ to find n_c, we obtain

$$1 + \tau g \ln\left(\frac{\pi}{\tau\theta g}\right) - \ln\left[\frac{\tau}{(1-\tau)^2\theta g}\right] - \frac{4}{3}g(1-\tau) = 0, \tag{4}$$

where the three dimensionless parameters: the order parameter $\tau \equiv Zen_c/\sigma_0$, the coupling constant $g \equiv Z^2 l_B/\lambda$ (where λ is the *bare* GC length), and the reduced temperature $\theta \equiv a/(Z^2 l_B)$, completely determine the equilibrium state of the system. It is straightforward to obtain the asymptotic solutions of Eq. (4) corresponding to the uncondensed, $\tau_1 \ll 1$, and condensed, $\tau_2 \approx 1$, state of the counterions: $\tau_1 \simeq g\,\theta \exp[1 - \frac{4}{3}g]$ and $\tau_2 \simeq 1 - [\pi \exp(1)]^{-1/2}(g\theta/\pi)^{(g-1)/2}$. For weak couplings, $g \ll 1$, τ_1 is the only consistent solution. On the other hand, for large coupling $g \gg 1$, where fluctuation free energies dominate the system, τ_1 and τ_2 are both consistent solutions for small θ, and a first-order transition takes place when $f(\tau_1) = f(\tau_2)$. Thus, a large fraction of counterions is condensed if g exceeds some threshold value $g > g_0$. For an estimate, taking $\theta = 0.02$ (divalent counterions at room temperature) we find $g_0 \sim 1.757$, corresponding to a surface charge of $\sigma_0 \sim e/10\ \text{nm}^{-2}$.

We emphasize that although there is a close analogy between our approach and the more familiar theory of counterion condensation, e.g., Manning condensation [8], the counterion condensation in our model has a different physical origin arising from charge fluctuations. In Manning condensation, the competition between entropy and electrostatics leads to an electrostatic potential at large distances that is independent of the charged density of the rod above the Manning threshold [8]. In this sense, for the geometry of a charged plate, counterions are always ‘‘Manning condensed’’ at the PB level [12]. On the other hand, in our model, we take one step further by showing that when correlation effects are taken into account, a finite fraction of the counterions is condensed to form a 2D Coulomb gas onto the charged plate. This paper is organized as follows: In Sec. II, we present in detail the two-fluid model and construct the total free energy of the system. In Sec. III we present the central results of this paper, followed by an extensive discussion.

II. COUNTERION FREE ENERGY IN THE ‘‘TWO-FLUID’’ MODEL

To study the condensation more rigorously, we compute total free energy by mapping the problem into a field theory. Consider an overall neutral system consisting of counterions and an oppositely charged surface immersed in an aqueous solution. The surface charge density on the plate is $\sigma_0 = en_0$. We model the aqueous solution with a uniform dielectric constant ϵ. This simplification allows us to study fluctuation and correlation effects analytically. In the spirit of the ‘‘two-fluid’’ model, we divide the counterions into a ‘‘condensed’’ and a ‘‘free’’ fraction. The condensed counterions are allowed to move only on the charged surface, while the free counterions distribute in the space on both sides of the plate. The electrostatic free energy for the whole system may be written as

$$\begin{aligned}\beta F_{el} = {} & \int d^2\mathbf{r}\, n_c(\mathbf{r})\{\ln[n_c(\mathbf{r})a^2]-1\} + \int d^3\mathbf{x}\,\rho(\mathbf{x}) \\ & \times\{\ln[\rho(\mathbf{x})a^3]-1\} \\ & + \frac{Z^2 l_B}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{n_c(\mathbf{r})\,\delta(z)\,n_c(\mathbf{r}')\,\delta(z')}{|\mathbf{x}-\mathbf{x}'|} \\ & + \frac{Z^2 l_B}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ & + Z l_B\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{n_c(\mathbf{r})\,\delta(z)[Z\rho(\mathbf{x}')-n_f(\mathbf{x}')]}{|\mathbf{x}-\mathbf{x}'|} \\ & - Z l_B\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{\rho(\mathbf{x})\,n_f(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ & + \frac{l_B}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{n_f(\mathbf{x})n_f(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|},\end{aligned} \tag{5}$$

