Pressure of correlated layer-charge and counterion fluctuations in charged thin films

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We predict the fluctuation contribution to the interaction between two surfaces with both mobile layer charges and delocalized counterions. The correlation (coupling) between the layer-charge fluctuations and the counterion fluctuations (around a piecewise homogeneous mean-field density profile) is taken into account in the Gaussian approximation. We find that this correlation significantly increases the magnitude of the interlayer fluctuation attraction. The counterion fluctuation pressure is calculated as a function of the intersurface distance and we show how the large and small distance limits correspond to three-dimensional (3D) and 2D fluctuations, respectively. In addition, we predict the charge density-density correlation functions. Experimental implications of the model are discussed. [S1063-651X(99)13911-4]

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I. INTRODUCTION AND SUMMARY OF RESULTS

Fluctuation-induced attractive forces may be important for many effects in charged systems, including membrane adhesion, DNA condensation, colloidal stability (see, e.g., references in [1]), shear response [2], and modification of bending rigidity [3]. Early direct measurements of forces between charged surfaces immersed in aqueous electrolyte solution suggested an anomalous long-range attractive component of the force [4]. Several experimental techniques developed recently have made it possible to measure very weak forces between charged objects on a variety of length scales and at various electrolyte concentrations [5,6]. The ideas of counterion-mediated attraction were applied to study the interaction between like-charged rigid polyelectrolytes [7]; the correlation effects in the counterion system with strong Coulomb coupling were investigated in Ref. [8].

Previous theoretical approaches to the problem of fluctuation-induced interactions in charged, thin films included both numerical and analytical methods. Guldbrand *et al.* [9] accounted for the correlated fluctuations in the ion clouds of the two surfaces using Monte Carlo simulations and found a net attractive interaction of the van der Waals type; however, no analytical law for the interaction was established at that time. Later, a number of numerical, integral equation studies confirmed their results [10,11]. Since, there have been several attempts to obtain the explicit analytical laws of attractive, double layer interactions [1,12–17]. All of them go beyond the mean-field Poisson-Boltzmann (PB) treatment that predicts only a repulsive contribution to the total interaction. The problem where all mobile charges are localized in the plane of the surface (we term these the layer-charge fluctuations) was first considered by Attard *et al.* [12] using a thermodynamic perturbation theory. In the regime of the asymptotically large intersurface separations they found a $-1/h^3$ scaling law for the fluctuation pressure between the surfaces separated by a distance h. Pincus and Safran [1] have recently addressed a similar problem, and using a different approach also considered the small distance limit. They found that the fluctuation pressure scales as $-1/(\lambda^2 h)$ in the limit of small intersurface separations $h \ll \lambda$, where $\lambda=(2\pi \ell \sigma_0)^{-1}$ is the Gouy-Chapman length and σ_0 is the total surface number density of mobile charges; we show below that the Bjerrum length $\ell = e^2/(\epsilon k_b T)$ should be small compared to h in order that the harmonic approximation used in Ref. [1] be applicable.

Several authors have addressed the problem with fluctuating *delocalized charges* within the volume between the surfaces [13–16]; however, the layer charges were fixed in these studies. The inhomogeneity of the mean-field counterion (and coion, if salt is added) density profile makes this problem extremely difficult to treat analytically. In the present work, we show how this inhomogeneity can be treated in a simple, analytical approximation. Our new results include predictions for the coupling of the layer-charge and counterion fluctuations; surprisingly, this contribution is larger than the fluctuations of either the layer charges or the counterions alone.

Our theory is based on an extension of the Gaussian fluctuation approach introduced by Pincus and Safran [1], to account self-consistently for the fluctuations of both layer charges and delocalized counterions (the correlation of the fluctuations of layer and delocalized charges was not considered in the references quoted above). We approximate the inhomogeneous mean-field counterion distribution by a piecewise uniform one in two asymptotic regimes: (i) in the regime $h \ll \lambda$, where the counterions are almost uniformly distributed between the surfaces; (ii) in the limit $h \gg \lambda$, where almost all counterions are localized in the vicinity of the surfaces (*condensed counterions*) and the remainder (*delocalized counterions*) are almost uniformly distributed in the space between the surfaces.

We find in Sec. II that the *total fluctuation pressure* Π may be represented as a sum of two contributions:

$$\Pi = \Pi^l + \Pi^c.$$

The first term $\Pi^l = \Pi_0^l + \Pi_{coup}^l$ is the pressure due to the layer-charge fluctuations (and condensed counterion fluctuations in the limit $h \gg \lambda$) Π_0^l, plus an additional contribution Π_{coup}^l due to their coupling with the counterion fluctuations (delocalized counterion fluctuations in the limit $h \gg \lambda$); note that only Π_0^l was considered in Ref. [1]. We find that Π_{coup}^l scales as $-1/(\lambda^2 h)$ and $-\ln(h/\lambda)/h^3$ in the limit $h \ll \lambda$ and

$h \gg \lambda$, respectively. While the last result $-\ln(h/\lambda)/h^3$ is similar to that obtained before for a system with only counterions [13,15], we show here that this largest contribution to the *total fluctuation pressure* comes from the coupling between the fluctuating condensed charges and the delocalized charges [18].

The second contribution to the fluctuation pressure, Π^c, represents the fluctuation pressure of the free plasma of counterions (delocalized counterions in the limit $h \gg \lambda$). Our approach shows in an intuitive manner that the counterion behavior goes continuously from two-dimensional-like (2D-like) to 3D-like, as h increases. The fluctuation pressure Π^c for small h can be derived by considering the counterions as a 2D Coulomb gas with the smallest length scale equal to that of the film thickness h; of course, we also present a more complex formula valid for the entire range of h/λ. In Sec. III we find that $\Pi^c \sim -1/(\lambda^2 h)$, if $h \ll \lambda$, and $\Pi^c \sim -1/h^3$, if $h \gg \lambda$. The scaling law in the limit $h \ll \lambda$ is different from that of an asymptotically large system. In Sec. IV we give a comprehensive picture of the scaling behavior of density-density inter- and intralayer correlation functions, and analyze the region of applicability of the model. Finally, the fluctuation attraction is compared numerically with the mean-field (Poisson-Boltzmann) repulsion.

II. TWO LAYERS WITH DELOCALIZED COUNTERIONS

We consider two overall neutral layers separated by a distance h with negative mobile layer charges (σ_0 is the average surface charge density) and positive counterions screening the layer charges. The layer charges are free to move within the planes and counterions are allowed to occupy the entire volume between the planes [19]. The surfaces are immersed in the solvent which is treated as a structureless continuum with a homogeneous dielectric constant ϵ. Our goal is to calculate the contribution to the pressure between the surfaces arising from the thermal fluctuations of all the mobile charges (both layer charges [1] and counterions, including their coupling).

The electrostatic free energy F of the system (the effective Hamiltonian in our problem) may be represented as a sum of the entropy of charges in an ideal gas approximation and the electrostatic interaction energy [20]:

$$\beta F = \sum_{i=1}^{3} \int d\mathbf{r}\, n_i(\mathbf{r})[\ln(n_i(\mathbf{r})v_0)-1] + \frac{\ell}{2}\sum_{i,j=1}^{3} z_i z_j \int d\mathbf{r}\; d\mathbf{r}' \frac{n_i(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \qquad (1)$$

where $n_1(\mathbf{r}) = \sigma_1(\boldsymbol{\rho})\,\delta(z-h)$ and $n_2(\mathbf{r}) = \sigma_2(\boldsymbol{\rho})\,\delta(z)$ are volume number densities of the layer charges in layers 1 and 2, respectively, and $n_3(\mathbf{r})$ is the counterion density, $\boldsymbol{\rho}=(x,y)$; z_i is the charge number of the ith species, $z_1 = z_2 = -1$, $z_3 = 1$; v_0 is the volume per ion, $\ell \simeq 7$ Å, $\beta \equiv 1/(k_b T)$, and $\epsilon \simeq 80$ for water.

