Electrolytic depletion interactions

M. N. Tamashiro* and P. Pincus

Materials Research Laboratory, University of California at Santa Barbara, Santa Barbara, California 93106-5130
(Received 8 July 1999)

We consider the interactions between two uncharged planar macroscopic surfaces, immersed in an electrolyte solution, which are induced by interfacial selectivity. These forces are taken into account by introducing a depletion free-energy density functional, in addition to the usual mean-field Poisson-Boltzmann functional. The minimization of the total free-energy functional yields the density profiles of the microions and the electrostatic potential. The disjoining pressure is obtained by differentiation of the total free energy with respect to the separation of the surfaces, holding the range and strength of the depletion forces constant. We find that the induced interaction between the two surfaces is always repulsive for sufficiently large separations, and becomes attractive at shorter separations. The nature of the induced interactions changes from attractive to repulsive at a distance corresponding to the range of the depletion forces. [S1063-651X(99)14012-1]

PACS number(s): 05.70.Np, 65.50.+m, 61.20.Qg, 87.10.+e

I. INTRODUCTION

Electrostatic interactions often play an important role in a variety of different systems, ranging from biological membranes to chemical industrial paint ingredients. In some cases, it provides the underlying mechanism for the stabilization of mesoscopic systems against flocculation and precipitation. When two macroscopic charged surfaces approach one another, the result is *usually* a repulsive force, which inhibits a further approach. For two flat charged plates, this effect can be understood in a physical picture in terms of the osmotic pressure generated by the difference of the ion concentration in the region between the two approaching surfaces and the electrolyte-reservoir concentration. On the other hand, attractive interactions, which lead to aggregation or fusion, are sometimes a desirable feature. This is the case, for example, in the adhesion and fusion of vesicles and membranes or in environmental sewage treatment. Furthermore, some experiments [1–5] and simulations [6–9] indicate that, for small separations and high surface-charge densities, two like-charged polyions can indeed attract.

From the theoretical point of view, several distinct mechanisms leading to attractive interactions have been proposed, which are based on charge fluctuations [10–12], strong positional charge correlations [13–15], anisotropic hypernetted chain calculations [16] or strong bulk-counterion correlations [17,18]. Very recently a unified treatment, taking into account quantum fluctuations and structural correlations of the Wigner crystals formed by the condensed counterions onto the charged surfaces, has been proposed [19]. Although the bare Coulomb force between two macroscopic surfaces is always repulsive, correlations and/or fluctuations can induce attractive interactions, which occasionally may overcome the electrostatic repulsion between the two equally charged surfaces. Correlations, which are entirely neglected within the mean-field Poisson-Boltzmann (PB) approximation (Gouy-Chapman theory [20,21]), are believed to be *es-*

sential ingredients for the appearance of attractive interactions. Thus most proposed mechanisms which lead to attraction always include a non-mean-field effect.

In this work we propose a mechanism for attraction between two identical plates. In contrast to the previous theoretical pictures, this mechanism is entirely at the mean-field level. However, nonpure electrostatic forces are taken into account by including depletion forces—for example, those associated with finite ionic radii—acting on one of the ion species surrounding the plates. For simplicity, we consider the case in which the identical plates are uncharged and infinitely large. By considering *uncharged* plates, we can discern the effect of the depletion forces separately from the usual electrostatic mean-field repulsion, which indeed turns out to be entropic and not strictly electrostatic. If we treat the *surface-charged* case, we are not able to separate the two contributions. Due to the simplicity of the model, it is possible to derive explicit, analytical expressions for all thermodynamical properties, including the disjoining pressure.

The remainder of this paper is organized as follows. In Sec. II the model is introduced and the general equations are obtained. Section III is devoted to solving the generalized PB equations for the nonoverlapping regime, when the depletion zones associated with the two plates do not overlap. The solution to the generalized PB equations for the overlapping regime, when the depletion zones associated with the two plates do overlap, is obtained in Sec. IV. Some concluding remarks are presented in Sec. V. The closed analytical expression for the disjoining pressure is obtained in the Appendix.

II. DEFINITION OF THE MODEL

We shall consider two uncharged macroscopic surfaces immersed in a symmetric 1:1 electrolyte within mean-field theory. The system is modeled by two planar, infinitely thin rigid and uncharged surfaces, separated by a distance h, in contact with a monovalent salt reservoir of bulk concentration n_0. A Cartesian coordinate system is chosen so that the surfaces are located at the $x = \pm h/2$ planes, in such a way that the x axis is perpendicular to the surfaces. At the mean-

---

*Electronic addresses: mtamash@mrl.ucsb.edu, fyl@physics.ucsb.edu

field level the microions are treated as an inhomogeneous ideal gas, with local number densities $n_+(x)$ and $n_-(x)$ for the positive and negative ions, respectively. We assume that, due to some *nonelectrostatic depletion* mechanism, these local densities become inhomogeneous in the region close to the infinite plates. These inhomogeneities are governed by the reduced (total) free-energy functional (per unit area), $\bar{f} = \beta f$, where $\beta = 1/k_B T$,

$$\bar{f} = \bar{f}_{\text{depletion}} + \bar{f}_{\text{PB}}, \tag{1}$$

which we split into two terms. The first term of Eq. (1) corresponds to a *nonelectrostatic depletion* free energy (per unit area),

$$\bar{f}_{\text{depletion}} = \epsilon \int_{-\infty}^{\infty} dx\, n_+(x) \left[w_s \left(x + \frac{h}{2} \right) + w_s \left(x - \frac{h}{2} \right) \right], \tag{2}$$

where ϵ is a depletion-strength parameter (which has dimensions of distance), and $w_s(\xi)$ can be considered a normalized external (nonelectrostatic) potential with a finite short range s. This term breaks the original degeneracy between cations and anions, penalizing positive particles that are closest from a distance s to the surfaces. It mimics, for example, the effect of different sizes for the microions. Smaller negative ions are allowed to come in direct contact with the neutral surfaces, whereas the positive particles, due to their larger size, are held apart from an effective distance s, related to their sizes. The effect of this term on the system is to yield an excess of anions in the region surrounding the plates, leading to an inhomogeneity of the local densities of microions in the vicinity of the uncharged plates. Thus, although the surfaces are themselves neutral, this imbalance of microions gives rise to a nonvanishing electric field. To allow analytical calculations, we shall hereafter assume that w_s has the step-function form

$$w_s(\xi) = \begin{cases} 0 & \text{for } |\xi| \geqslant s \\ \dfrac{1}{2s} & \text{for } |\xi| < s. \end{cases} \tag{3}$$

In the limit $s \to 0$, the function $w_s(\xi)$ corresponds to the Dirac delta function $\delta(\xi) = \lim_{s \to 0} w_s(\xi)$. Therefore, w_s has dimensions of inverse distance.

The second term of Eq. (1), $\bar{f}_{\text{PB}}$, represents the reduced *bulk excess* PB free-energy functional (per unit area),

$$\bar{f}_{\text{PB}} = \int_{-\infty}^{\infty} dx \{ n_+(x)(\ln[\Lambda^3 n_+(x)] - 1)$$

$$+ n_-(x)(\ln[\Lambda^3 n_-(x)] - 1) + \tfrac{1}{2}\phi(x)[n_+(x) - n_-(x)]$$

$$- \beta\mu[n_+(x) + n_-(x)] + \beta\Pi_0 \}$$

$$= \int_{-\infty}^{\infty} dx \{ n_+(x)\ln[n_+(x)/n_0] + n_-(x)\ln[n_-(x)/n_0]$$

$$+ \tfrac{1}{2}\phi(x)[n_+(x) - n_-(x)] - [n_+(x) + n_-(x) - 2n_0] \}, \tag{4}$$

where Λ is an arbitrary length scale. The electrochemical potential and the reference pressure were set, respectively, to $\beta\mu = \ln(\Lambda^3 n_0)$ and $\beta\Pi_0 = 2n_0$, since the system is in electrochemical equilibrium with the infinite salt reservoir. The reduced electrostatic potential, $\phi(x) = \beta e \psi(x)$, where e is the proton charge and $\psi(x)$ is the electrostatic potential, satisfies the Poisson equation

$$\frac{d^2\phi(x)}{dx^2} = -4\pi l [n_+(x) - n_-(x)], \tag{5}$$

where $l = \beta e^2/D$ is the Bjerrum length, and the solvent is treated as a continuum of dielectric constant D.

