Electrostatically Swollen Lamellar Stacks and Adiabatic Pair Potential of Highly Charged Platelike Colloids in an Electrolyte

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We show that describing the screened electrostatic interactions in a periodic stack of rigid parallel identical charged platelike colloids within a local density functional theory approach generically leads to a swelling behavior. Within the same framework, we find that the effective potential between a pair of such plates immersed in an electrolyte is repulsive at all distances. This general result is in contradiction with a theory put forward by Sogami, Shinohara, and Smalley, that we criticize and thoroughly reconsider to show how the two approaches can be reconciled.

I. Introduction

The counterintuitive phenomenon of effective attractions between like charges immersed in an electrolyte has recently attracted considerable attention and questions one of the fundamental tenets of colloid science.[1−5] The understanding of the underlying mechanism is crucial for a correct description of a vast variety of industrial and natural processes, in particular the stability and phase behavior of colloidal dispersions. In this article, we investigate the stability of electrostatically swollen stacks of regularly spaced planar colloids or membranes of infinite lateral extension in an electrolyte. Such a one-dimensional geometry describes the early stages of clay swelling[6] but is also relevant for lamellar phases of charged bilayers.[7] At the simplest level of mean-field description, with neglect of excluded volume and Coulomb correlation effects, the inhomogeneous density profiles of microscopic co- and counterions forming the electric double layers around the planar macroions can be obtained analytically.[8] The resulting Poisson−Boltzmann osmotic (or disjoining) pressure in the stack is invariably found positive,[9] which is the signature of the tendency to swell. This behavior is reminiscent of the repulsive nature of pair interactions (as we shall see below, the two phenomena are however distinct), established within the same mean-field framework[10,11] and recently extended beyond mean-field,[12] with the possible inclusion of approximate correlation contributions. Note that more refined incorporation of discrete solvent effects by adding a bilinear nonlocal term to the free energy of standard Poisson−Boltzmann theory has shown the possibility of a net attraction (negative pressure) at high surface charges.[13]

The purpose of the present investigation is twofold. First, we apply the general local density functional formalism of ref 12 to provide a prediction for the stability of stacked or lamellar phases. We show in section II that the interactions of electric double layers generically lead to swelling whereas describing an equilibrium spacing between the membranes requires either the inclusion of nonelectrostatic forces (usually van der Waals-like) or the consideration of more refined theories. Second, the pair potential problem is considered in section III with a resulting effective repulsion at all distances, within the same framework that encompasses in particular the nonlinear Poisson−Boltzmann theory. This statement is consequently in contradiction with the attractive behavior reported by Sogami, Shinohara, and Smalley.[14,15] We show that their controversial finding is attributable to a confusion in the thermodynamic potential describing the electrostatic situation under study.

II. Swelling of a Lamellar Stack

Before setting the framework of the analysis, it is worthwhile to point out that the results obtained in refs 10−12 for a pair of colloids do not apply to the regular stacked situation under scrutiny here (the precise definition of the geometry is given at the beginning of section IIA). First of all, the mechanical route followed in refs 10−12 (deriving the interactions by integration of the stress tensor over the colloids' surfaces) would yield a

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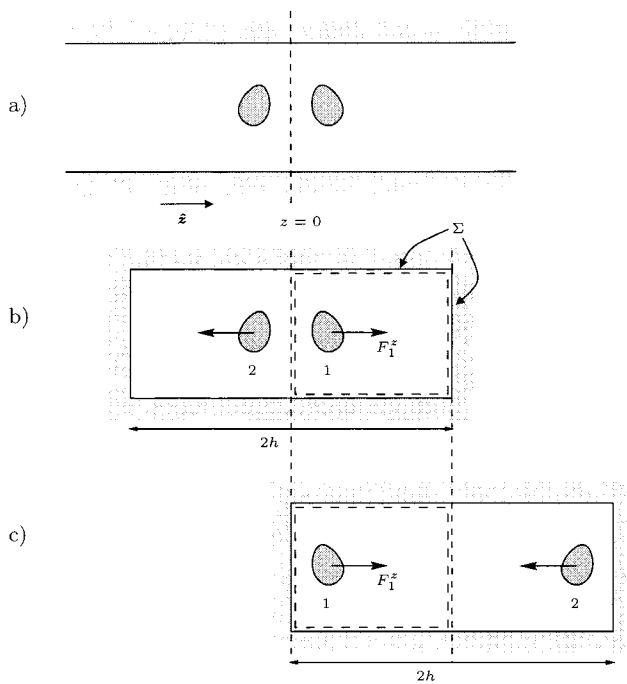
a)

b)