where a is the molecular size of the counterions, $l_B = e^2/(\epsilon k_B T)$ is the Bjerrum length, Z is the valence of the counterions, $\mathbf{r}$ is the in-plane position vector, and $\mathbf{x} = (\mathbf{r}, z)$. The first two terms in Eq. (5) are the two-dimensional entropy for the condensate and three-dimensional entropy for the ‘‘free’’ counterions, respectively, and the other terms represent the electrostatic interactions of counterions in the system. In Eq. (5), the two-dimensional density of the condensed counterions is denoted by $n_c(\mathbf{r})$, the ‘‘free’’ counterions with 3D density by $\rho(\mathbf{x})$, and the external fixed charges arising from the surface by $n_f(\mathbf{x}) = n_0\delta(z)$. Within the Gaussian fluctuation approximation, we consider the spatial dependent fluctuations of the 2D density of condensed counterions about a uniform mean $n_c(\mathbf{r}) = n_c + \delta n_c(\mathbf{r})$, and expand Eq. (5) to second order in $\delta n_c(\mathbf{r})$

$$\begin{aligned}\beta F_{el} = {} & n_c\{\ln[n_c a^2]-1\}\mathcal{A} + \int d^3\mathbf{x}\,\rho(\mathbf{x})\{\ln[\rho(\mathbf{x})a^3]-1\} \\ & + \frac{Z^2 l_B}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ & - Z l_B\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{\rho(\mathbf{x})n_R(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ & + \frac{1}{2}\int d^2\mathbf{r}\int d^2\mathbf{r}'\left[\frac{Z^2 l_B}{|\mathbf{r}-\mathbf{r}'|}\right. \\ & \left. + \frac{\delta(\mathbf{r}-\mathbf{r}')}{n_c}\right]\delta n_c(\mathbf{r})\,\delta n_c(\mathbf{r}') \\ & + Z l_B\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{\delta n_c(\mathbf{r})\,\delta(z)J(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ & + \frac{l_B}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\frac{n_R(\mathbf{x})n_R(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + \mathcal{O}(\delta n_c(\mathbf{r}))^3,\end{aligned}$$

where $\mathcal{A}$ is the area of the plane, $J(\mathbf{x}) \equiv Z\rho(\mathbf{x}') - n_R(\mathbf{x})$, and $n_R(\mathbf{x}) = n_f(\mathbf{x}) - Zn_c\delta(z)$. Note that $J(\mathbf{x})$ is linearly coupled to $\delta n_c(\mathbf{r})$ in the above equation. Summing over all the 2D fluctuations of the condensed counterions, i.e.,

$$e^{-\beta\mathcal{H}_e} = \int \mathcal{D}\delta n_c(\mathbf{r})e^{-\beta F_{el}},$$

we obtain two terms in the effective free energy: $\mathcal{H}_e = F_{2D} + \mathcal{H}_{3D}$. The first term F_{2D} is the free energy associated with the condensed counterions that can be written as

$$\beta F_{\mathrm{2D}} = n_c\{\ln[n_c\,a^2]-1\}\mathcal{A} + \frac{1}{2}\ln\det\hat{\mathbf{K}}_{\mathrm{2D}} - \frac{1}{2}\ln\det[-\nabla_{\mathbf{x}}^2], \tag{6}$$

where

$$\hat{\mathbf{K}}_{\mathrm{2D}}(\mathbf{x},\mathbf{y}) \equiv \left[-\nabla_{\mathbf{x}}^2 + \frac{2}{\lambda_D}\,\delta(z)\right]\delta(\mathbf{x}-\mathbf{y})$$