Minimization of the reduced total free-energy functional $\bar{f}[n_+(x), n_-(x)]$ with respect to the number densities,

$$\frac{\delta\bar{f}[n_+(x), n_-(x)]}{\delta n_+(x)} = \ln[n_+(x)/n_0] + \phi(x) + \epsilon \left[w_s \left(x + \frac{h}{2} \right) \right.$$

$$\left. + w_s \left(x - \frac{h}{2} \right) \right] = 0, \tag{6}$$

$$\frac{\delta\bar{f}[n_+(x), n_-(x)]}{\delta n_-(x)} = \ln[n_-(x)/n_0] - \phi(x) = 0, \tag{7}$$

leads to the Boltzmann distribution for the optimum microion profiles:

$$n_+(x) = n_0 \exp\left[-\phi(x) - \epsilon w_s \left(x + \frac{h}{2} \right) - \epsilon w_s \left(x - \frac{h}{2} \right) \right], \tag{8}$$

$$n_-(x) = n_0 \exp[\phi(x)]. \tag{9}$$

Replacing Eqs. (8) and (9) into the Poisson equation (5) leads to a generalized PB equation

$$\frac{d^2\phi(x)}{dx^2} = \frac{\kappa^2}{2} \left\{ \exp[\phi(x)] - \exp\left[-\phi(x) - \epsilon w_s \left(x + \frac{h}{2} \right) \right. \right.$$

$$\left. \left. - \epsilon w_s \left(x - \frac{h}{2} \right) \right] \right\}, \tag{10}$$

where $\kappa \equiv \sqrt{8\pi n_0 l}$ is the inverse of the Debye screening length.

The appropriate boundary conditions are the vanishing of the electrostatic potential and the electric field at infinity,

$$\phi(x \to \pm\infty) = \phi'(x \to \pm\infty) = 0; \tag{11}$$

the vanishing of the electric field at the midplane ($x = 0$),

$$\phi'(x = 0) = 0; \tag{12}$$

and the continuity of the electrostatic potential and the electric field across the planes located at $x = \pm(h/2) \pm s$,

$$\phi\left(x\uparrow\pm\frac{h}{2}\pm s\right)=\phi\left(x\downarrow\pm\frac{h}{2}\pm s\right), \qquad (13)$$

$$\phi'\left(x\uparrow\pm\frac{h}{2}\pm s\right)=\phi'\left(x\downarrow\pm\frac{h}{2}\pm s\right), \qquad (14)$$

where $\phi(x\uparrow y)\equiv\lim_{x\to y_+}\phi(x)$ and $\phi(x\downarrow y)\equiv\lim_{x\to y_-}\phi(x)$. The boundary conditions (13) and (14) are based on the fact that the charge distribution, which appears on the right-hand side of the Poisson equation (5), contains just a *finite jump* at the planes $x=\pm(h/2)\pm s$.

By symmetry we have $\phi(x)=\phi(-x)$, and we need only to consider the *positive* x axis. Because of the nonelectro-

static depletion of *cations* around the surfaces located at $x=\pm h/2$, the electrostatic potential $\phi(x)$ is *always negative*, since there is an effective excess of *anions* around the surfaces. We shall consider two regimes separately, namely, the nonoverlapping regime ($h>2s$) and the overlapping regime ($h<2s$).

III. NONOVERLAPPING REGIME, $h>2s$

In the nonoverlapping regime, which occurs when the separation between the surfaces is larger than the range of the depletion forces, $h>2s$, the depletion zones associated with the two interfaces *do not overlap,* and the generalized PB equation reads

$$\frac{d^2\phi(x)}{dx^2}=\begin{cases}\kappa^2\sinh\phi(x), & \text{for } 0\leq x\leq\frac{h}{2}-s \text{ and } x\geq\frac{h}{2}+s \\[2mm] e^{-2\alpha}\kappa^2\sinh[\phi(x)+2\alpha] & \text{for } \frac{h}{2}-s<x<\frac{h}{2}+s,\end{cases} \qquad (15)$$

where we introduced the parameter $\alpha\equiv\epsilon/8s$.

Using the identity $d^2\phi(x)/dx^2=\frac{1}{2}d[\phi']^2/d\phi$, the nonlinear second-order differential equation represented by Eq. (15) can be analytically integrated. Introducing the midplane electrostatic potential, $\phi_m=\phi(x=0)$, and the internal and external electrostatic potentials in the vicinity of the interface at $x=h/2$, $\phi_<=\phi(x=(h/2)-s)$ and $\phi_>=\phi(x=(h/2)+s)$, the solutions which satisfy the boundary conditions (11) and (12) can be written explicitly as

$$\phi'(x)=\begin{cases}\kappa\Delta[\phi_m,\phi(x)] & \text{for } 0\leq x\leq\frac{h}{2}-s \\[2mm] \kappa\,\text{sgn}(x-x_i)e^{-\alpha}\Delta_\alpha[\phi_i,\phi(x)] & \text{for } \frac{h}{2}-s<x<\frac{h}{2}+s \\[2mm] -2\kappa\sinh\frac{\phi(x)}{2} & \text{for } x\geq\frac{h}{2}+s,\end{cases} \qquad (16)$$

$$\phi(x)=\begin{cases}2\,\text{arcsinh}\left[\dfrac{\sinh\dfrac{\phi_m}{2}}{\text{cn}\left(\kappa x\cosh\dfrac{\phi_m}{2},1\Big/\cosh\dfrac{\phi_m}{2}\right)}\right] & \text{for } 0\leq x\leq\frac{h}{2}-s \\[6mm] 2\,\text{arcsinh}\left\{\dfrac{\sinh\left(\dfrac{\phi_i}{2}+\alpha\right)}{\text{cn}\left[e^{-\alpha}\kappa(|x|-x_i)\cosh\left(\dfrac{\phi_i}{2}+\alpha\right),1\Big/\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)\right]}\right\}-2\alpha & \text{for } \frac{h}{2}-s<x<\frac{h}{2}+s \\[6mm] 4\,\text{arctanh}\left\{\exp\left[-\kappa\left(\left|x\right|-\dfrac{h}{2}-s\right)\right]\tanh\dfrac{\phi_>}{4}\right\} & \text{for } x\geq\frac{h}{2}+s,\end{cases} \qquad (17)$$

where we introduced

$$\Delta(\phi_m,\phi)=-\sqrt{2\cosh\phi-2\cosh\phi_m}$$
$$=2\sinh\frac{\phi}{2}\sqrt{1-\left[\sinh\frac{\phi_m}{2}\Big/\sinh\frac{\phi}{2}\right]^2}, \qquad (18)$$

$$\Delta_\alpha(\phi_i,\phi)=\sqrt{2\cosh(\phi+2\alpha)-2\cosh(\phi_i+2\alpha)}. \qquad (19)$$

$\text{cn}(u,k)$ is the Jacobi cosine-amplitude elliptic function with modulus k [22,23], x_i is the inversion point where the electric field vanishes, $\phi'(x_i)=0$, and the electrostatic potential $\phi_i=\phi(x_i)$ is an integration constant to be determined by the boundary conditions (13) and (14).