The fluctuation contribution to the free energy G is determined by the average

$$e^{-\beta G} = \int \mathcal{D}\delta\sigma_1(\boldsymbol{\rho})\mathcal{D}\delta\sigma_2(\boldsymbol{\rho})\mathcal{D}\delta n_3(\mathbf{r}) e^{-\beta\Delta F}, \qquad (2)$$

and the corresponding fluctuation pressure between the layers is

$$\Pi = -\frac{1}{A_0}\frac{\partial G}{\partial h}, \qquad (3)$$

where A_0 is the surface area, with ΔF being the second variation of the effective Hamiltonian,

$$\begin{aligned}\beta\Delta F = {} & \frac{1}{2}\int \delta n_3(\mathbf{r})\left[\frac{\delta(\mathbf{r}-\mathbf{r}')}{n_0(z)} + \frac{\ell}{|\mathbf{r}-\mathbf{r}'|}\right]\delta n_3(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \\ & + \frac{1}{2}\sum_{i=1,2}\int \delta\sigma_i(\boldsymbol{\rho})\left[\frac{\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')}{\sigma_0} + \frac{\ell}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}\right] \\ & \times \delta\sigma_i(\boldsymbol{\rho}')\,d\boldsymbol{\rho}\,d\boldsymbol{\rho}' \\ & + \int \delta\sigma_1(\boldsymbol{\rho})\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+h^2}}\delta\sigma_2(\boldsymbol{\rho}')\,d\boldsymbol{\rho}\,d\boldsymbol{\rho}' \\ & - \int \delta\sigma_1(\boldsymbol{\rho})\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+(z'-h)^2}}\delta n_3(\mathbf{r}')\,d\boldsymbol{\rho}\,d\mathbf{r}' \\ & - \int \delta\sigma_2(\boldsymbol{\rho})\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+z'^2}}\delta n_3(\mathbf{r}')\,d\boldsymbol{\rho}\,d\mathbf{r}', \end{aligned} \qquad (4)$$

where $\delta\sigma_{1,2}(\boldsymbol{\rho}) = \sigma_{1,2}(\boldsymbol{\rho}) - \sigma_0$, and $\delta n_3(\mathbf{r}) = n_3(\mathbf{r}) - n_0(z)$ is the fluctuation of the counterion density around its mean-field profile $n_0(z)$ [20]:

$$n_0(z) = \frac{n_0}{\cos^2 k_0(z-h/2)}, \qquad (5)$$

where n_0 is the number density of counterions on the mid-plane $z=h/2$, and $k_0^2 = 2\pi n_0 \ell$; n_0 is determined by the total charge conservation condition

$$\int_0^h n_0(z)dz = 2\sigma_0, \qquad (6)$$

which gives $k_0 h \tan(hk_0/2) = h/\lambda$; here $\lambda = (2\pi\ell\sigma_0)^{-1}$ is the Gouy-Chapman length.

We proceed further by approximating the inhomogeneous distribution $n_0(z)$ in Eq. (4) by a piecewise uniform one (see below). There are two regimes in the problem associated with the magnitude of the parameter h/λ, when this approximation can be justified (see, e.g., [20]). These limits of $h \ll \lambda$ and $h \gg \lambda$ are analyzed in Secs. II A and II B, respectively.

Once one makes the approximation of a piecewise uniform counterion density distribution, one can represent the pressure Π in both asymptotic limits in the form

$$\Pi = \Pi^l + \Pi^c, \qquad (7)$$

where Π^c is the pressure due to those terms in the free energy corresponding to the thermal fluctuations of the *free* (i.e., not correlated with the layer-charge fluctuations) counterions (delocalized counterions in the limit $h \gg \lambda$) confined within the finite volume of the film (see the Appendix for a derivation):

$$\Pi^c = -\frac{k_b T}{2} \frac{\partial}{\partial h} \sum_{k_z} \int \frac{d\mathbf{q}}{(2\pi)^2} \ln\left[1 + \frac{4\pi \ell n_0}{k^2}[1-\omega(\mathbf{k})]\right], \tag{8}$$

with $\mathbf{q}=(q_x, q_y)$, $k^2=q^2+k_z^2$, $k_z=2\pi m/h$, m is an integer, and $\omega(\mathbf{k})$ is given by Eq. (A6); Π^c will be discussed in Sec. III. Here we note that argument of the logarithm in Eq. (8) is inversely proportional to the counterion density correlation function. Our result for this function interpolates between 3D behavior of the counterion fluctuations when $h \to \infty$ and the Fourier transform of the Coulomb interaction scales as $1/k^2$, and 2D behavior when $h \to 0$ (for $k_z=0$) and the Coulomb interaction scales as $1/q$. What is new in our expression for Π^l in Eq. (7) is the pressure due to the layer-charge fluctuations modified by their coupling with the counterion fluctuations:

$$\Pi^l = \Pi_0^l + \Pi_{coup}^l. \tag{9}$$

Here Π_0^l is the contribution exclusively due to the layer-charge fluctuations (only Π_0^l was analyzed in [1]), and Π_{coup}^l is the contribution due to the *coupling* of the layer-charge fluctuations with the counterion fluctuations. We now explain how we approximate the inhomogeneous counterion distribution by a piecewise uniform one and specify Π^l in the limits $h \ll \lambda$ (Sec. II A) and $h \gg \lambda$ (Sec. B).

A. Limit of small intersurface separations $h \ll \lambda$

In the limit $h \ll \lambda$ (ideal gas limit), the counterions are nearly uniformly distributed between the two layers. The total charge conservation condition, Eq. (6), then implies,

$$n_0 = 2\sigma_0/h.$$

The idea is thus to approximate $n_0(z)$ in Eq. (4) by $n_0 = 2\sigma_0/h$. After the calculation of Eqs. (2) and (3), where one expands in the small parameter h/λ, we obtain the asymptotic contributions to Π_0^l, Π_{coup}^l, and Π^l, respectively (see Appendix A1):

$$\Pi_0^l = -\frac{k_b T}{4\pi\lambda^2 h}, \tag{10}$$

$$\Pi_{coup}^l = -\frac{k_b T}{\pi\lambda^2 h}, \tag{11}$$

$$\Pi^l = -\frac{5 k_b T}{4\pi\lambda^2 h}. \tag{12}$$

We stress again that only Π_0^l was analyzed by Pincus and Safran [1] in the problem where the purely layer-charge fluctuations were considered (without coupling to the counterion fluctuations included). Our results show that the coupling contribution Π_{coup}^l is a factor of 4 larger than the direct layer-charge fluctuation attraction. This coupling leads to a significant increase of the pressure Π^l compared to Π_0^l: $\Pi^l = 5\Pi_0^l$.

We note that there is a contribution to the total pressure Π that comes from the thermal fluctuations of the *free* counterions, Π^c [see Eqs. (7) and (8) and explanation there]. As shown in detail in Sec. III, we find

$$\Pi^c = -\frac{k_b T}{2\pi\lambda^2 h}, \tag{13}$$

and note that Π^c has the same scaling $-1/h$ as Π^l. The coupling contribution is also larger than Π^c by a factor of 2.

B. Limit of large intersurface separations $h \gg \lambda$

In the opposite limit of $h \gg \lambda$ (high charge density limit), it follows from the analysis of a mean-field solution for $n_0(z)$ that most of the counterions are localized very near the surfaces (*condensed counterions*), and the remainder (*delocalized counterions*) are almost uniformly distributed in the space between the surfaces [21]. In this limit $h \gg \lambda$, we approximate [20] the delocalized counterion distribution between the surfaces by the volume number density equal to that on the midplane $z=h/2$:

$$n_0 = \pi/(2\ell h^2).$$

The surface number density of the condensed counterions σ_c in each layer (in addition to σ_0 due to the layer charges) is then

$$\sigma_c = \sigma_0(1-\pi^2\lambda/2h), \tag{14}$$

as implied by Eq. (6); of course, the condensed counterions are positively charged, while the layer charges are negative. Hence, in this limit $h \gg \lambda$, Eq. (1) should be extended to include condensed counterions as an additional species of positive layer charges. The details of the calculation for this scenario are reported in Appendix A 2. The principal contributions to Π_0^l and Π_{coup}^l are

$$\Pi_0^l = -\frac{\zeta(3)}{8\pi} \frac{k_b T}{h^3}, \tag{15}$$

$$\Pi_{coup}^l \simeq -\frac{k_b T}{h^3}\left(\frac{\pi}{2}\ln(2h/\lambda) - 2\right), \tag{16}$$

where ζ is the Riemann zeta function. We note that the amplitude $-\zeta(3)/(8\pi) \simeq -0.048$ is universal for this interaction, induced by the long-ranged fluctuations in the limit $h \gg \lambda$ [12,22].