is the 2D Debye-Hückel operator and $\lambda_D = 1/(2\pi Z^2 l_B n_c)$ is the Debye screening length in 2D. The first term in Eq. (6) is the entropy and the second term arises from the 2D charge fluctuations. Note that this fluctuation term can be evaluated analytically [9], with the result quoted in Eq. (2)

$$\beta f_{\mathrm{2D}}(n_c) = n_c\{\ln[n_c\,a^2]-1\} + \frac{1}{2}\int\frac{d^2\mathbf{q}}{(2\pi)^2} \times\left\{\ln\left[1+\frac{1}{q\lambda_{\mathrm{D}}}\right] - \frac{1}{q\lambda_{\mathrm{D}}}\right\}.$$

The second term $\mathcal{H}_{\mathrm{3D}}$ is the electrostatic free energy for the "free" counterions, taking into account of the presence of the fluctuating condensate; to within an additive constant, it may be written as

$$\begin{aligned}\beta\mathcal{H}_{\mathrm{3D}} = {} & \int d^3\mathbf{x}\,\rho(\mathbf{x})\{\ln[\rho(\mathbf{x})a^3]-1\} \\ & + \frac{1}{2}\int d^3\mathbf{x}\int d^3\mathbf{x}'\,\rho(\mathbf{x})G_{\mathrm{2D}}(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}') \\ & - \int d^3\mathbf{x}\,\phi(\mathbf{x})\,\rho(\mathbf{x}),\end{aligned} \tag{7}$$

where $\phi(\mathbf{x}) \equiv \int d^3\mathbf{x}'\,Z^{-1}\,G_{\mathrm{2D}}(\mathbf{x},\mathbf{x}')\,n_R(\mathbf{x}')$ is the "renormalized" external field arising from the charged plate. From Eq. (7), we can see that the presence of the condensate modifies the electrostatics of the free counterions in two ways. First, the condensate partially neutralizes the charged surface, effectively reducing the surface charge density from en_0 to $en_R = e(n_0 - Zn_c)$. Second, their fluctuations renormalize the electrostatic interaction of the system; thus, instead of the usual Coulomb potential, the free counterions and the charged surfaces interact via the interaction $G_{\mathrm{2D}}(\mathbf{x},\mathbf{x}')$, which is the inverse (the Green's function) of the 2D Debye-Hückel operator $\hat{\mathbf{K}}_{\mathrm{2D}}$ [13],

$$\left[-\nabla_{\mathbf{x}}^2 + \frac{2}{\lambda_D}\,\delta(z)\right]G_{\mathrm{2D}}(\mathbf{x},\mathbf{x}') = 4\pi l_B Z^2\,\delta(\mathbf{x}-\mathbf{x}'), \tag{8}$$

where the second term in the bracket takes the fluctuating 2D "condensate" into account. Hence, in the limit $n_c \to 0$ or $\lambda_D \to \infty, G_{\mathrm{2D}}(\mathbf{x},\mathbf{x}')$ reduces to the usual Coulomb interaction $G_0(\mathbf{x},\mathbf{x}') = 4\pi l_B Z^2/|\mathbf{x}-\mathbf{x}'|$.

After a Hubbard-Stratonovich transformation [14], the grand canonical partition function for the free counterions can be mapped onto a functional integral representation: $\mathcal{Z}_\mu[\phi] = \mathcal{N}_0\int\mathcal{D}\psi\,e^{-\mathcal{S}[\psi,\phi]}$ with the effective Hamiltonian [15]

$$\begin{aligned}\mathcal{S}[\psi,\phi] = \frac{1}{4\pi l_B Z^2}\int d^3\mathbf{x}\bigg\{ & \frac{1}{2}\,\psi(\mathbf{x})[-\nabla^2]\psi(\mathbf{x}) \\ & + \frac{1}{\lambda_D}\,\delta(z)\,[\psi(\mathbf{x})]^2 - \kappa^2\exp[i\,\psi(\mathbf{x}) + \phi(\mathbf{x})]\bigg\},\end{aligned} \tag{9}$$