Matching the electrostatic potential $\phi(x)$ at the planes x

$=(h/2)\pm s$ by imposing the boundary conditions (13) gives

$$\phi_< = 2\,\mathrm{arcsinh}\left\{ \frac{\sinh\dfrac{\phi_m}{2}}{\mathrm{cn}\left[\kappa\left(\dfrac{h}{2}-s\right)\cosh\dfrac{\phi_m}{2},1\left/\cosh\dfrac{\phi_m}{2}\right.\right]} \right\},$$
(20)

$$\kappa s = \frac{\mathcal{F}_\alpha(\phi_i,\phi_<)+\mathcal{F}_\alpha(\phi_i,\phi_>)}{2e^{-\alpha}\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)},$$
(21)

$$\kappa x_i = \frac{\mathcal{F}(\phi_m,\phi_<)}{\cosh\dfrac{\phi_m}{2}} + \frac{\mathcal{F}_\alpha(\phi_i,\phi_<)}{e^{-\alpha}\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)},$$
(22)

where we introduced

$$\mathcal{F}(\phi_m,\phi) = F\left(\arccos\left[\sinh\dfrac{\phi_m}{2}\left/\sinh\dfrac{\phi}{2}\right.\right],1\left/\cosh\dfrac{\phi_m}{2}\right.\right),$$
(23)

$$\mathcal{F}_\alpha(\phi_i,\phi) = \mathcal{F}(\phi_i+2\alpha,\phi+2\alpha)$$
$$= F\left\{\arccos\left[\sinh\left(\dfrac{\phi_i}{2}+\alpha\right)\left/\sinh\left(\dfrac{\phi}{2}+\alpha\right)\right.\right],\right.$$
$$\left.1\left/\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)\right.\right\},$$
(24)

and $F(\psi,k)=\int_0^\psi d\theta/\sqrt{1-k^2\sin^2\theta}$ is the elliptic integral of the first kind [22,23].

On the other hand, matching the electric field $\phi'(x)$ at the planes $x=(h/2)\pm s$ by imposing the boundary conditions (14) leads to

$$e^{-2\alpha}[\cosh(\phi_<+2\alpha)-\cosh(\phi_>+2\alpha)]$$
$$=\cosh\phi_<-\cosh\phi_m-2\sinh^2\dfrac{\phi_>}{2},$$
(25)

$$\cosh(\phi_i+2\alpha)=\cosh(\phi_>+2\alpha)-2e^{2\alpha}\sinh^2\dfrac{\phi_>}{2}.$$
(26)

Equations (21) and (25) represent a pair of coupled equations which can be solved for ϕ_m and $\phi_>$, since we can use Eqs. (20) and (26) to eliminate $\phi_<$ and ϕ_i, respectively. Once we have obtained ϕ_m and $\phi_>$ which solve Eqs. (21) and (25), the electrostatic potential $\phi(x)$ can be obtained by replacing them into the closed expression (17). To illustrate typical profiles for the nonoverlapping regime, in Fig. 1 we show the reduced electrostatic potential $\phi(x)$ and the density profiles $n_\pm(x)$ for fixed values of ϵ, s, and h. We also present the particle-density excess over the reservoir,

$$n(x)\equiv n_+(x)+n_-(x)-2n_0,$$
(27)

and the charge density,

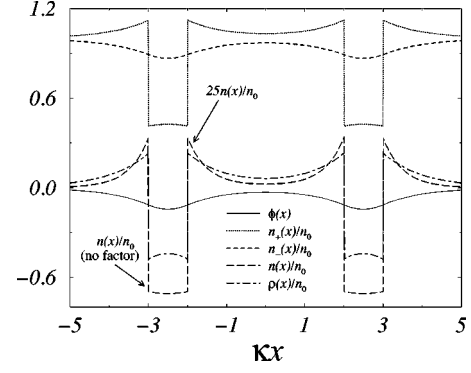$$\rho(x)\equiv n_+(x)-n_-(x).$$
(28)

FIG. 1. Reduced electrostatic potential $\phi(x)$ and density profiles as functions of the distance x for the set of parameters $\kappa\epsilon=1$, $\kappa s=1/2$, and $\kappa h=5$ (nonoverlapping regime). All densities are normalized to the salt reservoir density n_0. The positive portion of the particle-density excess $n(x)$ was amplified by a factor of 25.

The total free-energy density associated with the electrostatic potential (17) and the microion profiles (8) and (9) is obtained by replacing their closed forms into the total free-energy functional, given by Eq. (1), and performing the integrations. After some algebra, we obtain

$$\frac{\kappa}{n_0}\bar{f}=8\kappa s(1-e^{-2\alpha})+2\Delta(\phi_m,\phi_<)\left(\phi_<-4\coth\dfrac{\phi_<}{2}\right)$$

$$+16\mathcal{E}(\phi_m,\phi_<)\cosh\dfrac{\phi_m}{2}-8\mathcal{F}(\phi_m,\phi_<)\frac{\sinh^2\dfrac{\phi_m}{2}}{\cosh\dfrac{\phi_m}{2}}$$

$$+2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)\left[\phi_<-4\coth\left(\dfrac{\phi_<}{2}+\alpha\right)\right]$$

$$+2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)\left[\phi_>-4\coth\left(\dfrac{\phi_>}{2}+\alpha\right)\right]$$

$$+16e^{-\alpha}[\mathcal{E}_\alpha(\phi_i,\phi_<)+\mathcal{E}_\alpha(\phi_i,\phi_>)]\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)$$

$$-8e^{-\alpha}[\mathcal{F}_\alpha(\phi_i,\phi_<)+\mathcal{F}_\alpha(\phi_i,\phi_>)]\frac{\sinh^2\left(\dfrac{\phi_i}{2}+\alpha\right)}{\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)}$$

$$+4\sinh\dfrac{\phi_>}{2}\left(\phi_>-4\tanh\dfrac{\phi_>}{4}\right),$$
(29)

where we introduced

$$\mathcal{E}(\phi_m,\phi_<)=E\left(\arccos\left[\sinh\dfrac{\phi_m}{2}\left/\sinh\dfrac{\phi_<}{2}\right.\right],1\left/\cosh\dfrac{\phi_m}{2}\right.\right),$$
(30)

$$\mathcal{E}_\alpha(\phi_i,\phi)=\mathcal{E}(\phi_i+2\alpha,\phi+2\alpha)$$
$$=E\left\{\arccos\left[\sinh\left(\dfrac{\phi_i}{2}+\alpha\right)\left/\sinh\left(\dfrac{\phi}{2}+\alpha\right)\right.\right],\right.$$
$$\left.1\left/\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)\right.\right\},$$
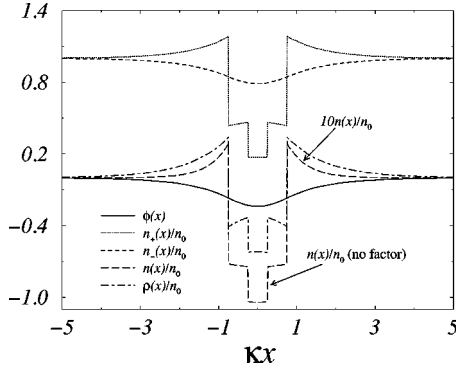(31)

FIG. 2. Reduced electrostatic potential $\phi(x)$ and density profiles as functions of the distance x for the set of parameters $\kappa\epsilon=1$, $\kappa s=1/2$, and $\kappa h=1/2$ (overlapping regime). All number densities are normalized to the salt reservoir density n_0. The positive portion of the particle-density excess $n(x)$ was amplified by a factor of 10.

and $E(\psi,k)=\int_0^\psi d\theta\sqrt{1-k^2\sin^2\theta}$ is the elliptic integral of the second kind [22,23]. The closed analytical expression (29) was checked against numerical integration of the free-energy density (1). In Fig. 3, we present the total free-energy density as a function of the separation of the surfaces h for a fixed value of the depletion strength ϵ and several values of the depletion range s.