$\hat{z}$

$z = 0$

Σ

F_1^z

2   1

2h

c)

F_1^z

1   2

2h

Figure 1. Illustrative side view of the cell models considered. Mirror symmetry with respect to the midplane $z = 0$ between the two colloids is enforced (this requirement is an important ingredient in the proofs [refs 10−12]).

vanishing effective force in a regular stack, with cancelling contributions acting on both sides of the platelets, and is thus uninformative about the stability of the array. Moreover, the situation considered in refs 10−12 is that of two colloids immersed in an electrolyte, confined in a cylinder with an axis parallel to the colloids' line of centers, and of infinite extension along this axis [see Figure 1a]. The assumption of infinite length is crucial for the validity of the effective repulsion (see Appendix A), and the corresponding confined two-body problem does not include the multibody stack geometry, for which the confining cylinder (Wigner−Seitz cell) would be a slab of finite length. This point is in contradiction with one erroneous conclusion reached in ref 21.

A. Density Functional Theory Formalism.[26] We consider a regular succession of rigid infinite parallel plates located at $z = 2nh$ ($n \in$ N). Each plate carries a uniform surface charge σ and releases its counterions in the electrolyte solution, considered to be a mixture of N microions, where species α has charge number e_α and local density $n_\alpha(z)$. We write the free energy of the total charge distribution in the Wigner−Seitz cell around a given platelet (e.g., that situated at $z = 0$ for which the cell is a slab extending between $−h$ and h) as

$$\mathcal{F}(\{n_\alpha\}) = \int_{-h}^{h} f[\{n_\alpha(z)\}] \, dz + \frac{1}{2} \int_{-h}^{h} \rho_c(z) \, \psi(z) \, dz \quad (1)$$

where $\rho_c(z)$ is the local total charge distribution, including the microions and the plate (with global electroneutrality $\int_{-h}^{h} \rho_c = 0$). $\mathcal{F}$ is expressed per unit area of the macroscopic surfaces. Within the primitive model of electrolytes,[22] whereby the solvent is regarded as a mere dielectric continuum of permittivity ϵ, the total electrostatic potential $\psi(z)$ is the solution of Poisson's equation

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \rho_c(z) = -\frac{4\pi}{\epsilon} [\sigma\delta(z) + \sum_\alpha e_\alpha \, n_\alpha(z)] \quad (2)$$

and can be cast in the form $\psi(z) = \int_{-h}^{h} \rho_c(z') \, G(z, z') \, dz'$ where G is the appropriate Green's function. The boundary condition of vanishing electric field at $z = \pm h$ is fulfilled by $\partial_z\psi$. This mean-field-like reduction of the problem materialized by the introduction of the Wigner−Seitz slab may be corrected by correlation terms included in the free energy density f. Moreover, even if the van der Waals energy term $\int \rho_c\psi = \int \rho_c G\rho_c$ is of mean-field form, correlation terms can be accounted for provided they translate into a local correction to the free energy, in the spirit of the approaches depicted in refs 23−25. Consequently, the term $\int f$ in eq 1 does not reduce in general to the entropic microions' contribution (as in Poisson-Boltzmann theory[22]) but may also include both non-mean-field energetic and entropic effects. Of course, the present formalism encompasses the nonlinear Poisson−Boltzmann and Modified Poisson−Boltzmann theories.[27,28]