where $\psi(\mathbf{x})$ is the fluctuating field, $\kappa^2 = 4\pi l_B Z^2\,e^{\mu}/a^3$, μ is the chemical potential, and $\mathcal{N}_0^{-2} \equiv \det\hat{\mathbf{K}}_{\mathrm{2D}}$ is the normalization factor. The minimum of the effective Hamiltonian, given by $[\delta\mathcal{S}/\delta\psi(\mathbf{x})]|_{\psi=\psi_0} = 0$, defines the saddle-point equation for $\psi_0(\mathbf{x})$, which reads

$$\nabla^2\varphi(\mathbf{x}) + \kappa^2 e^{-\varphi(\mathbf{x})} = 4\pi l_B Z n_R\,\delta(z) + \frac{2}{\lambda_D}\,\delta(z)\,\varphi(\mathbf{x}) \tag{10}$$

in terms of the mean-field potential $\varphi(\mathbf{x}) = -i\psi_0(\mathbf{x}) - \phi(\mathbf{x})$. The solution to Eq. (10) is $\varphi(\mathbf{x}) = 2\ln(1+\kappa|z|/\sqrt{2})$, which satisfies the boundary conditions: (i) $\varphi(0)=0$ and (ii) $d\varphi/dz|_{z=0} = 2\pi l_B Z n_R$, with $\kappa = 2\pi l_B Z n_R/\sqrt{2}$. Thus, at the mean-field level, the distribution of the free counterions

$$\rho_0(\mathbf{x}) \equiv \kappa^2 e^{-\varphi(\mathbf{x})}/4\pi l_B Z^2 = \frac{1}{2\pi l_B Z^2(|z|+\lambda_R)^2}$$

has exactly the same form as the PB distribution Eq. (1), but with a *renormalized* GC length $\lambda_R \equiv \sqrt{2}/\kappa = 1/(\pi l_B Z n_R)$. To obtain the mean-field free energy of the free counterions $F_0(n_R)$, we note that it is related to the Gibbs potential $\Gamma_0[\phi] \equiv \mathcal{S}[\psi_0,\phi]$ by a Legendre transformation: $F_0(n_R) = \Gamma_0[\phi] + \mu\int d^3\mathbf{x}\,\rho_0(\mathbf{x})$. Solving for the chemical potential μ from its definition, $\mu = \ln(n_R a^3/2Z\lambda_R)$ and using the mean-field solution $\varphi(\mathbf{x})$, we find

$$\beta F_0(n_R)/\mathcal{A} = \frac{n_R}{Z}\ln\left(\frac{n_R a^3}{2Z\lambda_R}\right) - \frac{n_R}{Z}, \tag{11}$$

where $\mathcal{A}$ is the area of the charged plane. Note that $F_0(n_R)$ has the form of an ideal gas entropy of a gas with concentration $n_R/(Z\lambda_R)$ confined to a slab of thickness λ_R, the renormalized GC length.

Next, to capture correlation effects, we must also include the fluctuations of the free counterions, thereby treating the "free" and "condensed" counterions on the same level. To this end, we expand the action $\mathcal{S}[\psi,\phi]$ about the saddle point $\psi_0(\mathbf{x})$ to second order in $\Delta\psi(\mathbf{x}) = \psi(\mathbf{x}) - \psi_0(\mathbf{x})$

$$\mathcal{S}[\phi,\psi] = \mathcal{S}[\phi,\psi_0] + \frac{1}{2}\int d^3\mathbf{x}\int d^3\mathbf{y}\,\Delta\psi(\mathbf{x}) \times \hat{\mathbf{K}}_{3\mathrm{D}}(\mathbf{x},\mathbf{y})\,\Delta\psi(\mathbf{y}) + \cdots, \tag{12}$$