The disjoining pressure Π is given by the negative derivative of the total free energy with respect to the separation of the surfaces, h, for constant depletion strength ϵ and range s,

$$\beta\Pi\equiv-\kappa\frac{\partial\bar{f}}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}}, \qquad (32)$$

where we introduced the dimensionless distances $\bar{h}=\kappa h$ and $\bar{s}=\kappa s$. After a lengthy calculation (see the Appendix), we obtain a very simple final expression for the disjoining pressure:

$$\beta\Pi=4n_0\sinh^2\frac{\phi_m}{2}=n(x=0). \qquad (33)$$

The above simple analytical expression was checked against numerical differentiation of the free-energy density for the nonoverlapping regime (29). Thus, it turns out that the disjoining pressure for the nonoverlapping regime is given simply by the excess osmotic pressure of the microions at the midplane over the bulk (reservoir) pressure. Although it might be tempting to attribute this simple result to the contact-value theorem for charged plates [24–26], we stress that this is not the case. Actually, an expression for the particle-density excess similar to the charged-plates case,

$$n(x)=n(x=0)+\frac{n_0}{\kappa^2}[\phi'(x)]^2, \qquad (34)$$

holds only for $0\leq|x|\leq|(h/2)-s|$. Since there are nonvanishing discontinuities for the density of cations $n_+(x)$ upon crossing the surfaces at $x=\pm(h/2)\pm s$,
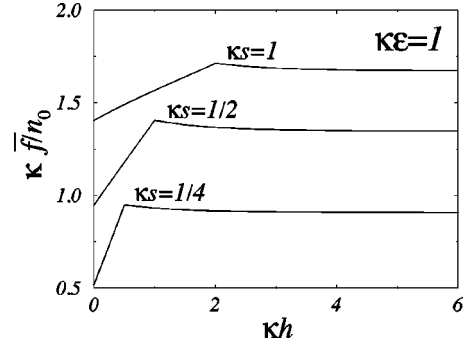

FIG. 3. Reduced total free-energy density $\bar{f}$ as a function of the separation of the surfaces h for a fixed value of the depletion strength ($\kappa\epsilon=1$) and three values of the depletion range ($\kappa s=1/4$, $1/2$, and 1). Although the free-energy density itself is continuous upon crossing the separation $h=2s$, it has a kink at this special value, giving rise to a change between attractive and repulsive forces (see Fig. 4).

$$\Delta n_+\left(x=\left|\frac{h}{2}-s\right|\right)\equiv n_+\left(x\uparrow\left|\frac{h}{2}-s\right|\right)-n_+\left(x\downarrow\left|\frac{h}{2}-s\right|\right), \qquad (35)$$

$$\Delta n_+\left(x=\left|\frac{h}{2}+s\right|\right)\equiv n_+\left(x\uparrow\left|\frac{h}{2}+s\right|\right)-n_+\left(x\downarrow\left|\frac{h}{2}+s\right|\right), \qquad (36)$$

the corrected expressions for the particle-density excess for $|x|>|(h/2)-s|$ are

$$n(x)=n(x=0)+\Delta n_+\left(x=\left|\frac{h}{2}-s\right|\right)+\frac{n_0}{\kappa^2}[\phi'(x)]^2$$

$$=n(x=x_i)+\frac{n_0}{\kappa^2}[\phi'(x)]^2 \quad \text{for}$$

$$\left|\frac{h}{2}-s\right|<x<\left|\frac{h}{2}+s\right|, \qquad (37)$$

$$n(x)=n(x=0)+\Delta n_+\left(x=\left|\frac{h}{2}-s\right|\right)+\Delta n_+\left(x=\left|\frac{h}{2}+s\right|\right)$$

$$+\frac{n_0}{\kappa^2}[\phi'(x)]^2$$

$$=\frac{n_0}{\kappa^2}[\phi'(x)]^2 \quad \text{for} \quad x>\left|\frac{h}{2}+s\right|, \qquad (38)$$

where we used Eqs. (25) and (26) to simplify the above expressions. However, these additional contributions cancel when we evaluate the disjoining pressure (for the nonoverlapping regime), and we obtain Eq. (33), a result similar to the contact-value theorem expression for charged plates. Since the disjoining pressure (33) is always positive, the interaction between the surfaces for the nonoverlapping regime is *always repulsive*. At the end of Sec. IV, in Fig. 4, we present the disjoining pressure as a function of the separation of the surfaces h for a fixed value of the depletion strength ϵ and several values of the depletion range s.

IV. OVERLAPPING REGIME, $h < 2s$

In the overlapping regime, which occurs when the separation between the surfaces is smaller than the range of the depletion forces, $h < 2s$, the depletion zones associated with the two interfaces *do overlap,* and the generalized PB equation reads

$$\frac{d^2\phi(x)}{dx^2} = \begin{cases} e^{-4\alpha}\kappa^2\sinh[\phi(x)+4\alpha] & \text{for} \quad 0 \leqslant x \leqslant s - \dfrac{h}{2} \\[2mm] e^{-2\alpha}\kappa^2\sinh[\phi(x)+2\alpha] & \text{for} \quad s - \dfrac{h}{2} < x < s + \dfrac{h}{2} \\[2mm] \kappa^2\sinh\phi(x) & \text{for} \quad x \geqslant s + \dfrac{h}{2}. \end{cases} \tag{39}$$

The calculation is analogous to the case when there is no overlapping of the depletion zones, $h > 2s$. Now the pair of coupled equations to be solved for $\phi_m = \phi(x=0)$ and $\phi_> = \phi(x = s + (h/2))$ is given by

$$\kappa s = \frac{\mathcal{F}_{2\alpha}(\phi_m, \phi_<)}{e^{-2\alpha}\cosh\left(\dfrac{\phi_m}{2} + 2\alpha\right)} + \frac{\mathcal{F}_\alpha(\phi_i, \phi_>) - \mathcal{F}_\alpha(\phi_i, \phi_<)}{2e^{-\alpha}\cosh\left(\dfrac{\phi_i}{2} + \alpha\right)} \tag{40}$$

and

$$e^{-2\alpha}[\cosh(\phi_< + 2\alpha) - \cosh(\phi_> + 2\alpha)] = e^{-4\alpha}[\cosh(\phi_< + 4\alpha) - \cosh(\phi_m + 4\alpha)] - 2\sinh^2\frac{\phi_>}{2}, \tag{41}$$

where $\phi_< = \phi(x = s - (h/2))$ and $\phi_i = \phi(x = x_i)$ are eliminated by using the relations

$$\phi_< = 2\,\mathrm{arcsinh}\left\{\frac{\sinh\left(\dfrac{\phi_m}{2} + 2\alpha\right)}{\mathrm{cn}\left[e^{-2\alpha}\kappa\left(s - \dfrac{h}{2}\right)\cosh\left(\dfrac{\phi_m}{2} + 2\alpha\right), 1\left/\cosh\left(\dfrac{\phi_m}{2} + 2\alpha\right)\right.\right]}\right\} - 4\alpha, \tag{42}$$

$$\cosh(\phi_i + 2\alpha) = \cosh(\phi_> + 2\alpha) - 2e^{2\alpha}\sinh^2(\phi_>/2). \tag{43}$$