The pressure Π^c, Eq. (8), due to the thermal fluctuations of the *free delocalized counterions* in this limit $h \gg \lambda$ (see Sec. III for details), is

$$\Pi^c \simeq -\frac{4 k_b T}{h^3},$$

and the total fluctuation pressure Π in the limit $h \gg \lambda$ is thus

$$\Pi=\Pi^{l}+\Pi^{c}\simeq-\frac{k_bT}{h^3}\left(\frac{\zeta(3)}{8\pi}+2+\frac{\pi}{2}\ln(2h/\lambda)\right). \quad (17)$$

For the case where the layer charges are fixed (nonfluctuating), our results are similar to that obtained by Attard using a more complicated approach [Eq. (3.14) in [13]]:

$$\Pi^{Attard}\simeq-\frac{k_bT}{h^3}\left(\frac{\zeta(3)}{8\pi}+2+\frac{\pi}{2}\ln(h/\lambda)\right). \quad (18)$$

The extra factor of 2 in the logarithm of Eqs. (16) and (17) compared to Eq. (18) is due to the extra fluctuating layer-charge component considered in our model, with an average surface number density of charge σ_0 (see Appendix A 2). We emphasize that only the coupling contribution Π^{l}_{coup} to the *total fluctuation pressure* Π depends on λ (and, hence, on σ_0) in this limit $h\gg\lambda$. While our result, Eq. (17), is not new, we believe that it is still important because (i) it shows that the limit $h\gg\lambda$ may be thought of as a piecewise uniform system of fluctuating delocalized counterions coupled to the purely two-dimensional system of the fluctuating condensed counterions (and the layer charges); (ii) our approach may be easily generalized to any number of the fluctuating species within the surfaces; (iii) we show explicitly and intuitively that the largest contribution $\sim -k_bT\ln(h/\lambda)/h^3$ to the pressure Π comes from the coupling between the condensed counterion fluctuations and the delocalized counterion fluctuations. This is somewhat surprising, since the density of the delocalized counterions is extremely low: $n_0\sim 1/(\ell h^2)$ in this limit. One should note finally that the $-k_bT\ln(h/\lambda)/h^3$ law for the fluctuation pressure of the counterions was also obtained in Ref. [15] with different numerical prefactors.

III. FINITE-SIZE EFFECTS ON COUNTERION PRESSURE

In the previous section, we showed that within the approximation of a mean-field homogeneous counterion density $n_0(z)=n_0$, the total fluctuation pressure Π can be represented as a sum of two contributions: $\Pi=\Pi^{l}+\Pi^{c}$. Here we consider in more detail the contribution Π^c due to the fluctuations of the *free* counterion gas, Eq. (8). We stress again that ''*free*'' includes those terms in the free energy corresponding to the fluctuations of the counterions that are *not correlated* with the layer-charge fluctuations (this correlation is captured by Π^{l}_{coup} term as explained in the previous section); this result is the direct consequence of the approximation of piecewise homogeneity of the mean-field counterion distribution, with no further assumptions. We report here the results for Π^c in both asymptotic limits $h\ll\lambda$ and $h\gg\lambda$ as derived from Eq. (8) (these results have been already quoted in Secs. II A and II B, respectively). Of course, the theory yields a (numerical) interpolation formula as well.

A. Π^c in the limit of small intersurface separation

In the limit $h\ll\lambda$, where $n_0=2\sigma_0/h$, the straightforward calculation of Eq. (8) yields the asymptotic contribution to Π^c, expanded as a function of the small parameter h/λ:

$$\Pi^{c}=-\frac{k_bT}{2\pi\lambda^2 h}. \quad (19)$$

We now discuss a less formal and more intuitive derivation of Eq. (19). Consider the uniformly negatively charged surface layer with charge number density $2\sigma_0$ and the screening *fluctuating* positive counterions localized within the layer approximated as a two-dimensional system, with the same mean surface number density $2\sigma_0$, as required by total charge neutrality. The fluctuation free energy G^{2d} of this two-dimensional system is [1]

$$G^{2d}=\frac{A_0k_bT}{2}\int_0^{q_m}\frac{dq\,q}{2\pi}\ln\left(1+\frac{2}{\lambda q}\right)$$

$$=-\frac{A_0k_bT}{2\pi\lambda^2}\ln(\lambda q_m), \quad (20)$$

where q_m is an upper cutoff for the wave vector $\mathbf{q}$. The self-energy is subtracted from Eq. (20); in any case it is independent of h. The approximation of a two-dimensional system for the counterions is appropriate for length scales much larger than h. We thus replace the cutoff q_m by $q_m=b/h$ where b is a constant of order unity. We then find that Eq. (19) for the pressure Π^c arises from the derivative of the free energy of Eq. (20) with respect to h, independent of the value of b. We note that G^{2d} in Eq. (20) follows from $\Pi^c=-(1/A_0)\partial G^c/\partial h$ of Eq. (8), if we expand for $hq\ll 1$ at $k_z=0$ [the contribution from all the other modes $k_z\neq 0$, $\sim k_bT/(h^2\lambda)$, is irrelevant; it corresponds to the self-energy and is canceled by the contribution for $hq\gg 1$].

In conclusion, we have shown that in the limit $h\ll\lambda$, Π^c may be obtained from the fluctuation free energy of the *two-dimensional* counterion system, provided the minimal length scale is set to be of order h.

B. Π^c in the limit of large intersurface separation

In the limit $h\gg\lambda$, one approximates the density of the *delocalized counterions* as $n_0=\pi/(2\ell h^2)$. It thus follows from Eq. (8) that

$$\Pi^{c}\simeq-\frac{4k_bT}{h^3}. \quad (21)$$

This is the scaling one would predict [24] from the expression for the fluctuation free energy of a 3D system: $G^{c}_{\inf}\sim -k_bTA_0h(n_0\ell)^{3/2}$, where $n_0\sim 1/(\ell h^2)$. If one considers only the delocalized counterions, there is an extra, cutoff-dependent term coming from Eq. (8), corresponding to the self-energy $G_c^{self}\sim k_bTA_0hq_mn_0\ell$, where $q_m\sim 1/a$ and a is an atomic length scale. However, this is exactly canceled by the contribution of the *condensed counterions.* If they are approximated as two thin slabs of thickness $\lambda_c=1/(2\pi\ell\sigma_c)$, where $\sigma_c=\sigma_0(1-\pi^2\lambda/2h)$, the volume number density n_c of the counterions within each slab is then $n_c=\sigma_c/\lambda_c$, and the volume of each slab is $A_0\lambda_c$. Calculation of Eq. (8) with $n_0\equiv n_c$ and $h\equiv\lambda_c$ for each slab yields a contribution to the free energy exactly equal to $-G_c^{self}/2$, providing an exact cancellation of the self-energy of the delocalized counterions.

IV. DISCUSSION

In Sec. II we observed that there was long-range scaling behavior of the interlayer fluctuation pressure Π^l in both asymptotic limits $h \ll \lambda$ and $h \gg \lambda$. This corresponds to scale free density fluctuations. In this section, we trace the connection between the pressure Π^l and the interlayer- and intralayer-charge correlation functions. We shall first define all the correlation functions and then summarize the results for their scaling in Table I. After doing that, we analyze the range of validity of the results obtained so far within the model and of the model itself.