B. Osmotic Pressure. For both canonical (fixed ionic content of the electrolyte solution) and semi-grand-canonical (when the solution is in osmotic equilibrium with a salt reservoir) descriptions, the optimal density profiles $n_\alpha^*(z)$ are obtained by minimizing the functional

$$\Omega(\{n_\alpha\}) = \mathcal{F}(\{n_\alpha\}) - \sum_\alpha \mu_\alpha N_\alpha \qquad (N_\alpha = \int_{-h}^{h} n_\alpha \, dz) \quad (3)$$

where μ_α is either the Lagrange multiplier associated with the constraint of fixed average concentration or the chemical potential of species α in the reservoir. The resulting stationary equations read for all species α

$$\frac{\partial f}{\partial n_\alpha} + e_\alpha\psi(z) = \mu_\alpha \quad (4)$$

These implicit relations between the electrostatic potential and the densities $\{n_\alpha\}$ allow us to solve Poisson's equation (eq 2) and compute the optimal profile $n_\alpha^*(z)$ (hereafter denoted $n_\alpha(z)$ without ambiguity), from which we deduce

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(21) Trizac, E.; Raimbault, J. L. *Phys. Rev. E* **1999**, *60*, 6530. In this article, eq 14 [and therefore eq 16] is erroneous as extra terms arise from the application of Green's theorem. Consequently, while the effective interactions remain repulsive when the specific size of the microions is taken into account via the Modified Poisson−Boltzmann theory put forward in ref 27, a similar conclusion cannot be reached for the situation of complete confinement (finite length of the confining cylinder). Appendix A provides a simple counterexample showing that effective attraction can result from complete lateral confinement. The above error has been corrected in the more general analysis of ref 12.

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the Helmholtz free energy $F(h, \sigma, T, \{N_\alpha\}) = \mathcal{F}(\{n_\alpha^*\})$, with $F = U - TS$ (U is the total internal energy, T is the absolute temperature, and S is the entropy of the total microion charge distribution in the cell).

From the knowledge of F, the definition of the thermodynamic potential $\mathcal{R}$ (whose variations correspond to the reversible work performed by an operator and thus define the osmotic pressure) requires the specification of the thermodynamic situation under consideration. In the canonical case with constant charge plates, $\mathcal{R} = F$.[29] If, on the other hand, the platelets are held at constant potential (e.g., by an external generator), $\mathcal{R}$ is the Legendre transform of F with respect to the surface charge,[29,30] namely,

$$\mathcal{R} = F(\sigma, h, T) - \sigma \frac{\partial F}{\partial \sigma}\Big|_{h,T} = F(\sigma, h, T) - \sigma \psi_\mathcal{P}(\sigma, h, T) \quad (5)$$

where $\psi_\mathcal{P} = \psi(z=0)$ denotes the surface potential. In the opposite case of a system in equilibrium with a salt reservoir,

$$\mathcal{R} = \mathcal{R}_\sigma = \Omega(\{n_\alpha\}) = F - \sum_\alpha \mu_\alpha \int_{-h}^{h} n_\alpha(z)\, dz$$
$$\text{at constant charge } \sigma \quad (6)$$

$$\mathcal{R} = \mathcal{R}_\psi = F - \sum_\alpha \mu_\alpha \int_{-h}^{h} n_\alpha(z)\, dz - \sigma \frac{\partial F}{\partial \sigma}$$
$$\text{at constant potential } \psi_\mathcal{P} \quad (7)$$

In any case, the osmotic pressure is defined as

$$\Pi = -\frac{1}{2} \frac{\partial \mathcal{R}}{\partial h} \quad (8)$$

where $\mathcal{R}$ depends on the electrostatic situation considered, as explained above. It is however important to stress that the osmotic pressure should not depend on the electrostatic situation under study, as becomes clear below. Theories that do not result in the above fundamental invariance of Π can consequently be disposed of.