Once solved the system of Eqs. (40) and (41), the electric field, and the electrostatic potential can be obtained by replacing the solution $(\phi_m, \phi_>)$ into the closed expressions

$$\phi'(x) = \begin{cases} \kappa e^{-2\alpha}\Delta_{2\alpha}[\phi_m, \phi(x)] & \text{for} \quad 0 \leqslant x \leqslant s - \dfrac{h}{2} \\[2mm] \kappa\,\mathrm{sgn}(x - x_i)e^{-\alpha}\Delta_\alpha[\phi_i, \phi(x)] & \text{for} \quad s - \dfrac{h}{2} < x < s + \dfrac{h}{2} \\[2mm] -2\kappa\sinh\dfrac{\phi(x)}{2} & \text{for} \quad x \geqslant s + \dfrac{h}{2}, \end{cases} \tag{44}$$

$$\phi(x) = \begin{cases} 2\,\mathrm{arcsinh}\left\{\dfrac{\sinh\left(\dfrac{\phi_m}{2} + 2\alpha\right)}{\mathrm{cn}\left[e^{-2\alpha}\kappa x\cosh\left(\dfrac{\phi_m}{2} + 2\alpha\right), 1\left/\cosh\left(\dfrac{\phi_m}{2} + 2\alpha\right)\right.\right]}\right\} - 4\alpha & \text{for} \quad 0 \leqslant x \leqslant s - \dfrac{h}{2} \\[4mm] 2\,\mathrm{arcsinh}\left\{\dfrac{\sinh\left(\dfrac{\phi_i}{2} + \alpha\right)}{\mathrm{cn}\left[e^{-\alpha}\kappa(|x| - x_i)\cosh\left(\dfrac{\phi_i}{2} + \alpha\right), 1\left/\cosh\left(\dfrac{\phi_i}{2} + \alpha\right)\right.\right]}\right\} - 2\alpha & \text{for} \quad s - \dfrac{h}{2} < x < s + \dfrac{h}{2} \\[4mm] 4\,\mathrm{arctanh}\left\{\exp\left[-\kappa\left(|x| - \dfrac{h}{2} - s\right)\right]\tanh\dfrac{\phi_>}{4}\right\} & \text{for} \quad x \geqslant s + \dfrac{h}{2}, \end{cases} \tag{45}$$

with the inversion point given by

$$\kappa x_i = \frac{\mathcal{F}_{2\alpha}(\phi_m,\phi_<)}{e^{-2\alpha}\cosh\left(\dfrac{\phi_m}{2}+2\alpha\right)} - \frac{\mathcal{F}_{\alpha}(\phi_i,\phi_<)}{e^{-\alpha}\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)}. \tag{46}$$

To illustrate typical profiles for the overlapping regime, in Fig. 2 we show the reduced electrostatic potential $\phi(x)$ and the density profiles $n_\pm(x)$, $n(x)$, and $\rho(x)$ for fixed values of ϵ, s, and h.

Again, it is possible to obtain a closed analytical expression for the total free-energy density,

$$\frac{\kappa}{n_0}\overline{f} = 4\left(\overline{s}-\frac{\overline{h}}{2}\right)(1-e^{-4\alpha}) + 4\overline{h}(1-e^{-2\alpha}) + \frac{\kappa}{n_0}\overline{f}_{\text{aux}}, \tag{47}$$

$$\frac{\kappa}{n_0}\overline{f}_{\text{aux}} = 2e^{-2\alpha}\Delta_{2\alpha}(\phi_m,\phi_<)\left[\phi_< - 4\coth\left(\frac{\phi_<}{2}+2\alpha\right)\right] + 16e^{-2\alpha}\mathcal{E}_{2\alpha}(\phi_m,\phi_<)\cosh\left(\frac{\phi_m}{2}+2\alpha\right)$$

$$- 8e^{-2\alpha}\mathcal{F}_{2\alpha}(\phi_m,\phi_<)\frac{\sinh^2\left(\dfrac{\phi_m}{2}+2\alpha\right)}{\cosh\left(\dfrac{\phi_m}{2}+2\alpha\right)} - 2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)\left[\phi_< - 4\coth\left(\frac{\phi_<}{2}+\alpha\right)\right]$$

$$+ 2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)\left[\phi_> - 4\coth\left(\frac{\phi_>}{2}+\alpha\right)\right] - 16e^{-\alpha}[\mathcal{E}_\alpha(\phi_i,\phi_<) - \mathcal{E}_\alpha(\phi_i,\phi_>)]\cosh\left(\frac{\phi_i}{2}+\alpha\right)$$

$$+ 8e^{-\alpha}[\mathcal{F}_\alpha(\phi_i,\phi_<) - \mathcal{F}_\alpha(\phi_i,\phi_>)]\frac{\sinh^2\left(\dfrac{\phi_i}{2}+\alpha\right)}{\cosh\left(\dfrac{\phi_i}{2}+\alpha\right)} + 4\sinh\frac{\phi_>}{2}\left(\phi_> - 4\tanh\frac{\phi_>}{4}\right), \tag{48}$$

which leads, after some algebra (see the Appendix), to a simple expression for the disjoining pressure:

$$\beta\Pi \equiv -\kappa\frac{\partial\overline{f}}{\partial\overline{h}}\bigg|_{\alpha,\overline{s}} = 2n_0[e^{-4\alpha}\cosh(\phi_m+4\alpha) - 1$$

$$+ 2e^{-\phi_< - 6\alpha}\sinh 2\alpha]$$

$$= n(x=0) + 2\Delta n_+\left(x=s-\frac{h}{2}\right). \tag{49}$$

The above simple analytical expression was checked against numerical differentiation of the free-energy density for the overlapping regime (47). It should be remarked that, in this case, the disjoining pressure *does not have the form* of the expression given by the contact-value theorem for charged plates [24–26]. An additional contribution due to the discontinuity $\Delta n_+(x=s-(h/2))$ of the density of cations upon crossing the surface located at $x=s-(h/2)$, appears. Contrary to the nonoverlapping regime, this additional contribution does not cancel when we evaluate the disjoining pressure. According to this imbalanced pressure acting onto the neutral surfaces, this leads to an effective attraction between them.

Figures 3 and 4 show the total free-energy density and the associated pressure as a function of the separation of the surfaces h for a fixed value of the depletion strength ϵ and several values of the depletion range s. The nature of the interactions changes from attractive to repulsive at a separation $h=2s$.

V. CONCLUDING REMARKS

We have proposed a mechanism for attraction between neutral plates immersed in a monovalent electrolyte solution, which does not include any correlation or fluctuation effects. The electrostatic potential and the density profiles of the microions are obtained from analytical solutions of the generalized PB equations, which include nonelectrostatic depletion interactions. Explicit analytical expressions of all thermodynamic properties, including the disjoining pressure, were obtained.
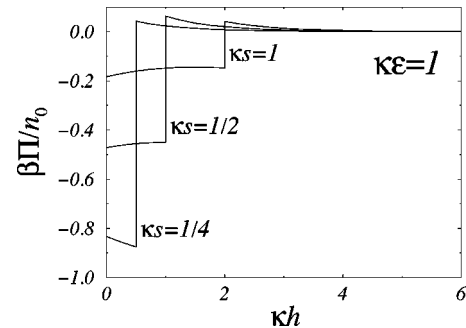
We found that the repulsive interactions at large separa-

FIG. 4. Disjoining pressure Π as a function of the separation of the surfaces h for a fixed value of the depletion strength ($\kappa\epsilon=1$) and three values of the depletion range ($\kappa s=1/4$, $1/2$, and 1). This graph corresponds to the negative derivative of the curves of Fig. 3. Note the discontinuity of the pressure at the separation $h=2s$, associated with the kink of the free energy.

tions become attractive when the separation between the plates is decreased. The range of the attractive forces is closely related to the range of the nonelectrostatic depletion interactions introduced in the formulation of the model. Although this result is not at all surprising, since the attraction is induced by the imbalanced pressure originated from the ionic depletion in the region between the two approaching surfaces, we found that the disjoining pressure *does not have the form* of the expression given by the contact-value theorem for charged plates.