where the differential operator

$$\hat{\mathbf{K}}_{3\mathrm{D}}(\mathbf{x},\mathbf{y}) \equiv \left[-\nabla_{\mathbf{x}}^2 + \frac{2}{\lambda_D}\delta(z) + \frac{2}{(|z|+\lambda_R)^2}\right]\delta(\mathbf{x}-\mathbf{y}), \tag{13}$$

is the second variation of the action $\mathcal{S}[\psi,\phi]$. Note that the linear term in $\Delta\psi(\mathbf{x})$ does not contribute to the expansion since $\psi_0(\mathbf{x})$ satisfies the saddle-point equation, Eq. (10). Performing the Gaussian integrals in the functional integral, we obtain an expression for the change in the free energy due to fluctuations of the free counterions,

$$\beta\Delta F_{3\mathrm{D}} = \frac{1}{2}\ln\det\hat{\mathbf{K}}_{3\mathrm{D}} - \frac{1}{2}\ln\det\hat{\mathbf{K}}_{2\mathrm{D}}, \tag{14}$$

where the second term comes from the normalization factor $\mathcal{N}_0$. To evaluate $\beta\Delta F_{3\mathrm{D}}$ explicitly, we first differentiate it with respect to l_B by making use of the identity $\delta\ln\det\hat{\mathbf{X}} = \mathrm{Tr}\,\hat{\mathbf{X}}^{-1}\,\delta\hat{\mathbf{X}}$ to obtain

$$\begin{aligned} 4\pi l_B Z^2\frac{\partial\beta\Delta F_{3\mathrm{D}}}{\partial l_B} = &-\frac{\partial\lambda_R}{\partial l_B}\int d^3\mathbf{x}\frac{2G_{3\mathrm{D}}(\mathbf{x},\mathbf{x})}{(|z|+\lambda_R)^3} \\ &-\frac{\partial\lambda_D}{\partial l_B}\int d^3\mathbf{x}\left[G_{3\mathrm{D}}(\mathbf{x},\mathbf{x})\right. \\ &\left.-G_{2\mathrm{D}}(\mathbf{x},\mathbf{x})\right]\frac{\delta(z)}{\lambda_D^2}, \end{aligned} \tag{15}$$

where $G_{2\mathrm{D}}(\mathbf{x},\mathbf{x})$ is the diagonal part of the 2D Green's function, satisfying

$$G_{2\mathrm{D}}(\mathbf{x},\mathbf{x}) = \int\frac{d^2\mathbf{q}}{(2\pi)^2}\,\frac{2\pi l_B Z^2}{q}\left[1-\frac{e^{-2q|z|}}{1+q\lambda_D}\right]$$

and $G_{3\mathrm{D}}(\mathbf{x},\mathbf{x}')$ is the Green's function for the 3D free counterions. It satisfies

$$\left[-\nabla_{\mathbf{x}}^2 + \frac{2}{\lambda_D}\delta(z) + \frac{2}{(|z|+\lambda_R)^2}\right]G_{3\mathrm{D}}(\mathbf{x},\mathbf{x}') = 4\pi l_B Z^2\delta(\mathbf{x}-\mathbf{x}'), \tag{16}$$

which can be solved to yield,

$$\begin{aligned} G_{3\mathrm{D}}(\mathbf{x},\mathbf{x}) = \int\frac{d^2\mathbf{q}}{(2\pi)^2}\frac{2\pi l_B Z^2}{q}\Bigg\{ & 1 - \frac{1}{q^2(|z|+\lambda_R)^2} + \frac{e^{-2q|z|}\left[1+\frac{1}{q(|z|+\lambda_R)}\right]^2}{(1+q\lambda_R)[1+q\lambda_R+(q\lambda_R)^2]} \\ & - \frac{\gamma(q\lambda_R)^3 e^{-2q|z|}\left[1+\frac{1}{q(|z|+\lambda_R)}\right]^2}{[1+q\lambda_R+(q\lambda_R)^2]\,[(1+q\lambda_R)(1+\gamma)+(q\lambda_R)^2]}\Bigg\}, \end{aligned} \tag{17}$$