The free energy variation induced by changing the intermembrane distance is computed in Appendix B with the result

$$\delta F = \left[f - \sum_\alpha n_\alpha \frac{\partial f}{\partial n_\alpha} \right]_{z=h} 2\delta h + \sum_\alpha \mu_\alpha \delta N_\alpha + \psi_\mathcal{P} \delta \sigma \quad (9)$$

so that the osmotic pressure reads

$$\Pi = \left[-f + \sum_\alpha n_\alpha \frac{\partial f}{\partial n_\alpha} \right]_{z=h} \quad (10)$$

independently of the situation of constant potential or constant charge considered. Not surprisingly, the pressure is related to the Legendre transform of the free energy density, as for ordinary homogeneous gases,[30] and equals the local stress $\pi(z)$ at the midplane between the membranes:

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$\Pi = \pi(z=h)$ where $\pi(z) =$

$$-f[\{n_\alpha\}(z)] + \sum_\alpha n_\alpha(z) \frac{\partial f}{\partial n_\alpha}(z) \quad (11)$$

C. Stability Analysis. When the stack is in osmotic equilibrium with a salt reservoir, the comparison of Π obtained in section IIB with the pressure exerted by the reservoir quantifies the tendency toward swelling ($\Pi > \Pi_{res}$) or collapse ($\Pi < \Pi_{res}$). For consistency, the (neutral) reservoir needs to be described within the same framework as the electrolyte around the platelet. The remainder of this section is devoted to the proof that Π is extremal in the reservoir and that this extremum is a minimum under fairly general conditions. We first analyze the ψ dependence of the pressure π, defined by $\pi(\psi) = \pi(z)$ where $\psi = \psi(z)$ is the solution of Poisson's equation (eq 2). From eq 11, we have

$$\frac{\partial \pi}{\partial \psi} = \sum_\alpha n_\alpha \frac{\partial}{\partial \psi}\left(\frac{\partial f}{\partial n_\alpha} \right) \quad (12)$$

that can be recast making use of the stationary condition in (4):

$$\frac{\partial \pi}{\partial \psi} = -\sum_{\alpha=1}^{N} n_\alpha e_\alpha \quad (13)$$

$$= -\rho_c(z) \quad \text{outside the plate } (z \neq 0) \quad (14)$$

π thus goes through an extremum in the reservoir (Π_{res} by definition) where the charge density vanishes (unlike at the midplane $z = h$ where $\rho_c \neq 0$). Relation 14 together with Poisson's equation implies that the local stress introduced in eq 11 fulfills the mechanical equilibrium condition for the fluid of microions:

$$\pi(z) - \frac{\epsilon}{8\pi}\left(\frac{\partial \psi}{\partial z} \right)^2 = \Pi \quad (15)$$

which is the simple form taken in a one-dimensional problem by the condition of vanishing divergence for the generalized Maxwell stress tensor in the dielectric medium.[29]

The second derivative of π can be obtained by introducing the Hessian matrix $N \times N$

$$H_{\alpha\beta} = \frac{\partial^2 f}{\partial n_\alpha \partial n_\beta} \quad (16)$$

that obeys the relation

$$\sum_{\beta=1}^{N} H_{\alpha\beta} \frac{\partial n_\beta}{\partial \psi} = -e_\alpha \quad (17)$$

as can be seen from eq 4. We thus have

$$\frac{\partial^2 \pi}{\partial \psi^2} = \sum_{\alpha\beta} H_{\alpha\beta} \frac{\partial n_\alpha}{\partial \psi} \frac{\partial n_\beta}{\partial \psi} \quad (18)$$

which is a positive quantity when the matrix of second derivatives $H_{\alpha\beta}$ is positive definite. Under this assumption, π is a convex-up function of the potential and the extremum attained in the reservoir is therefore a minimum, so that $\Pi > \Pi_{res}$.

Despite the differences outlined at the beginning of section II between the pair potential and the multibody

stacked problems, the method employed here is close to that of ref 12, and we shall also distinguish two different situations to conclude with the stability analysis:

Case a. The free energy density does not depend on the elementary charge e (as in mere mean-field treatments[8,22,27,28]). In the limit $e \rightarrow 0$ (at fixed valency e_α/e), we obtain a locally neutral mixture where the total free energy functional reduces to the contribution $\int f$. The thermodynamic stability criterion of this neutral mixture implies the positive definiteness of the matrix $H_{\alpha\beta}$ that is independent of e.