The proposed mechanism could mimic neutral surfaces immersed in an electrolyte solution containing ions of different sizes. We expect to observe attraction when the separation between the two surfaces is comparable to the size of the smaller ions. We stress the fact that we do not include any non-mean-field effects to obtain attractive forces. Surely, for short separations, other features should be taken into account, as for example, the discreteness of the charges and ionic correlations. However, using an exactly solvable model, we showed that the inclusion of non-mean-field effects is not a *necessary condition* to obtain attractive interactions.

ACKNOWLEDGMENTS

APPENDIX: DISJOINING PRESSURE

The disjoining pressure Π is given by the negative derivative of the total free energy with respect to the separation of the surfaces, h, for constant depletion strength ϵ and range s,

$$\frac{\beta\Pi}{n_0} \equiv -\frac{\kappa}{n_0}\frac{\partial\bar{f}}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}} = -\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_m}\frac{\partial\phi_m}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}}$$
$$-\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_<}\frac{\partial\phi_<}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}} -\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_i}\frac{\partial\phi_i}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}}$$
$$-\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_>}\frac{\partial\phi_>}{\partial\bar{h}}\bigg|_{\alpha,\bar{s}}, \quad \text{(A1)}$$

where we introduced, for convenience, the dimensionless distances $\bar{h}=\kappa h$ and $\bar{s}=\kappa s$. The (four) derivatives of the free energy which appears in Eq. (A1), $d\bar{f}/d\varphi$, with $\varphi = (\phi_m,\phi_<,\phi_i,\phi_>)$, can be obtained directly by using the free-energy expressions (29) and (47). On the other hand, the partial derivatives $\partial\varphi/\partial\bar{h}|_{\alpha,\bar{s}}$ are obtained by the matrix product

$$\left(\frac{\partial\phi_m}{\partial\bar{h}}, \frac{\partial\phi_<}{\partial\bar{h}}, \frac{\partial\phi_i}{\partial\bar{h}}, \frac{\partial\phi_>}{\partial\bar{h}}\right)_{\alpha,\bar{s}}$$
$$= \left[\frac{\partial(\bar{h},\bar{s},u,v)}{\partial(\phi_m,\phi_<,\phi_i,\phi_>)}\right]^{-1}(1,0,0,0), \quad \text{(A2)}$$

where u and v are the boundary conditions (14) written in a parametric form involving ϕ_m, $\phi_<$, ϕ_i, and $\phi_>$. We will give the explicit expressions of u and v (and their derivatives) when we separately treat the nonoverlapping and the overlapping regimes.

1. Nonoverlapping regime

For the nonoverlapping regime, the total free-energy density is given by Eq. (29), with derivatives

$$\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_m} = 4\mathcal{E}(\phi_m,\phi_<)\sinh\frac{\phi_m}{2}$$
$$-\frac{2\sinh\phi_m}{\Delta(\phi_m,\phi_<)}\left(\phi_< - 2\tanh^2\frac{\phi_m}{2}\coth\frac{\phi_<}{2}\right), \quad \text{(A3)}$$

$$\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_<} = \frac{2\sinh\phi_<}{\Delta(\phi_m,\phi_<)}\left(\phi_< - 2\tanh\frac{\phi_<}{2}\right)$$
$$+\frac{2e^{-\alpha}\sinh(\phi_<+2\alpha)}{\Delta_\alpha(\phi_i,\phi_<)}\left[\phi_< - 2\tanh\left(\frac{\phi_<}{2}+\alpha\right)\right], \quad \text{(A4)}$$

$$\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_i} = 4e^{-\alpha}[\mathcal{E}_\alpha(\phi_i,\phi_<)+\mathcal{E}_\alpha(\phi_i,\phi_>)]\sinh\left(\frac{\phi_i}{2}+\alpha\right)$$
$$-\frac{2e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_<)}\left[\phi_< - 2\tanh^2\left(\frac{\phi_i}{2}+\alpha\right)\right.$$
$$\left.\times\coth\left(\frac{\phi_<}{2}+\alpha\right)\right] - \frac{2e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)}$$
$$\times\left[\phi_> - 2\tanh^2\left(\frac{\phi_i}{2}+\alpha\right)\coth\left(\frac{\phi_>}{2}+\alpha\right)\right], \quad \text{(A5)}$$

$$\frac{\kappa}{n_0}\frac{d\bar{f}}{d\phi_>} = \frac{2e^{-\alpha}\sinh(\phi_>+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)}\left[\phi_> - 2\tanh\left(\frac{\phi_>}{2}+\alpha\right)\right]$$
$$+2\cosh\frac{\phi_>}{2}\left(\phi_> - 2\tanh\frac{\phi_>}{2}\right). \quad \text{(A6)}$$

The defining equations for $\bar{h}$, $\bar{s}$, u, and v are

$$\bar{h} = \frac{2\mathcal{F}(\phi_m,\phi_<)}{\cosh\frac{\phi_m}{2}} + \frac{\mathcal{F}_\alpha(\phi_i,\phi_<)+\mathcal{F}_\alpha(\phi_i,\phi_>)}{e^{-\alpha}\cosh\left(\frac{\phi_i}{2}+\alpha\right)}, \quad \text{(A7)}$$

$$\bar{s} = \frac{\mathcal{F}_\alpha(\phi_i,\phi_<)+\mathcal{F}_\alpha(\phi_i,\phi_>)}{2e^{-\alpha}\cosh\left(\frac{\phi_i}{2}+\alpha\right)}, \quad \text{(A8)}$$

$$u = e^{-\alpha} \Delta_\alpha(\phi_i, \phi_<) + \Delta(\phi_m, \phi_<) = 0, \tag{A9}$$

$$v = e^{-\alpha} \Delta_\alpha(\phi_i, \phi_>) + 2 \sinh \frac{\phi_>}{2} = 0, \tag{A10}$$

and their derivatives necessary for the evaluation of the Jacobian $\partial(\bar{h}, \bar{s}, u, v)/\partial(\phi_m, \phi_<, \phi_i, \phi_>)$:

$$\frac{d\bar{h}}{d\phi_m} = -\frac{\mathcal{E}(\phi_m, \phi_<)}{\sinh \frac{\phi_m}{2}} - \frac{2 \tanh \frac{\phi_m}{2} \coth \frac{\phi_<}{2}}{\Delta(\phi_m, \phi_<)}, \tag{A11}$$

$$\frac{d\bar{h}}{d\phi_<} = \frac{2}{\Delta(\phi_m, \phi_<)} + \frac{1}{e^{-\alpha} \Delta_\alpha(\phi_i, \phi_<)}, \tag{A12}$$

$$\frac{d\bar{h}}{d\phi_i} = -\frac{[\mathcal{E}_\alpha(\phi_i, \phi_<) + \mathcal{E}_\alpha(\phi_i, \phi_>)]}{2e^{-\alpha} \sinh\left(\frac{\phi_i}{2} + \alpha\right)} - \left[\frac{\coth\left(\frac{\phi_<}{2} + \alpha\right)}{e^{-\alpha} \Delta_\alpha(\phi_i, \phi_<)}\right.$$
$$\left. + \frac{\coth\left(\frac{\phi_>}{2} + \alpha\right)}{e^{-\alpha} \Delta_\alpha(\phi_i, \phi_>)}\right] \tanh\left(\frac{\phi_i}{2} + \alpha\right), \tag{A13}$$