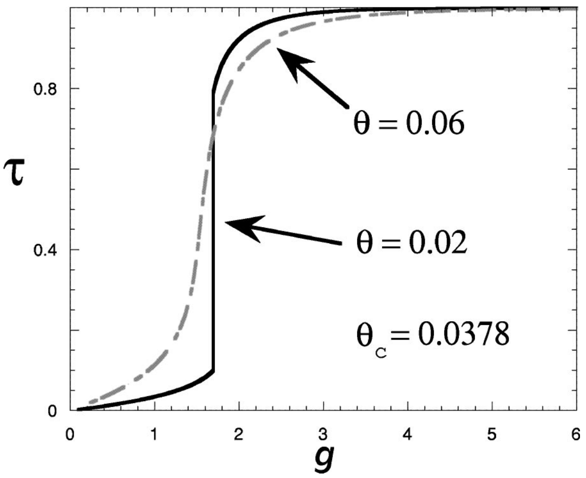

FIG. 1. The fraction of condensed counterions $\tau \equiv Zen_c/\sigma_0$ as a function of $g \equiv Z^2 l_B/\lambda$ for different values of $\theta \equiv a/(Z^2 l_B)$. At low surface charge $g \ll 1$, the counterion distribution is well described by PB theory since $\tau \ll 1$. However, at high surface charge, correlation effects lead to a large fraction of counterion condensed. The condensation is first order for $\theta < \theta_c$ and smooth for $\theta > \theta_c$, where $\theta_c \approx 0.0378$. The solid line $\theta = 0.02$ corresponds to divalent counterions where a finite jump occurs at $g_0 \sim 1.7$ or $\sigma_0 \sim 0.1\, e\ \mathrm{nm}^{-2}$.

where $\gamma \equiv \lambda_R/\lambda_D = 2\,\tau/(1-\tau)$. Note that the first term in $G_{3D}(\mathbf{x},\mathbf{x})$ is just the Coulomb self-energy $G_0(\mathbf{0}) = \int [d^2\mathbf{q}/(2\pi)^2]\,(2\pi l_B Z^2/q)$, which must be subtracted. Inserting $G_{2\mathrm{D}}(\mathbf{x},\mathbf{x})$ and $G_{3\mathrm{D}}(\mathbf{x},\mathbf{x})$ into Eq. (15), we obtain

$$\frac{1}{\mathcal{A}} \frac{\partial \beta \Delta F_{3\mathrm{D}}}{\partial l_B} = \frac{\mathcal{I}_1(\gamma)}{4\pi\lambda_R^3} \frac{\partial \lambda_R}{\partial l_B} + \frac{\mathcal{I}_2(\gamma)/\gamma}{4\pi\lambda_{\mathrm{D}}^3} \frac{\partial \lambda_D}{\partial l_B} + (\text{self-energy}), \tag{18}$$

where the functions $\mathcal{I}_{1,2}(\gamma)$ are given by

$$\mathcal{I}_1(\gamma) = \frac{1}{2}\ln(1+\gamma) + 3\left| \sqrt{\frac{1+\gamma}{3-\gamma}} \tan^{-1} \sqrt{\frac{3-\gamma}{1+\gamma}} \right|,$$

$$\mathcal{I}_2(\gamma) = \frac{\gamma}{2}\ln\frac{\gamma^2}{1+\gamma} + (2-\gamma)\left| \sqrt{\frac{1+\gamma}{3-\gamma}} \tan^{-1} \sqrt{\frac{3-\gamma}{1+\gamma}} \right|.$$