A. Inter- and intralayer correlation functions

The inter- and intralayer correlation functions provide insight into the fluctuations due to the layer charges (and *condensed counterions* in the limit $h \gg \lambda$) as modified by the coupling with the fluctuations of the counterions (*delocalized counterions* in the limit $h \gg \lambda$). For simplicity, in what follows until the end of this section, whenever we consider the limit $h \gg \lambda$, we calculate the fluctuations of the *condensed counterions* correlated with the *delocalized counterions*, with the layer charges held fixed (see Sec. II B). The density-density interlayer $\mathcal{K}_{12}(\rho)$ and intralayer $\mathcal{K}_{11}(\rho)$ correlation functions $\mathcal{K}_{ij}(\rho) \equiv \langle \delta\sigma_i(\rho)\delta\sigma_j(0)\rangle$ are defined as the average of the product of the charge fluctuations $\delta\sigma_i(\rho)\delta\sigma_j(0)$ with the probability density proportional to $e^{-\beta\Delta F}$, where $\boldsymbol{\rho} \equiv (x,y)$ is the in-plane vector. This averaging yields

$$\mathcal{K}_{ij}(\rho) = \int_0^\infty \frac{dq\, q}{2\pi} \mathcal{K}_{ij}(q) J_0(q\rho), \tag{22}$$

with $\mathcal{K}_{ij}(q) \equiv \langle \delta\sigma_i(\mathbf{q})\delta\sigma_j(-\mathbf{q})\rangle$ being a 2D Fourier transform of $\mathcal{K}_{ij}(\rho)$, where

$$\mathcal{K}_{12}(q) = \frac{\lambda_1 - \lambda_2}{\lambda_1\lambda_2}, \qquad \mathcal{K}_{11}(q) = \frac{\lambda_1 + \lambda_2}{\lambda_1\lambda_2}, \tag{23}$$

J_0 is the Bessel function, and $\lambda_1, \lambda_2, \lambda_1^0$, λ_2^0 are eigenvalues of the free energy as defined in the Appendix for both asymptotic limits. We stress that in the case *without coupling* between the layer-charge fluctuations and the counterion fluctuations, the interlayer $\mathcal{K}_{12}^0(\rho) \equiv \langle \delta\sigma_1(\rho)\delta\sigma_2(0)\rangle_0$ and intralayer $\mathcal{K}_{11}^0(\rho) \equiv \langle \delta\sigma_1(\rho)\delta\sigma_1(0)\rangle_0$ correlation functions are defined by the same expressions [i.e., Eqs. (22) and (23)] as $\mathcal{K}_{12}(\rho)$ and $\mathcal{K}_{11}(\rho)$, respectively, provided the substitution $\lambda_i \to \lambda_i^0$ is performed. The intralayer correlation function $\mathcal{K}_{11}^0(\rho)$ is divergent. This artificial divergence is due to the infinite increase of fluctuations due to the self-interaction of charges as $\rho \to 0$ $(q \to \infty)$. Instead of $\mathcal{K}_{11}^0(\rho)$ we will consider the renormalized correlation function K_{11}^0: $K_{11}^0(q) = \mathcal{K}_{11}^0(q) - \lim_{q\to\infty} \mathcal{K}_{11}^0(q) = \mathcal{K}_{11}^0(q) - 2\sigma_0$. This procedure is equivalent to the formal definition [25] $K_{11}^0(\rho) = \mathcal{K}_{11}^0(\rho) - 2\sigma_0\delta(\rho)$, so that the nonphysical self-interaction of the charges is subtracted out. In what follows, this renormalization will be applied to all intralayer correlation functions. The results for $\mathcal{K}_{12}^0(\rho)$ and $K_{11}^0(\rho)$ are shown in Table I.

TABLE I. Scaling results for the inter- and intralayer charge density-density correlation functions, where $\alpha \simeq 2.1$, $\alpha' \simeq 2.37$, and $\tau \simeq 0.15$. $\mathcal{K}_{12}^0(\rho)$ and $K_{11}^0(\rho)$ are the interlayer and intralayer correlation functions, respectively, for the system with purely lateral charge fluctuations (no coupling with the counterion fluctuations). $\mathcal{K}^{coup}(\rho)$ is the contribution to the layer charge correlation functions exclusively due to the correlation between the layer charge fluctuations and the counterion fluctuations. The definitions and detailed discussion of all correlation functions, including $\mathcal{K}_{11}^{in}(\rho)$, are given in Sec. IV.

$\mathcal{K}^{coup}(\rho)$	$\frac{2\sigma_0}{\pi\lambda^2}\left(\ln\frac{\lambda}{h} - \alpha\right)$	$h \ll \lambda,\ \rho \ll h$
	$\frac{\pi\sigma_0}{2h^2}$	$h \gg \lambda,\ \rho \ll h$
$\mathcal{K}_{12}^0(\rho)$	$-\frac{\sigma_0}{\pi\lambda h}$	$h \ll \lambda,\ \rho \ll h$
	$-\frac{\sigma_0}{\pi\lambda\rho}$	$h \ll \lambda,\ \rho \gg h$
	$-\frac{1}{\pi^2 \ell h^3}$	$h \gg \lambda,\ \rho \ll h$
	$\frac{1}{2\pi^2 \ell \rho^3}$	$h \gg \lambda,\ \rho \gg h$
$K_{11}^0(\rho)$	$-\frac{\sigma_0}{\pi\lambda\rho}$	$h \ll \lambda,\ \rho < \lambda$
	$-\frac{\sigma_0}{\pi\lambda\rho}$	$h \gg \lambda,\ \rho \ll \lambda$
$\mathcal{K}_{12}(\rho) = \mathcal{K}_{12}^0(\rho) + \mathcal{K}^{coup}(\rho)$	$-\frac{\sigma_0}{\pi\lambda h} \simeq \mathcal{K}_{12}^0(\rho)$	$h \ll \lambda,\ \rho \ll h$
	$\frac{\pi\sigma_0}{2h^2}$	$h \gg \lambda,\ \rho \ll h$
$K_{11}(\rho) = K_{11}^0(\rho) + \mathcal{K}^{coup}(\rho)$	$-\frac{\sigma_0}{\pi\lambda\rho} \simeq K_{11}^0(\rho)$	$h \ll \lambda,\ \rho \ll h$
	$-\frac{\sigma_0}{\pi\lambda\rho} \simeq K_{11}^0(\rho)$	$h \gg \lambda,\ \rho \ll \lambda$
$\mathcal{K}_{11}^{in}(\rho)$	$\frac{\sigma_0}{\pi\lambda^2}\left(\ln\frac{\lambda}{h} - \alpha'\right)$	$h \ll \lambda,\ \rho < h$
	$\frac{\tau}{\pi^2 \ell h^3}$	$h \gg \lambda,\ \rho \ll h$

In order to capture the effects exclusively due to the correlation between the counterion fluctuations and the layer-charge fluctuations, we consider the difference

$$\mathcal{K}_{ij}^{coup}(\rho) = \mathcal{K}_{ij}(\rho) - \mathcal{K}_{ij}^0(\rho), \tag{24}$$

in analogy with what was done before for the pressure Π^l_{coup}; this difference $\mathcal{K}^{coup}_{ij}(\rho)=\mathcal{K}^{coup}(\rho)$, $i,j=1,2$, is the same for inter- and intralayer correlation functions in both asymptotic limits. The leading order terms in $\mathcal{K}^{coup}(\rho)$ are the following (see Table I):

$$\mathcal{K}^{coup}(\rho)\simeq\frac{2\sigma_0}{\pi\lambda^2}(\ln(\lambda/h)-\alpha),\quad h\ll\lambda,\quad \rho\ll h, \tag{25}$$

$$\mathcal{K}^{coup}(\rho)=\frac{\pi\sigma_0}{2h^2},\quad h\gg\lambda,\quad \rho\ll h, \tag{26}$$

where $\alpha\simeq 2.1$.

In order to gain a more physical, intuitive understanding of the coupling contribution $\mathcal{K}^{coup}(\rho)$, let us consider a new correlation function $\mathcal{K}^{in}_{11}$:

$$\mathcal{K}^{in}_{11}(q)=\mathcal{K}^{0}_{11}(q)-\lim_{h\to\infty}\mathcal{K}^{0}_{11}(q); \tag{27}$$

here ''*in*'' stands for ''induced''; this is the correlation function of the charge fluctuations within the first layer induced by the direct interaction with the charge fluctuations within the second layer (no coupling to the counterion fluctuations). In the limit $h\ll\lambda$, the correlation function $\mathcal{K}^{in}_{11}(\rho)$ has the same scaling behavior,

$$\mathcal{K}^{in}_{11}(\rho)\simeq\frac{\sigma_0}{\pi\lambda^2}[\ln(\lambda/h)-\alpha'],\quad h\ll\lambda,\quad \rho\ll h, \tag{28}$$

as $\mathcal{K}^{coup}(\rho)$ when $\rho\ll h$ [compare with Eq. (25), see also Table I], where $\alpha'\simeq 2.37$. Thus, we see that as long as $h\ll\lambda$, the counterion fluctuations modify the layer-charge fluctuations in much the same way as purely lateral charge fluctuations in one plane modify the lateral charge fluctuations in the other plane.