$$\frac{d\bar{h}}{d\phi_>} = \frac{1}{e^{-\alpha} \Delta_\alpha(\phi_i, \phi_>)}, \tag{A14}$$

$$\frac{d\bar{s}}{d\phi_m} = 0, \tag{A15}$$

$$\frac{d\bar{s}}{d\phi_<} = \frac{1}{2e^{-\alpha} \Delta_\alpha(\phi_i, \phi_<)}, \tag{A16}$$

$$\frac{d\bar{s}}{d\phi_i} = -\frac{[\mathcal{E}_\alpha(\phi_i, \phi_<) + \mathcal{E}_\alpha(\phi_i, \phi_>)]}{4e^{-\alpha} \sinh\left(\frac{\phi_i}{2} + \alpha\right)} - \left[\frac{\coth\left(\frac{\phi_<}{2} + \alpha\right)}{2e^{-\alpha} \Delta_\alpha(\phi_i, \phi_<)}\right.$$
$$\left. + \frac{\coth\left(\frac{\phi_>}{2} + \alpha\right)}{2e^{-\alpha} \Delta_\alpha(\phi_i, \phi_>)}\right] \tanh\left(\frac{\phi_i}{2} + \alpha\right), \tag{A17}$$

$$\frac{d\bar{s}}{d\phi_>} = \frac{1}{2e^{-\alpha} \Delta_\alpha(\phi_i, \phi_>)}, \tag{A18}$$

$$\frac{du}{d\phi_m} = -\frac{\sinh \phi_m}{\Delta(\phi_m, \phi_<)}, \tag{A19}$$

$$\frac{du}{d\phi_<} = \frac{\sinh \phi_<}{\Delta(\phi_m, \phi_<)} + \frac{e^{-\alpha} \sinh(\phi_< + 2\alpha)}{\Delta_\alpha(\phi_i, \phi_<)}, \tag{A20}$$

$$\frac{du}{d\phi_i} = -\frac{e^{-\alpha} \sinh(\phi_i + 2\alpha)}{\Delta_\alpha(\phi_i, \phi_<)}, \tag{A21}$$

$$\frac{du}{d\phi_>} = \frac{dv}{d\phi_m} = \frac{dv}{d\phi_<} = 0, \tag{A22}$$

$$\frac{dv}{d\phi_i} = -\frac{e^{-\alpha} \sinh(\phi_i + 2\alpha)}{\Delta_\alpha(\phi_i, \phi_>)}, \tag{A23}$$

$$\frac{dv}{d\phi_>} = \frac{e^{-\alpha} \sinh(\phi_> + 2\alpha)}{\Delta_\alpha(\phi_i, \phi_>)} + \cosh \frac{\phi_>}{2}. \tag{A24}$$

Putting all these together into the expression for the disjoining pressure [Eq. (A1)], leads to a very simple final result:

$$\beta\Pi = 4n_0 \sinh^2 \frac{\phi_m}{2} = n(x = 0). \tag{A25}$$

Although it might be tempting to attribute this simple final result to the contact-value theorem for charged plates, this is not the case (see the discussion at the end of Sec. III).

2. Overlapping regime

For the overlapping regime, it is convenient to apply the parametric differentiation just on the last term, $\bar{f}_{aux}$, of the total free energy (47), since the two first terms yield a constant contribution to the disjoining pressure:

$$\frac{\beta\Pi}{n_0} \equiv -\frac{\kappa}{n_0} \frac{\partial \bar{f}}{\partial \bar{h}}\bigg|_{\alpha, \bar{s}} = 2(1 - e^{-4\alpha}) - 4(1 - e^{-2\alpha})$$
$$- \frac{\kappa}{n_0} \frac{\partial \bar{f}_{aux}}{\partial \bar{h}}\bigg|_{\alpha, \bar{s}}. \tag{A26}$$

The derivatives of the last term [Eq. (48)] of the total free energy $\bar{f}_{aux}$ are given by

$$\frac{\kappa}{n_0} \frac{d\bar{f}_{aux}}{d\phi_m} = 4e^{-2\alpha} \mathcal{E}_{2\alpha}(\phi_m, \phi_<) \sinh\left(\frac{\phi_m}{2} + 2\alpha\right)$$
$$- \frac{2e^{-2\alpha} \sinh(\phi_m + 4\alpha)}{\Delta_{2\alpha}(\phi_m, \phi_<)} \left[\phi_< - 2 \tanh^2\left(\frac{\phi_m}{2} + 2\alpha\right)\right.$$
$$\left. \times \coth\left(\frac{\phi_<}{2} + 2\alpha\right)\right], \tag{A27}$$

$$\frac{\kappa}{n_0} \frac{d\bar{f}_{aux}}{d\phi_<} = \frac{2e^{-2\alpha} \sinh(\phi_< + 4\alpha)}{\Delta_{2\alpha}(\phi_m, \phi_<)} \left[\phi_< - 2 \tanh\left(\frac{\phi_<}{2} + 2\alpha\right)\right]$$
$$- \frac{2e^{-\alpha} \sinh(\phi_< + 2\alpha)}{\Delta_\alpha(\phi_i, \phi_<)} \left[\phi_< - 2 \tanh\left(\frac{\phi_<}{2} + \alpha\right)\right], \tag{A28}$$

$$\frac{\kappa}{n_0}\frac{d\bar{f}_{\text{aux}}}{d\phi_i} = -4e^{-\alpha}[\mathcal{E}_\alpha(\phi_i,\phi_<)-\mathcal{E}_\alpha(\phi_i,\phi_>)]\sinh\left(\frac{\phi_i}{2}+\alpha\right)$$
$$+\frac{2e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_<)}\left[\phi_<-2\tanh^2\left(\frac{\phi_i}{2}+\alpha\right)\right.$$
$$\left.\times\coth\left(\frac{\phi_<}{2}+\alpha\right)\right]-\frac{2e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)}$$
$$\times\left[\phi_>-2\tanh^2\left(\frac{\phi_i}{2}+\alpha\right)\coth\left(\frac{\phi_>}{2}+\alpha\right)\right],$$
(A29)

$$\frac{\kappa}{n_0}\frac{d\bar{f}_{\text{aux}}}{d\phi_>} = \frac{2e^{-\alpha}\sinh(\phi_>+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)}\left[\phi_>-2\tanh\left(\frac{\phi_>}{2}+\alpha\right)\right]$$
$$+2\cosh\frac{\phi_>}{2}\left(\phi_>-2\tanh\frac{\phi_>}{2}\right).$$
(A30)