Because $\mathcal{I}_{1,2}(\gamma)$ are independent of l_B, we can integrate Eq. (15) back to obtain $\beta \Delta F_{3D}$; thus, the total free energy per unit area for the free counterions is

$$\beta f_{3\mathrm{D}}(\tau) = \frac{n_R}{Z} \ln\left(\frac{n_R a^3}{2Z\lambda_R} \right) - \frac{n_R}{Z} - \frac{\mathcal{I}_1(\gamma)}{8\pi\lambda_R^2} - \frac{\mathcal{I}_2(\gamma)}{8\pi\lambda_D\lambda_R}. \tag{19}$$

Incidentally, in the limit of vanishing density of the condensed counterions, $n_c \to 0$ (or $\lambda_R \to \lambda$), $\mathcal{I}_1(0) = \pi/\sqrt{3}$, and we obtain the fluctuation correction to the mean-field PB free energy: $\Delta f_{\mathrm{PB}} = -k_B T/(8\sqrt{3}\,\lambda^2)$. This result may be understood physically as follows. According to PB theory, the counterions are confined to a slab of thickness λ, and thus may be considered as an ideal gas with a 3D concentration of $c \sim n_0/\lambda$. This implies that the inverse of the 3D "screening" length is $\kappa_s \sim \sqrt{c\, l_B} \sim 1/\lambda$. Using the 3D Debye-Hückel free energy (per unit volume) $\beta\Delta f \sim -\kappa_s^3$, the correction to the mean-field PB free energy (per unit area) scales like $\beta\Delta f_{\mathrm{PB}} \sim -\lambda \times \lambda^{-3} \sim -\lambda^{-2}$, in agreement with Eq. (3). Therefore, the precise calculation leading to Eq. (19) justifies the use of the simple picture to illustrate the physics behind the counterion condensation presented in the Introduction. We note finally that Eq. (19) also contains additional couplings among the fluctuations of the "condensed" and "free" counterions.

III. RESULTS AND DISCUSSION

The central results of this paper follow from the minimization of the total free energy $f(\tau) = f_{2\mathrm{D}}(\tau) + f_{3\mathrm{D}}(\tau)$, obtained, respectively, in Eqs. (2) and (19), with respect to the order parameter τ. Figure 1 summarizes the behavior of τ as a function of the coupling constant related to the surface charge density $g = Z^2 l_B/\lambda$ and the reduced temperature $\theta \equiv a/(Z^2 l_B)$. For weak coupling $g \ll 1$, where fluctuation corrections are negligibly small, the counterions prefer to be free to gain entropy; there are almost no condensed counterions so that $\tau \approx 0$. This is not surprising since PB theory is a weak-coupling theory that becomes exact as $g \to 0$. However, for higher surface charge density, where correlation effects become more important, the behavior of τ depends crucially on θ. In particular, for $\theta < \theta_c \approx 0.0378$, τ displays a finite jump at $g_0(\theta)$, e.g., $g_0 = 1.695$ at $\theta = 0.02$. [This corresponds to divalent counterions at room temperature with $\sigma_0 \sim 0.1e$ nm^{-2}.] Thus, the system exhibits a first-order phase transition, in which a large fraction of counterions is condensed (about 80%). The physical mechanism leading to this counterion condensation is the additional binding arising from 2D charge fluctuations, which dominates the system at lower temperatures. However, for $\theta > \theta_c$ the behavior of τ is completely different; in this regime, there is *no phase transition* and the condensation occurs smoothly. Thus, the condensation transition is similar to the liquid-gas transition, which has a line of first-order transitions terminating at the critical point where a *second-order* transition occurs. In our case, the critical point is found to be $\tau_c \simeq 0.4$, $g_c \simeq 1.605$, and $\theta_c \simeq 0.0378$. Furthermore, if one takes $l_B \sim 10$ Å, i.e., room temperature, and $a \sim 1$ Å, it follows from the definition of θ that there is a critical value of counterion valence $Z_c = \sqrt{a/(l_B \theta_c)} \simeq 1.62$, below which no first-order condensation transition is possible. Therefore, divalent counterions behave *qualitatively* differently from monovalent counterions. In fact, significant differences between monovalent and divalent ions are observed in various biophysical processes.