To trace the connection between the pressure Π^l and the layer-charge correlation functions, we note that the scaling for the short-distance ($\rho\ll h$) density correlations of $\mathcal{K}^0_{12}(\rho)$ coincides with the scaling for the pressure Π^l_0 within the corresponding regimes: $\mathcal{K}^0_{12}(\rho)\sim-\sigma_0/(\lambda h)$, if $h\ll\lambda$, and $\mathcal{K}^0_{12}(\rho)\sim-1/(\ell h^3)$, if $h\gg\lambda$. This again is not an accidental coincidence. One can check that the pressure Π^l_0 is expressed through the interlayer correlation function $\mathcal{K}^0_{12}(q)$:

$$\Pi^l_0=-\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^2}\mathcal{K}^0_{12}(q)\frac{\partial\Lambda^0_{12}}{\partial h}, \tag{29}$$

where $\Lambda^0_{12}=(2\pi\ell/q)e^{-qh}$ is the Fourier transform of the direct interaction between the charge fluctuations $\delta\sigma_1(\rho)$ and $\delta\sigma_2(\rho)$ within the two layers [third term of Eq. (4)], and the integral, Eq. (29), is proportional to $\mathcal{K}^0_{12}(\rho)$ in the limit $\rho\ll h$. Therefore, only interlayer correlations contribute to the pressure Π^l_0, while Π^l is determined by both inter- and intralayer correlation functions, in fact:

$$\Pi^l=-\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^2}\left[\mathcal{K}_{11}(q)\frac{\partial\tilde{\Lambda}_{11}}{\partial h}+\mathcal{K}_{12}(q)\frac{\partial\tilde{\Lambda}_{12}}{\partial h}\right], \tag{30}$$

where $\tilde{\Lambda}_{11}$ and $\tilde{\Lambda}_{12}$ in both regimes are defined in the Appendix; they would be equal to Λ^0_{11} and Λ^0_{12}, respectively, if no coupling of the *condensed-charge* fluctuations with the *delocalized-charge* fluctuations [18] would exist in the system. Hence, one concludes that the correlation (coupling) of the layer-charge fluctuations and the counterion fluctuations results in a contribution from the intralayer correlations to the pressure Π^l that leads to an additional attraction.

B. Applicability of the theory

We now discuss the range of applicability of the results. Here we address two questions: (i) Under what conditions are the fluctuations weak enough that the harmonic approximation we adopt is valid for our model (ii) Under what conditions is the effective Hamiltonian, Eq. (1) (i.e., the model itself), applicable and how are these conditions consistent with (i)?

The inter- and intralayer fluctuations of the layer charges are weak if the correlation functions for their fluctuations obey $\mathcal{K}_{12}(\rho)/\sigma_0^2\ll 1$ and $K_{11}(\rho)/\sigma_0^2\ll 1$. The former condition implies a restriction on the minimal intersurface separation h (in the limit $h\ll\lambda$) when the pressure is $\Pi^l\sim-1/(\lambda^2 h)$ and the interlayer correlation function is $\mathcal{K}_{12}(\rho)\sim-\sigma_0^2\ell/h$, while the latter condition determines the lower bound on ρ in the intralayer correlation function $K_{11}(\rho)\sim-\sigma_0^2\ell/\rho$ (in both asymptotic limits $h\ll\lambda$ and $h\gg\lambda$). It follows from Table I that these conditions are equivalent to $h\gg\ell$ and $\rho\gg\ell$, respectively; in the limit of large intersurface separations, $h\gg\lambda$, the interlayer-charge fluctuations (correlations) are always weak, of course.

Returning to the total free energy of Eq. (1) we note that the first term is the ideal gas entropy of counterions and layer charges. The condition that $h\gg\ell$ and $\rho\gg\ell$ means that the layer-charge surface density σ_0 and the counterion volume density n_0 should be dilute enough; i.e., the mean electrostatic energy of two ions, $\sim e^2/r_0$ (r_0 is the mean distance between ions, $r_0\sim\sigma_0^{-1/2}$ for layer charges, and $r_0\sim n_0^{-1/3}$ for counterions), should be small compared with the entropy $\sim k_bT$; this implies $r_0\gg\ell$; i.e., the system is entropy dominated. One can check that the last inequality is equivalent to $\lambda\gg\ell$.

Summarizing these conditions, one estimates the region of validity of the results: (i) in the limit $h\ll\lambda$ we require $h\gg\ell$ ($\lambda\gg\ell$ is satisfied automatically); (ii) in the limit $h\gg\lambda$ we require $\lambda\gg\ell$. Thus all length scales must be larger than the Bjerrum length for the fluctuations to be considered as small.

The experimentally interesting situation where the fluctuation attraction is largest, corresponding to the limit $h<\lambda$, may be realized, e.g., in the measurements of forces between surfactant bilayers, adsorbed on mica surfaces [26] or within a black film [6,27]. Taking the reasonable [5,26] values $\sigma_0\sim 10^{13}$ cm^{-2} (this corresponds to one charge per 1000 Å^2, $\lambda\simeq 22$ Å) and $h\sim 10$ Å, one can estimate the fluctuation attractive pressure $\Pi=\Pi^l+\Pi^c$, Eqs. (12) and (13):

$$\Pi=-\frac{7}{4}\frac{k_bT}{\pi\lambda^2 h}\simeq-5\times 10^6\frac{\text{dyn}}{\text{cm}^2}.$$

The Poisson-Boltzmann repulsive pressure Π^{PB} is (see, however, Ref. [28])

$$\Pi^{PB}=k_bTn_0=\frac{k_bT}{\pi\lambda\ell h}\simeq 8\times 10^6\,\frac{\text{dyne}}{\text{cm}^2},$$

[this is derived in Ref. [20], Eq. (5.96)]; the values of h and λ are at the upper bound of the limit $h\ll\lambda$ and, of course, the corresponding scaling results for pressure Π and correlation functions are accurate deep inside this region and only approximately correct at its boundaries. We also note that the pressure of the order of 10^6 dyne/cm^2 is measurable in current force balance experiments [4–6]. Even in the case when the fluctuation attraction is not dominant, it is still of the same order of magnitude as Poisson-Boltzmann repulsion, and combined with van der Waals interaction at $h\leqslant 50$ Å, it may overcome the repulsive interaction completely, or may combine with the repulsion to give an optimal, minimal energy interlayer spacing.

V. CONCLUSION

In summary, we derived the fluctuation contributions to the pressure between surfaces with mobile layer charges in the presence of delocalized counterions without added salt. The correlation of the layer-charge fluctuations (and the *condensed counterion* fluctuations in the limit $h\gg\lambda$) with the counterion fluctuations (*delocalized counterion* fluctuations in the limit $h\gg\lambda$) was taken into account; this correlation (coupling) gives rise to a different significant contribution Π^l_{coup} to the fluctuation pressure in each asymptotic regime: $h\ll\lambda$ $[\Pi^l_{coup}\sim -1/(\lambda^2 h)]$ and $h\gg\lambda$ $[\Pi^l_{coup}\sim -\ln(h/\lambda)/h^3]$; we stress that the term $-\ln(h/\lambda)/h^3$ arising from the coupling represents the dominant contribution to the total fluctuation pressure Π in this limit. We also showed in an intuitive way that the counterion fluctuation pressure Π^c goes continuously from 2D-like to 3D-like behavior as h increases; for small h, Π^c can be derived by considering the counterions as a 2D Coulomb gas with the smallest length scale equal to that of the film thickness h. The correlation functions obtained within the model show long-range power law behavior but no indication of the phase transitions was obtained.