Now the defining equations for $\bar{h}$, $\bar{s}$, u, and v are

$$\bar{h}=\frac{\mathcal{F}_\alpha(\phi_i,\phi_>)-\mathcal{F}_\alpha(\phi_i,\phi_<)}{e^{-\alpha}\cosh\left(\frac{\phi_i}{2}+\alpha\right)},$$
(A31)

$$\bar{s}=\frac{\mathcal{F}_{2\alpha}(\phi_m,\phi_<)}{e^{-2\alpha}\cosh\left(\frac{\phi_m}{2}+2\alpha\right)}+\frac{\mathcal{F}_\alpha(\phi_i,\phi_>)-\mathcal{F}_\alpha(\phi_i,\phi_<)}{2e^{-\alpha}\cosh\left(\frac{\phi_i}{2}+\alpha\right)},$$
(A32)

$$u=e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)-e^{-2\alpha}\Delta_{2\alpha}(\phi_m,\phi_<)=0,\quad(A33)$$

$$v=e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)+2\sinh\frac{\phi_>}{2}=0,\quad(A34)$$

and their associated derivatives for the evaluation of the Jacobian $\partial(\bar{h},\bar{s},u,v)/\partial(\phi_m,\phi_<,\phi_i,\phi_>)$:

$$\frac{d\bar{h}}{d\phi_m}=0,$$
(A35)

$$\frac{d\bar{h}}{d\phi_<}=-\frac{1}{e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)},$$
(A36)

$$\frac{d\bar{h}}{d\phi_i}=\frac{[\mathcal{E}_\alpha(\phi_i,\phi_<)-\mathcal{E}_\alpha(\phi_i,\phi_>)]}{2e^{-\alpha}\sinh\left(\frac{\phi_i}{2}+\alpha\right)}+\left[\frac{\coth\left(\frac{\phi_<}{2}+\alpha\right)}{e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)}\right.$$
$$\left.-\frac{\coth\left(\frac{\phi_>}{2}+\alpha\right)}{e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)}\right]\tanh\left(\frac{\phi_i}{2}+\alpha\right),$$
(A37)

$$\frac{d\bar{h}}{d\phi_>}=\frac{1}{e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)},$$
(A38)

$$\frac{d\bar{s}}{d\phi_m}=-\frac{\mathcal{E}_{2\alpha}(\phi_m,\phi_<)}{2e^{-2\alpha}\sinh\left(\frac{\phi_m}{2}+2\alpha\right)}$$
$$-\frac{\tanh\left(\frac{\phi_m}{2}+2\alpha\right)\coth\left(\frac{\phi_<}{2}+2\alpha\right)}{e^{-2\alpha}\Delta_{2\alpha}(\phi_m,\phi_<)},\quad(A39)$$

$$\frac{d\bar{s}}{d\phi_<}=\frac{1}{e^{-2\alpha}\Delta_{2\alpha}(\phi_m,\phi_<)}-\frac{1}{2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)},$$
(A40)

$$\frac{d\bar{s}}{d\phi_i}=\frac{[\mathcal{E}_\alpha(\phi_i,\phi_<)-\mathcal{E}_\alpha(\phi_i,\phi_>)]}{4e^{-\alpha}\sinh\left(\frac{\phi_i}{2}+\alpha\right)}+\left[\frac{\coth\left(\frac{\phi_<}{2}+\alpha\right)}{2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_<)}\right.$$
$$\left.-\frac{\coth\left(\frac{\phi_>}{2}+\alpha\right)}{2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)}\right]\tanh\left(\frac{\phi_i}{2}+\alpha\right),$$
(A41)

$$\frac{d\bar{s}}{d\phi_>}=\frac{1}{2e^{-\alpha}\Delta_\alpha(\phi_i,\phi_>)},$$
(A42)

$$\frac{du}{d\phi_m}=\frac{e^{-2\alpha}\sinh(\phi_m+4\alpha)}{\Delta_{2\alpha}(\phi_m,\phi_<)},$$
(A43)

$$\frac{du}{d\phi_<}=-\frac{e^{-2\alpha}\sinh(\phi_<+4\alpha)}{\Delta_{2\alpha}(\phi_m,\phi_<)}+\frac{e^{-\alpha}\sinh(\phi_<+2\alpha)}{\Delta_\alpha(\phi_i,\phi_<)},$$
(A44)

$$\frac{du}{d\phi_i}=-\frac{e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_<)},$$
(A45)

$$\frac{du}{d\phi_>}=\frac{dv}{d\phi_m}=\frac{dv}{d\phi_<}=0,$$
(A46)

$$\frac{dv}{d\phi_i}=-\frac{e^{-\alpha}\sinh(\phi_i+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)},$$
(A47)

$$\frac{dv}{d\phi_>}=\frac{e^{-\alpha}\sinh(\phi_>+2\alpha)}{\Delta_\alpha(\phi_i,\phi_>)}+\cosh\frac{\phi_>}{2}.$$
(A48)

Putting all these together into the disjoining pressure expression (A26), for the overlapping regime we obtain

$$\beta\Pi=n_0(e^{-\phi_m-8\alpha}+e^{\phi_m}-2+2e^{-\phi_<-4\alpha}-2e^{-\phi_<-8\alpha})$$
$$=2n_0[e^{-4\alpha}\cosh(\phi_m+4\alpha)-1+2e^{-\phi_<-6\alpha}\sinh 2\alpha]$$
$$=n(x=0)+2\Delta n_+\left(x=s-\frac{h}{2}\right),$$
(A49)

where the discontinuity of the density of cations Δn_+ upon crossing the surface located at $x=s-(h/2)$ is defined by Eq. (35). We remark that, due to this additional term, in this case the disjoining pressure *does not have the form* of the expression given by the contact-value theorem for charged plates.

[1] N. Ise, Angew. Chem. **25**, 323 (1986).

[2] V. A. Bloomfield, Biopolymers **31**, 1471 (1991).

[3] R. Podgornik, D. C. Rau, and V. A. Parsegian, Biophys. J. **66**, 962 (1994).

[4] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **77**, 1897 (1996).

[5] A. E. Larsen and D. G. Grier, Nature (London) **385**, 230 (1997).

[6] L. Guldbrand, B. Jönsson, H. Wennerström, and P. Linse, J. Chem. Phys. **80**, 2221 (1984).

[7] N. Grønbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997).

[8] N. Grønbech-Jensen, K. M. Beardmore, and P. Pincus, Physica A **261**, 74 (1998).

[9] E. Allahyarov, I. D'Amico, and H. Löwen, Phys. Rev. Lett. **81**, 1334 (1998).

[10] O. Spalla and L. Belloni, Phys. Rev. Lett. **74**, 2515 (1995); J. Chem. Phys. **107**, 465 (1997).

[11] P. A. Pincus and S. A. Safran, Europhys. Lett. **42**, 103 (1998).

[12] Y. Levin, Physica A **265**, 432 (1999).

[13] I. Rouzina and V. A. Bloomfield, J. Phys. Chem. **100**, 9977 (1996).

[14] B. I. Shklovskii, Phys. Rev. Lett. **82**, 3268 (1999).

[15] J. J. Arenzon, J. F. Stilck, and Y. Levin, Eur. Phys. J. B **12**, 79 (1999).

[16] H. Greberg and R. Kjellander, J. Chem. Phys. **108**, 2940 (1998), and references therein.

[17] M. J. Stevens and M. O. Robbins, Europhys. Lett. **12**, 81 (1990).

[18] A. Diehl, M. N. Tamashiro, M. C. Barbosa, and Y. Levin, Physica A **274**, 433 (1999).

[19] A. W. C. Lau, P. Pincus, D. Levine, and H. A. Fertig (unpublished).

[20] G. Gouy, J. Phys. Paris **9**, 457 (1910).

[21] D. L. Chapman, Philos. Mag. **25**, 475 (1913).

[22] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products,* 5th ed., edited by Alan Jeffrey (Academic Press, San Diego, 1994).

[23] P. F. Byrd and M. D. Friedman, *Handbook of Elliptic Integrals for Engineers and Scientists,* 2nd ed. (Springer-Verlag, Berlin, 1971).

[24] D. Andelman, in *Handbook of Biological Physics*, edited by R. Lipowsky and E. Sackmann, Structure and Dynamics of Membranes, Generic and Specific Interactions Vol. 1B (Elsevier, Amsterdam, 1995).

[25] J. N. Israelachvili, *Intermolecular and Surface Forces,* 2nd ed. (Academic Press, London, 1992).

[26] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces and Membranes* (Addison-Wesley, Reading, MA, 1994).