Case b. Correlation or fluctuation effects are taken into account with a resulting e-dependent free energy density. It is no longer possible to find an uncharged mixture of microspecies described by the same density f. The thermodynamic stability condition of the full functional (eq 1) involves Green's function $G(z, z')$ and does not imply the positive definiteness of the Hessian H. However, the convexity of f with respect to density variations is generally fulfilled by the approaches proposed in the literature, either in the full density range[25] or for the small plasma coupling parameters relevant to colloidal dispersions.[24]

From the above discussion and the positive definiteness of the Hessian matrix H, we conclude that the stack generically exhibits a tendency toward swelling.

III. Adiabatic Pair Potential

In this section, we consider within the density functional formalism of eq 1 the problem of the effective interactions between a pair of parallel charged plates immersed in an electrolyte solution of infinite volume (no confinement). The two rigid plates with distance $2h$ are supposed to be of negligible thickness and uniform surface charge (as in section II); they divide the electrolyte solution into two disconnected regions (inner region with $|z| < h$ and outer region with $|z| > h$), which does not correspond to the situation analyzed in refs 10–12. However, the generalization to the present case is straightforward and yields an effective repulsion as long as both regions are in contact with salt reservoirs imposing the same chemical potential for microspecies. Indeed, from the computation of the free energy variation detailed in section IIB, the effective force can be written

$$F_z = -\frac{1}{2}\frac{\delta \mathcal{R}}{\delta h} = \Pi_{in} - \Pi_{out} \qquad (19)$$

From the vanishing of the electric field at $z = 0$ and $|z| \rightarrow \infty$, we have $\Pi_{in} = \pi(z=0)$ and $\Pi_{out} = \pi(|z| \rightarrow \infty)$. For $|z| \rightarrow \infty$, the charge density vanishes so that Π_{out} equals the osmotic pressure in the salt reservoir under consideration. The argument of section IIC indicates that $\Pi_{in} > \Pi_{out}$ and that the interactions are repulsive under the assumption of positive definiteness for the stability matrix $\partial^2_{\alpha\beta} f$. This last condition is obeyed by Poisson–Boltzmann (PB) theory independently of the valency of the microions [see eq 20 below]. Our result is consequently in contradiction with the "long-range weak attractive part of the free energy" reported in refs 14 and 15 for the same system treated at the level of Poisson–Boltzmann. The work of Sogami et al. has already been criticized,[16–19] but in our opinion, the subsequent controversy[20] dwells on ambiguities on the thermodynamic potential that should be considered, which to our knowledge have not been explicitly pointed out so far. It thus seems worthwhile to restrict to PB theory and devote the remainder of this article to briefly revisit the model of refs 14 and 15, introduced to describe the swelling behavior of *n*-butylammonium vermiculite gels.

Within PB mean-field theory, the microions are considered as an ideal gas and density fluctuations are discarded, so that the free energy density does not include any correlation term and reduces to the entropy of an ideal mixture:

$$f(\{n_\alpha\}) = \beta^{-1} \sum_{\alpha=1}^{N} n_\alpha [\ln(n_\alpha \Lambda_\alpha^3) - 1] \qquad (20)$$

where the (irrelevant) lengths $\{\Lambda_\alpha\}$ involve the masses of microions and $\beta = 1/(kT)$ is the inverse temperature. The stationary condition in (4) translates into

$$n_\alpha(z) = n_\alpha^0 \exp(-\beta e_\alpha \psi) \qquad (21)$$

and the local osmotic stress in (11) is given by the ideal equation of state $\pi(z) = kT\sum_\alpha n_\alpha(z)$. The electrostatic potential ψ is chosen to vanish for $|z| \rightarrow \infty$, so that n_α^0 is the density of species α far from the plates with a corresponding chemical potential