We stress that fluctuation effects are crucial for this counterion condensation transition to occur. In fact, it may be viewed as a surface analog of the bulk transition discussed by Fisher and Levin [16]. These authors predicted a phase separation, where a strongly correlated, dense phase coexists with a weakly correlated dilute phase in an ionic system dominated by Coulomb interactions and charge fluctuations. In our case, the surface breaks the translational symmetry and similar phase separation occurs in its vicinity. Indeed, using Eq. (19) in the limit of $\tau \to 0$, i.e., without assuming the existence of 2D condensate, the system shows a thermodynamic instability at $g \sim 4.4$. The inclusion of an additional degree of freedom, i.e., allowing the counterions to condense, can only lower the total free energy, suggesting a phase transition in which the condensate (''liquid'') near the surface coexists with the more dilute, delocalized counterion (''gas'') distribution. Indeed, a recent simulation [17] clearly shows that at low temperature, most of the counterions reside on the surface, consistent with our two-fluid picture. However, our calculation based on the Gaussian fluctuation theory may break down for very large $g > 10$. In this regime, a complementary treatment is considered by Shklovskii in Ref. [4], in which the condensed counterions are assumed to form a 2D strongly correlated liquid. That theory also predicts a strongly reduced surface charge and an exponentially large renormalized Gouy-Chapmann length, qualitatively similar to our results. In contrast, by treating the fluctuations of the condensed and free counterions on an equal footing, we are able to capture the onset of the condensation (at $g \sim 2$), which bridges between the regime where PB theory is appropriate, $g \rightarrow 0$, and the very strong coupling regime, $g \rightarrow \infty$ [4,17].

In summary, we have presented a mechanism by which the counterions become condensed so as to neutralize the surface charge of a macroion. It has been known experimentally that an effective surface charge, which is always lower than the actual charge, must be introduced in order to fit experimental data to the PB theory [18]. Thus, our theory offers a possible scenario to account for this experimental fact. In addition, for the case of two highly charged surfaces, the PB repulsions between them are greatly reduced due to strong condensation, and the dominant interaction will be the charge fluctuation attractions. Thus, this condensation picture may also be crucial to understanding the like-charged attraction [19]. Furthermore, there are some recent experimental [20] and simulation [21] indications that are consistent with the predicted condensation effect. The experiments [20] were performed with a monolayer of cationic surfactant where surface density of the surfactant and the counterion/salt density are controlled with high accuracy. The experiments measured a rapid neutralization (about 90%) of the charged surfactant monolayer by increasing its surface density (by about 10%). In some cases, a discontinuous neutralization process is observed [20]. Also, recent extensive simulation studies of uniformly charged surfaces performed in Ref. [21] report two interesting observations: First, when $g \gg 1$ there appears a coexistence between two distinct counterion density distributions: an exponentially decaying distribution near the immediate vicinity of the charged surface and an algebraic decaying distribution far away from the the surface. Note that the exponentially decaying distribution might be associated with our condensed counterions, which we have assumed to be a δ-function distribution. Second, the specific heat of the simulated system shows a pronounced hump in the region $10 < g < 100$, though no rigorous proof of the condensation transition from simulations (and experiments) has been obtained so far. Indeed, there remains some fundamental issues to be addressed in the future, for example, the role of excluded volumes, the discreteness of the surface charge and its mobility, and higher order (beyond Gaussian) corrections. A recent calculation and simulation shows that charge discreteness also induces charge localization [22]. Therefore, it is possible that these neglected effects may smooth out the first-order transition. However, we believe that a rapid variation of the condensation with the surface charge, reflecting the predicted effect, should remain.

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