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APPENDIX: DETAILS OF CALCULATIONS FOR SEC. II

In this appendix we summarize the details of calculations performed in Sec. II. Let us rewrite Eq. (4) in the form

$$\begin{aligned}\beta\Delta F=&\frac{1}{2}\int \delta n_3(\mathbf{r})\Lambda^0_{33}(\mathbf{r}-\mathbf{r}')\,\delta n_3(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'\\&+\frac{1}{2}\sum_{i,j=1,2}\int \delta\sigma_i(\boldsymbol{\rho})\Lambda^0_{ij}(\boldsymbol{\rho}-\boldsymbol{\rho}')\,\delta\sigma_j(\boldsymbol{\rho}')d\boldsymbol{\rho}\,d\boldsymbol{\rho}'\\&+\sum_{i=1,2}\int \delta\sigma_i(\boldsymbol{\rho})\Lambda^0_{i3}(\boldsymbol{\rho}-\boldsymbol{\rho}',z')\,\delta n_3(\mathbf{r}')d\boldsymbol{\rho}\,d\mathbf{r}',\end{aligned}\tag{A1}$$

where Λ^0_{ij} is a 3×3 symmetric matrix:

$$\begin{aligned}\Lambda^0_{11}(\boldsymbol{\rho}-\boldsymbol{\rho}')=\Lambda^0_{22}(\boldsymbol{\rho}-\boldsymbol{\rho}')&=\frac{\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')}{\sigma_0}+\frac{\ell}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|},\\ \Lambda^0_{12}(\boldsymbol{\rho}-\boldsymbol{\rho}')&=\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+h^2}},\\ \Lambda^0_{13}(\boldsymbol{\rho}-\boldsymbol{\rho}',z')&=-\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+(z'-h)^2}},\\ \Lambda^0_{23}(\boldsymbol{\rho}-\boldsymbol{\rho}',z')&=-\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+z'^2}},\\ \Lambda^0_{33}(\mathbf{r}-\mathbf{r}')&=\frac{\delta(\mathbf{r}-\mathbf{r}')}{n_0(z)}+\frac{\ell}{|\mathbf{r}-\mathbf{r}'|}.\end{aligned}\tag{A2}$$

The integration with respect to the z coordinate in Eq. (A1) (and everywhere in the text) is performed within the finite width h of the film: $\int_0^h dz$. As explained in Sec. II, we approximate the counterion density $n_0(z)$ by a piecewise uniform one; we thus approximate: $n_0(z)=n_0$. In order to perform the functional integration in Eq. (2), we can rewrite the free energy (shifting δn_3) of Eq. (A1) in Fourier representation with periodic boundary conditions, so that it is a quadratic function of $\delta\tilde{n}_3$ and $\delta\sigma_i$ separately:

$$\beta\Delta F=\frac{1}{2A_0}\sum_{i,j=1,2}\sum_{\mathbf{q}}\delta\sigma_i(\mathbf{q})\tilde{\Lambda}_{ij}(\mathbf{q})\,\delta\sigma_j(-\mathbf{q})+\beta\Delta F^c,\tag{A3}$$

where

$$\beta\Delta F^c=\frac{1}{2A_0h}\sum_{\mathbf{k}}\delta\tilde{n}_3(\mathbf{k})\Lambda^0_{33}(\mathbf{k})\,\delta\tilde{n}_3(-\mathbf{k}),\tag{A4}$$

with

$$\Lambda^0_{33}(\mathbf{k})=\frac{1}{n_0}+\frac{4\pi\ell}{k^2}[1-\omega(\mathbf{k})];\tag{A5}$$

here $\mathbf{k}\equiv(\mathbf{q},k_z)$, $k^2=q^2+k_z^2$, $k_z=2\pi m/h$, m is an integer, and $\omega(\mathbf{k})$ is the contribution due to the finite size of the film:

$$\omega(\mathbf{k})=\frac{(1-e^{-hq})}{hq}\,\frac{q^2-k_z^2}{k^2}.\tag{A6}$$

We note that the Fourier transform of the counterion fluctuation free energy [the first term of Eq. (A1)] also includes the nondiagonal (coupling wave vectors k_z and k_z') contribution due to the finite size of the system. This nondiagonal term is omitted in Eq. (A4) for the following reasons: Finite-size corrections reduce the free energy of the fluctuations; the lowest fluctuation contributions are obtained for wave vectors $k_z \simeq 0$. Thus, the nondiagonal terms do not contribute to the lowest free energy modes of the system. More detailed calculations show that the largest contribution to the pressure comes from the term $k_z = 0$. Because of the finite size, there is a gap in the spectrum. In the limit $h \ll \lambda$ all the higher modes contribute to terms in the pressure that are high order in h/λ. In the opposite limit $h \gg \lambda$, the nondiagonal term is higher order in $1/h$ for any $k_z \neq 0$.

The layer-charge interaction (renormalized by the coupling with the counterion fluctuations) matrix elements $\tilde{\Lambda}_{ij}(\mathbf{q})$ are

$$\tilde{\Lambda}_{ij}(\mathbf{q}) = \Lambda^0_{ij}(\mathbf{q}) - \Gamma_{ij}(\mathbf{q}), \quad i,j = 1,2, \tag{A7}$$

with

$$\Lambda^0_{11}(\mathbf{q}) = \Lambda^0_{22}(\mathbf{q}) = \frac{1}{\sigma_0} + \frac{2\pi\ell}{q},$$

$$\Lambda^0_{12}(\mathbf{q}) = \frac{2\pi\ell}{q} e^{-qh}; \tag{A8}$$

$\Lambda^0_{11}(\mathbf{q}), \Lambda^0_{12}(\mathbf{q})$ are the Fourier transforms of the corresponding matrix elements due to the purely layer-charge fluctuations in Eq. (A2); $\Gamma_{ij}(\mathbf{q})$ is the contribution which modifies the layer-charge interactions, due to the coupling of the layer-charge fluctuations with the counterion fluctuations; $\Gamma_{ij}(\mathbf{q})$ is specified below in both asymptotic limits.

Having obtained ΔF, Eq. (A3), in diagonalized form, one can perform the functional integration in Eq. (2). Integrating out $\delta\tilde{n}_3$ first (note that $\mathcal{D}\delta\tilde{n}_3 = \mathcal{D}\delta n_3$), one can obtain Π^c in the following form:

$$\Pi^c = -\frac{k_b T}{2}\frac{\partial}{\partial h}\sum_{k_z}\int \frac{d\mathbf{q}}{(2\pi)^2}\ln[n_0 \Lambda^0_{33}(\mathbf{k})]. \tag{A9}$$

Equation (A9) is identical to Eq. (8) quoted in Sec. II without derivation. Integrating in Eq. (2) with respect to $\delta\sigma_1()$ and $\delta\sigma_2(\rho)$, we immediately find

$$\Pi^l = -\frac{k_b T}{2}\frac{\partial}{\partial h}\int \frac{d\mathbf{q}}{(2\pi)^2}\ln(\lambda_1\lambda_2/a_0^2), \tag{A10}$$

where a_0 is a microscopic area, and λ_1, λ_2 are the eigenvalues of 2×2 matrix $\tilde{\Lambda}_{ij}(\mathbf{q})$:

$$\lambda_1 = \tilde{\Lambda}_{11}(\mathbf{q}) - \tilde{\Lambda}_{12}(\mathbf{q}),$$

$$\lambda_2 = \tilde{\Lambda}_{11}(\mathbf{q}) + \tilde{\Lambda}_{12}(\mathbf{q}). \tag{A11}$$

The contribution *exclusively due to the layer charge fluctuations* Π^l_0 is similar to Eq. (A10), provided the substitution $\lambda_1 \to \lambda^0_1$ and $\lambda_2 \to \lambda^0_2$ is performed,

$$\Pi^l_0 = -\frac{k_b T}{2}\frac{\partial}{\partial h}\int \frac{d\mathbf{q}}{(2\pi)^2}\ln(\lambda^0_1\lambda^0_2/a_0^2), \tag{A12}$$

with λ^0_1, λ^0_2 being the eigenvalues of 2×2 matrix $\Lambda^0_{ij}(\mathbf{q})$ Eq. (A8):

$$\lambda^0_1 = \frac{1}{\sigma_0} + \frac{2\pi\ell}{q}(1 - e^{-qh}),$$

$$\lambda^0_2 = \frac{1}{\sigma_0} + \frac{2\pi\ell}{q}(1 + e^{-qh}). \tag{A13}$$

We stress again that $\Pi^l_{coup} = \Pi^l - \Pi^l_0$ would be equal to zero if *no coupling* of the layer-charge fluctuations with the counterion fluctuations would exist in the system. In what follows, we specify in detail how Π^l is obtained in both asymptotic regimes $h \ll \lambda$ and $h \gg \lambda$.