$$\mu_\alpha = kT \ln (n_\alpha^0 \Lambda_\alpha^3) \qquad (22)$$

As a result of the global electroneutrality condition, it can be checked that the final free energy [expression 23 below] is independent of an arbitrary shift of the potential ψ [in which case the densities appearing in eq 22 are simply the prefactors of the exponentials in (21)]. It is convenient to use the relation between the local ionic densities and the electrostatic potential to recast the Helmholtz free energy $F = U - TS$ in the form

$$\begin{aligned} F &= \mathcal{F}(\{n_\alpha\}) \\ &= \sigma\psi_\mathcal{P} - \frac{\epsilon}{8\pi}\int_{-\infty}^{\infty}\left(\frac{\partial\psi}{\partial z}\right)^2 dz + \sum_\alpha N_\alpha(\mu_\alpha - kT) \\ &= \sigma\psi_\mathcal{P} + \int_{-\infty}^{\infty}\Pi\, dz + \sum_\alpha N_\alpha(\mu_\alpha - 2kT) \qquad (23) \end{aligned}$$

where eq 15 and the ideal equation of state for $\pi(z)$ have been used in going from the first to the second line. Note that it is understood that the osmotic term Π in (23) takes the value Π_{in} (respectively Π_{out}) for $|z| < h$ (respectively $|z| > h$). Strictly speaking, expression 23 diverges (if salt is added to the electrolyte, some of the quantities N_α are extensive with system size). This feature can be circumvented by computing the excess free energy with respect to a well-chosen reference system (for instance, the system with same bulk densities in the absence of the plates). Once the solution of Poisson's equation is known (see ref 9 for a review of the standard solutions, including the present geometry), F may be computed from eq 23. Following this route, we readily recover the Helmholtz free energy obtained by Sogami et al. by means of a charging process. In eq 23, $\sigma = \sigma_{in} + \sigma_{out}$ stands for the total surface charge on a platelet, including both the different inner (σ_{in} from $z = h^-$) and outer (σ_{out} from $z = h^+$) contributions, denoted Z_i and Z_o, respectively, in refs 14 and 15.

In the model of refs 14 and 15, the electrostatic potential is imposed to be continuous throughout the system and the surface potential $\psi_\mathcal{P}$ is independent of the distance $2h$ between the plates. Moreover, the numbers of microions between the plates also depend on h with a fixed chemical potential, given by (22) where the n_α^0 can be considered as

the ionic densities of a reservoir in chemical equilibrium with both the inner and outer parts of the electrolyte solution around the plates. Consequently, the thermodynamic potential $\mathcal{R}_\psi$ defined in eq 7 should be used in computing the force whereas F has been considered in refs 14 and 15. The definition of the model imposes that when h changes at fixed ψ_ρ, Z_0 is constant while Z_i varies, so that the two situations of constant charge and constant potential are equivalent for the outer part of the system ($|z| > h$) but not for the inner part. The reversible work performed by an operator changing the distance $2h$ between the charged plates is therefore given by the variations of

$$\mathcal{R}_\psi = F_{\text{in}} + F_{\text{out}} - \sum_\alpha \mu_\alpha \int_{-\infty}^{+\infty} n_\alpha(z)\, \mathrm{d}z - \sigma_{\text{in}}\psi_\rho \quad (24)$$

whereas $F = F_{\text{in}} + F_{\text{out}}$ has been considered in refs 14 and 15. Omission of the chemical potential terms $\mu_\alpha n_\alpha$ in the right-hand side of eq 24 leads the force computed in refs 14 and 15 to depend on the masses (through the lengths Λ_α), which is impossible in an equilibrium statistical mechanics theory, as already pointed out in ref 31. With the aid of the relations given in ref 14 [e.g., eqs 63, 64, and 65 valid in the case of counterion dominance between the plates], an explicit computation of the force $F_z = -\partial\mathcal{R}_\psi/\partial(2h)$ yields the standard expression

$$F_z = \pi(h^-) - \frac{\epsilon}{8\pi}\left(\frac{\partial\psi}{\partial z}\right)^2_{z=h^-} - \left[\pi(h^+) - \frac{\epsilon}{8\pi}\left(\frac{\partial\psi}{\partial z}\right)^2_{z=h^+}\right] \quad (25)$$

$$= \frac{\epsilon}{8\pi}\left[\left(\frac{\partial\psi}{\partial z}\right)^2_{z=h^+} - \left(\frac{\partial\psi}{\partial z}\right)^2_{z=h^-}\right] \quad (26)$$

where the continuity of the co- and counterion charge density across the membrane (resulting from the imposed continuity of the potential) has been used in going from (25) to (26). The compatibility of eq 25 with eq 19 is transparent. In terms of the variables used in refs 14 and 15, where $\Phi(0)$ denotes the reduced potential at mid-distance between the plates, we get

$$F_z = \frac{2\pi}{\epsilon}e^2(Z_0^2 - Z_i^2) = 4n_0kT\sinh^2\left[\frac{\Phi(0)}{2}\right] \geq 0 \quad (27)$$

hence an effective repulsion at all distances, that is in the present case entirely due to the electrostatic pressure (the osmotic contribution cancelling on both sides of the plates).

It can be checked that in the dual situation where both the inner σ_{in} are outer σ_{out} surface charges are held constant, the effective force is still given by (25). This translates into the Legendre identity

$$\frac{\partial\mathcal{R}_\psi}{\partial h}\bigg|_{\psi_\rho,\sigma_{\text{out}}} = \frac{\partial}{\partial h}\left[\mathcal{R}_\psi - \psi_\rho\frac{\partial\mathcal{R}_\psi}{\partial\psi_\rho}\bigg|_{\psi_\rho,\sigma_{\text{out}}}\right]_{\sigma_{\text{in}},\sigma_{\text{out}}} =$$
$$\frac{\partial(\mathcal{R}_\psi + \sigma_{\text{in}}\psi_\rho)}{\partial h}\bigg|_{\sigma_{\text{in}},\sigma_{\text{out}}} \quad (28)$$

that can be considered as a test for the consistency of the thermodynamic potential used. In the limit of counterion dominance between the plates investigated in ref 14, the identity in (28) can be checked explicitly with the thermodynamic potential $\mathcal{R}_\psi$ used here.

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IV. Conclusion

Describing the interactions between the electric double layers around charged planar colloids with a local density functional theory for ionic screening and the primitive model of electrolytes, we have shown that a regular stack of such plates generally displays a swelling behavior when electrostatic forces alone are taken into account. Within the same framework, the effective pair potential is found to be repulsive at all distances, in contradistinction with the results derived in refs 14 and 15. The repulsive interactions are evidenced without resort to an explicit solution of Poisson's equation and are related to the convexity of the underlying free energy functional, as already noted in ref 12.

Of course, the present result does not preclude the possibility of effective attractive pair potentials. In particular, a drawback of the theories encompassed by eq 1 is that the direct correlation function $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ defined as the second functional derivative of $\mathcal{F}$ is necessarily mean-field-like:

$$c^{(2)}_{\alpha,\beta}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\partial^2 f}{\partial n_\alpha \partial n_\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2) - e_\alpha e_\beta G(\mathbf{r}_1, \mathbf{r}_2) \quad (29)$$

with a δ-correlated short-range part. This shortcoming may be circumvented by the inclusion of nonlocal terms in the theory, for example, in the spirit of the weighted density approximation.[33,34] However, we expect the local formalism considered here to be instructive for interplate separations much larger than the ionic size.

Appendix A

References 10−12 proved that the effective interactions between a pair of like-charged colloids immersed with counterions and salt in a confining cylinder of infinite extension [see Figure 1a] were repulsive. We show here that the result does not hold for a finite-length cylinder.