1. Limit of small intersurface separations

In the limit $h \ll \lambda$ analyzed in Sec. II A, one has $n_0 = 2\sigma_0/h$. In this limit $\Gamma = \Gamma_{ij}$ is

$$\Gamma = \frac{2\varepsilon^2}{\sigma_0}\frac{(1 - e^{-x})^2}{x[x^3 + 4\varepsilon(x - 1 + e^{-x})]}, \tag{A14}$$

where $x = qh$, and $\varepsilon = h/\lambda$ is a small parameter in the limit $h \ll \lambda$. The coupling contribution Π^l_{coup} is then

$$\Pi^l_{coup} = \Pi^l - \Pi^l_0 = -\frac{k_b T}{2}\frac{\partial}{\partial h}\int \frac{d\mathbf{q}}{(2\pi)^2}\ln\left(1 - \frac{2\Gamma}{\lambda^0_2}\right). \tag{A15}$$

The explicit scaling laws for Π^l_0, Π^l_{coup}, and Π^l reported in Sec. II A, Eqs. (10), (11), and (12) are obtained from Eqs. (A12), (A15), and (A10), respectively, where one uses Γ determined by Eq. (A14), and

$$\lambda_1 = \lambda^0_1,$$

$$\lambda_2 = \lambda^0_2 - 2\Gamma, \tag{A16}$$

and expands in the small parameter h/λ.

2. Limit of large intersurface separations

As we explained in Sec. II B, in the limit $h \gg \lambda$ one should reformulate the problem to include *condensed counterions* as an additional species of positive charges localized within the layers (the layer charges are negative) with the average surface number density of charge $\sigma_c = \sigma_0(1 - \pi^2\lambda/2h)$. Therefore, instead of Eq. (1), the effective Hamiltonian in this limit is the following:

$$\beta F=\sum_{\substack{i=1,2\\ \alpha=\pm}}\int d\mathbf{r}\, n_i^\alpha(\mathbf{r})\{\ln[n_i^\alpha(\mathbf{r})v_0]-1\}+\int d\mathbf{r}\, n_3(\mathbf{r})\{\ln[n_3(\mathbf{r})v_0]-1\}+\frac{\ell}{2}\sum_{\substack{i,j=1,2\\ \alpha,\gamma=\pm}} z_i^\alpha z_j^\gamma\int d\mathbf{r}\, d\mathbf{r}'\frac{n_i^\alpha(\mathbf{r})n_j^\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\ell\sum_{\substack{i=1,2\\ \alpha=\pm}} z_i^\alpha\int d\mathbf{r}\, d\mathbf{r}'\frac{n_i^\alpha(\mathbf{r})n_3(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{\ell}{2}\int d\mathbf{r}\, d\mathbf{r}'\frac{n_3(\mathbf{r})n_3(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{A17}$$

with $n_1^\alpha(\mathbf{r})=\sigma_1^\alpha(\boldsymbol{\rho})\delta(z-h)$, $n_2^\alpha(\mathbf{r})=\sigma_2^\alpha(\boldsymbol{\rho})\delta(z)$, $\alpha=\pm$, $z_1^+=z_2^+=1$, and $z_1^-=z_2^-=-1$; here $\sigma_1^-(\boldsymbol{\rho})=\sigma_1(\boldsymbol{\rho})$, $\sigma_2^-(\boldsymbol{\rho})=\sigma_2(\boldsymbol{\rho})$ are the surface number densities of the negative layer charges on layers 1 and 2, respectively, and $\sigma_1^+(\boldsymbol{\rho})$, $\sigma_2^+(\boldsymbol{\rho})$ are the corresponding surface number densities of the positive *condensed counterions*; $n_3(\mathbf{r})$ is the volume number density of the *delocalized counterions*.

One defines the thermal fluctuation contribution G to the free energy in analogy with Eq. (2),

$$e^{-\beta G}=\prod_{\substack{i=1,2\\ \alpha=\pm}}\int \mathcal{D}\delta\sigma_i^\alpha(\boldsymbol{\rho})\mathcal{D}\delta n_3(\mathbf{r})e^{-\beta\Delta F}, \tag{A18}$$

where the second variation ΔF of F has a form similar to Eq. (4) [compare with Eqs. (A1) and (A2)]:

$$\beta\Delta F=\frac{1}{2}\int \delta n_3(\mathbf{r})\Lambda_{33}^0(\mathbf{r}-\mathbf{r}')\delta n_3(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'+\frac{1}{2}\sum_{\substack{i,j=1,2\\ \alpha,\beta=\pm}}\int \delta\sigma_i^\alpha(\boldsymbol{\rho})\Lambda_{ij}^{\alpha\beta}(\boldsymbol{\rho}-\boldsymbol{\rho}')\delta\sigma_j^\beta(\boldsymbol{\rho}')d\boldsymbol{\rho}\,d\boldsymbol{\rho}'+\sum_{\substack{i=1,2\\ \alpha=\pm}}\int \delta\sigma_i^\alpha(\boldsymbol{\rho})\Lambda_{i3}^\alpha(\boldsymbol{\rho}-\boldsymbol{\rho}',z')\delta n_3(\mathbf{r}')d\boldsymbol{\rho}\,d\mathbf{r}', \tag{A19}$$

with

$$\Lambda_{11}^{\alpha\alpha}(\boldsymbol{\rho}-\boldsymbol{\rho}')=\Lambda_{22}^{\alpha\alpha}(\boldsymbol{\rho}-\boldsymbol{\rho}')=\frac{\delta(\boldsymbol{\rho}-\boldsymbol{\rho}')}{\sigma_0^\alpha}+\frac{\ell}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|},$$

$$\Lambda_{12}^{\alpha\beta}(\boldsymbol{\rho}-\boldsymbol{\rho}')=z_1^\alpha z_2^\beta\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+h^2}},$$

$$\Lambda_{11}^{+-}(\boldsymbol{\rho}-\boldsymbol{\rho}')=\Lambda_{22}^{+-}(\boldsymbol{\rho}-\boldsymbol{\rho}')=-\frac{\ell}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}$$

$$\Lambda_{13}^{\alpha}(\boldsymbol{\rho}-\boldsymbol{\rho}',z')=z_1^\alpha\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+(z'-h)^2}},$$

$$\Lambda_{23}^{\alpha}(\boldsymbol{\rho}-\boldsymbol{\rho}',z')=z_2^\alpha\frac{\ell}{\sqrt{(\boldsymbol{\rho}-\boldsymbol{\rho}')^2+z'^2}},$$

$$\Lambda_{33}^{0}(\mathbf{r}-\mathbf{r}')=\frac{\delta(\mathbf{r}-\mathbf{r}')}{n_0}+\frac{\ell}{|\mathbf{r}-\mathbf{r}'|}, \tag{A20}$$

where $\sigma_0^-=\sigma_0$ and $\sigma_0^+=\sigma_c=\sigma_0(1-\pi^2\lambda/2h)$ are the average surface number densities of the layer charges and the condensed counterions respectively, in each layer (σ_c is explained in Sec.II B); $n_0=\pi/(2\ell h^2)$ is the volume number density of the delocalized counterions.

One finds ΔF in Fourier representation:

$$\beta\Delta F=\frac{1}{2A_0}\sum_{\substack{i,j=1,2\\ \alpha,\beta=\pm}}\sum_{\mathbf{q}}\delta\sigma_i^\alpha(\mathbf{q})\tilde{\Lambda}_{ij}^{\alpha\beta}(\mathbf{q})\delta\sigma_j^\beta(-\mathbf{q})+\beta\Delta F^c, \tag{A21}$$

where

$$\tilde{\Lambda}_{ij}^{\alpha\beta}(\mathbf{q})=\Lambda_{ij}^{\alpha\beta}(\mathbf{q})-\Gamma_{ij}^{\alpha\beta}(\mathbf{q}) \tag{A22}$$

and

$$\Gamma_{ij}^{\alpha\beta}(\mathbf{q})=z_i^\alpha z_j^\beta\Gamma. \tag{A23}$$

Within this limit $n_0=\pi/(2\ell h^2)$ (see Sec. II B), and Γ can be represented in the form

$$\Gamma=\frac{\pi^3 h\ell(1-e^{-x})^2}{x^2}\frac{\coth(\frac{1}{2}\sqrt{x^2+2\pi^2})}{\sqrt{x^2+2\pi^2}}, \tag{A24}$$

where $x=qh$. In Eq. (A22), $\Lambda_{ij}^{\alpha\beta}(\mathbf{q})$ is a 4×4 symmetric matrix, analogous to Eq. (A8):

$$\Lambda_{11}^{\alpha\alpha}(\mathbf{q})=\Lambda_{22}^{\alpha\alpha}(\mathbf{q})=\frac{1}{\sigma_0^\alpha}+\frac{2\pi\ell}{q},$$

$$\Lambda_{11}^{+-}(\mathbf{q})=\Lambda_{22}^{+-}(\mathbf{q})=-\frac{2\pi\ell}{q},$$

$$\Lambda_{12}^{\alpha\beta}(\mathbf{q})=z_1^\alpha z_2^\beta\frac{2\pi\ell}{q}e^{-qh}. \tag{A25}$$

Substituting Eq. (A21) into Eq. (A18), and first integrating out δn_3 ($\mathcal{D}\delta\tilde{n}_3=\mathcal{D}\delta n_3$), one obtains Π^c, Eqs. (8) and (A9), with $n_0=\pi/(2\ell h^2)$ in this limit. Integrating out the layer-charge and condensed counterion contributions $\delta\sigma_i^\alpha(\rho)$, $i=1,2$, $\alpha=\pm$, we find expressions analogous to Eqs. (A10), (A12), and (A15), respectively:

$$\Pi^l=-\frac{k_bT}{2}\frac{\partial}{\partial h}\int\frac{d\mathbf{q}}{(2\pi)^2}\ln(\det[\tilde{\Lambda}_{ij}^{\alpha\beta}]/a_0^4), \tag{A26}$$

$$\Pi_0^l=-\frac{k_bT}{2}\frac{\partial}{\partial h}\int\frac{d\mathbf{q}}{(2\pi)^2}\ln(\det[\Lambda_{ij}^{\alpha\beta}]/a_0^4), \tag{A27}$$

$$\Pi^{l}_{coup}=-\frac{k_bT}{2}\frac{\partial}{\partial h}\int\frac{d\mathbf{q}}{(2\pi)^2}\ln\left(1-\frac{2\Gamma}{\lambda_2^{large}}\right), \quad \text{(A28)}$$

where Γ is determined by Eq. (A24), and

$$\lambda_2^{large}=\frac{1}{2\sigma_0}+\frac{2\pi\ell}{q}(1+e^{-qh}), \quad \text{(A29)}$$

is similar to λ_2^0, Eq. (A13), provided the substitution $\sigma_0 \to 2\sigma_0$ in λ_2^0 is performed. Therefore, the effect of the extra layer-charge component, i.e., due to the *condensed counterions*, results is just to double the surface number density of charge, compared to the case of the single layer-charge component. The results reported in Sec. II B for Π^l_0, Eq. (15), and Π^l_{coup}, Eq. (16), may be found from Eqs. (A27) and (A28), respectively, by expansion with respect to the small parameter λ/h. We stress that Eq. (A28) is obtained within the approximation $\sigma^c \simeq \sigma_0$; the corrections to Eq. (A28) are of higher order in λ/h.

Finally we note that the eigenvalues λ_1,λ_2 that should be substituted in Eq. (23) for the correlation functions $\mathcal{K}_{12}(q)$ and $\mathcal{K}_{11}(q)$ in the limit $h \gg \lambda$ are analogous to Eq. (A16) with Γ determined by Eq. (A24).

[1] P. Pincus and S.A. Safran, Europhys. Lett. **42**, 103 (1998).
[2] S.A. Safran, Phys. Rev. Lett. **81**, 4768 (1998).
[3] A.W.C. Lau and P. Pincus, Phys. Rev. Lett. **81**, 1338 (1998).
[4] J.N. Israelachvili and G.E. Adams, Nature (London) **262**, 774 (1976); J. Chem. Soc., Faraday Trans. 1 **74**, 975 (1978).
[5] J.C. Crocker and D.G. Grier, Phys. Rev. Lett. **77**, 1897 (1996).
[6] D. Sentenac and J.J. Benattar, Phys. Rev. Lett. **81**, 160 (1998).
[7] N. Gronbech-Jensen, R.J. Mashl, R.F. Bruinsma, and W.M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997); B.-Y. Ha and A.J. Liu, *ibid.* **79**, 1289 (1997).
[8] I. Rouzina and V.A. Bloomfield, J. Phys. Chem. **100**, 9977 (1996); B.I. Shklovskii, Phys. Rev. Lett. **82**, 3268 (1999).
[9] L. Guldbrand, B. Jonsson, H. Wennerstrom, and P. Linse, J. Chem. Phys. **80**, 2221 (1984).
[10] R. Kjellander and S. Marcelja, Chem. Phys. Lett. **112**, 49 (1984); J. Chem. Phys. **82**, 2122 (1985).
[11] S. Marcelja, Biophys. J. **61l**, 1117 (1992), and references therein.
[12] P. Attard, R. Kjellander, and J. Mitchel, Chem. Phys. Lett. **139**, 219 (1987).
[13] P. Attard, D.J. Mitchell, and B.W. Ninham, J. Chem. Phys. **88**, 4987 (1988).
[14] P. Attard, D.J. Mitchell, and B.W. Ninham, J. Chem. Phys. **89**, 4358 (1988).
[15] R. Podgornik and B. Zeks, J. Chem. Soc., Faraday Trans. 2 **84**, 611 (1988).
[16] R. Podgornik, Chem. Phys. Lett. **156**, 71 (1989); J. Chem. Phys. **91**, 5840 (1989).
[17] M. Kardar and R. Golestanian, Rev. Mod. Phys. **71**, 1233 (1999); see Appendix II of this reference.
[18] We stress that by *condensed charges* we mean *layer charges* in the limit $h \ll \lambda$, and *layer charges plus condensed counterions* in the opposite limit $h \gg \lambda$. By *delocalized charges* we mean *counterions* in the limit $h \ll \lambda$ and *delocalized counterions* in the limit $h \gg \lambda$.
[19] The counterions are assumed to be confined to the volume between the planes which are taken to have infinitely large area; this is also applicable to a system consisting of a lamellar stack of many such membranes where there is no reservoir to which charges can escape. The other interesting case is where the counterions can escape; this case is beyond the scope of the present work (see, however, Ref. [28]).
[20] S.A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA, 1994), pp. 158–159.
[21] Monte Carlo simulations providing mean-field results for $n_0(z)$ were performed by B. Jonsson, H. Wennerstrom, and B. Halle, J. Phys. Chem. **84**, 2179 (1980); see also S.A. Safran, P.A. Pincus, M.E. Cates, and F.C. MacKintosh, J. Phys. (Paris) **51**, 503 (1990) and references therein, where a variational calculation for the counterion distribution around a cylinder showed that splitting up the charge into 2D and 3D components gives results comparable with the exact results.
[22] H. Li and M. Kardar, Phys. Rev. Lett. **67**, 3275 (1991); see also the review in Ref. [17].
[23] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, New York, 1980), reviewed and enlarged by E.M. Lifshitz and L.P. Pitaevskii.
[24] The result for the fluctuation free energy of classical plasma is obtained in, e.g., Ref. [23] in Chap. 78.
[25] Textbook explanations of the definition of $K^0_{11}(\rho)$ may be found in, e.g., Ref. [23], Eqs. (116.2) and (116.3), p. 351.
[26] J. Marra, Biophys. J. **50**, 815 (1986).
[27] O. Krichevsky and J. Stavans, Phys. Rev. E **55**, 7260 (1997).
[28] Note that in the case where the counterions can be squeezed out of the surfaces [in this case $n_0 \sim 1/(\lambda^2\ell)$ instead of $n_0 \sim 1/(\lambda\ell h)$ where the counterions are confined, in the limit $h \ll \lambda$], the mean-field repulsive PB pressure Π^{PB} is weaker and scales as $\Pi^{PB}=k_bT/(2\pi\lambda^2\ell)$ [this is obtained in, e.g., V.A. Parsegian and D. Gingell, Biophys. J. **12**, 1192 (1972); see the Appendix], instead of $k_bT/(\pi\lambda\ell h)$. However, in distinction to Π^{PB}, the layer-charge fluctuation pressure $\Pi^l_0 \sim -k_bT/(\lambda^2 h)$ will not change its scaling behavior even in the case where the counterions can escape because it is determined exclusively by the surface concentration of the mobile layer charges σ_0, while Π^l_{coup} and Π^c do depend on n_0 and will be smaller than Π^l_0 in this case; thus the total fluctuation pressure Π will have the same scaling $\Pi \sim -k_bT/(\lambda^2 h)$, but reduced amplitude compared to the case where the counterions are confined within the volume between the surfaces.