We consider two colloids confined in the cylinder of length $2h$ represented in Figure 1b, in the specific case of Neumann boundary conditions on the surface Σ (vanishing normal electric field). Due to the mirror symmetry of the charge distribution, the electric field has no z-component in the plane $z = 0$, and the problem is equivalent to that of a unique colloid (say colloid 1) in a subcell cylinder of length h, with again Neumann boundary conditions [the right half of the cylinder, indicated by a dotted rectangle in Figure 1b]. We assume the effective force acting on colloid 1 to be repulsive ($F_1^z \geq 0$). Then, we translate along the z-axis the left half cell ($-h \leq z \leq 0$) by a distance $2h$, keeping the right half fixed, to obtain the configuration of Figure 1c. The electrostatic potential around colloid 1 is unaffected, so that the effective force is unchanged, corresponding now to an effective attraction. Any repulsive configuration with Neumann boundary conditions on the confining cylinder can then be mapped onto an attractive one (from the construction of the mapping, it appears that this feature disappears in the limit $h \rightarrow \infty$). The hypothesis of infinite length is thus a key ingredient of the proofs in refs 10−12. Moreover, numerical solutions of the nonlinear Poisson−Boltzmann equation for finite-size disklike clay platelets confined in a finite-length Wigner−Seitz cylinder

(32) Marcus, R. A. *J. Chem. Phys.* **1955**, *23*, 1057. Trizac, E.; Hansen, J.-P. *Phys. Rev. E* **1997**, *56*, 3137.
(33) Diehl, A.; Tamashiro, M. N.; Barbosa, M. C.; Levin, Y. *Physica A* **1999**, *274*, 433.
(34) Groot, R. D. *J. Chem. Phys.* **1991**, *95*, 9191.

show repulsive effective pair forces when the distance between the clay particles is smaller than the half length h of the cylinder.[35]

Appendix B

It will be shown that upon modifying the distance between the plates ($h \rightarrow h + \delta h$), the Helmholtz free energy changes according to eq 9. The present derivation bears some similarities with other ones in the related context of Poisson−Boltzmann cell theory.[32] From the definition of the free energy, eq 1, and the symmetry $z \leftrightarrow -z$, we have

$$\delta F = \int_{-h}^{h} \delta f \, dz + 2 \int_{h}^{h+\delta h} f \, dz + \frac{1}{2} \int_{-h}^{h} \delta(\rho_c \psi) \, dz + \int_{h}^{h+\delta h} \rho_c \psi \, dz \quad (B1)$$

Consider first the energetic contribution. Making use of Poisson's equation (eq 2), two integrations by parts [with vanishing terms $(\partial_z \psi)^2_{z=\pm h}$] yield

(35) Leote de Carvalho, R. J. F.; Trizac, E.; Hansen, J.-P. *Phys. Rev. E* **2000**, *61*, 1634.

$$\frac{1}{2} \int_{-h}^{h} \delta(\rho_c \psi) \, dz$$

$$= \int_{-h}^{h} \psi \delta \rho_c \, dz + \int_{h}^{h+\delta h} \rho_c \psi \, dz \quad (B2)$$

$$= \int_{-h}^{h} \psi \delta \rho_c \, dz + \sum_{\alpha=1}^{N} \int_{h}^{h+\delta h} n_\alpha \left(\mu_\alpha - \frac{\partial f}{\partial n_\alpha} \right) dz \quad (B3)$$

The stationary condition (4) was used in going from (B2) to (B3). Similarly, with $N_\alpha = \int_{-h}^{h} n_\alpha \, dz$ and since ρ_c reduces to the microion charge distribution $\sum_\alpha e_\alpha n_\alpha$ outside the platelets (in particular between h and $h + \delta h$),

$$\int_{-h}^{h} \delta f \, dz = \sum_{\alpha=1}^{N} \int_{-h}^{h} (\mu_\alpha - e_\alpha \psi) \delta n_\alpha \, dz =$$

$$\sum_{\alpha=1}^{N} \mu_\alpha \left(\delta N_\alpha - 2 \int_{h}^{h+\delta h} n_\alpha \right) - \int_{-h}^{h} \psi \delta \rho_c \, dz + \psi(z=0) \delta \sigma$$

$$(B4)$$

Gathering results, we obtain eq 9.