Electrostatically swollen lamellar stacks and adiabatic pair potential of highly charged plate-like 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 plate-like colloids within a local density functional theory approach, generically leads to a swelling behaviour. 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 counter-intuitive 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 behaviour 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 counter-ions 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 behaviour 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 non local 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 either requires the inclusion of non electrostatic 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 non-linear Poisson-Boltzmann theory. This statement is consequently in contradiction with the attractive behaviour 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 [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 II A). 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 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 [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

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These implicit relations between the electrostatic potential and the densities of charge distribution in the Wigner-Seitz cell around a given platelet (e.g. that situated at $-h$ slab extending between $-h$ and $h$) may be corrected by correlation terms included in the free energy $F$ 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

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

(1)

where $\rho_c(z)$ is the local total charge distribution, including the microions and the plate (with global electroneutrality $\int_{-h}^{h} \rho_c = 0$). $F$ 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 $\varepsilon$, the total electrostatic potential $\psi(z)$ is the solution of Poisson’s equation

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

(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. 23–24. Consequently, the term $\int f$ in Equation (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 non-linear Poisson-Boltzmann and Modified Poisson-Boltzmann theories [21,22].

### A. Density functional theory formalism

We consider a regular succession of rigid infinite parallel plates located at $z = 2nh$ ($n \in \mathbb{N}$). Each plate carries a uniform surface charge $\sigma$, and releases its counter-ions in the electrolyte solution, considered to be a mixture of $N$ microions, where species $\alpha$ has charge number $e_{\alpha}$ and local density $n_{\alpha}(z)$. We write the free energy $F$ 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

$$\Omega\{\{n_{\alpha}\}\} = F\{\{n_{\alpha}\}\} - \sum_{\alpha} \mu_\alpha N_\alpha; \quad \left( N_\alpha = \int_{-h}^{h} n_{\alpha} dz \right),$$

(3)

where $\mu_{\alpha}$ is either the Lagrange multiplier associated with the constraint of fixed average concentration, or the chemical potential of species $\alpha$ in the reservoir. The resulting stationary equations read for all species $\alpha$

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

(4)

These implicit relations between the electrostatic potential and the densities $\{n_{\alpha}\}$ allow to solve Poisson’s equation (3) and compute the optimal profile $n_{\alpha}^*(z)$ (hereafter noted $n_{\alpha}(z)$ without ambiguity), from which we deduce the Helmholtz free energy $F(h, \sigma, T, \{N_{\alpha}\}) = F\{\{n_{\alpha}^*\}\}$, with $F = U - TS$ ($U$ is the total internal energy, $T$ the absolute temperature and $S$ the entropy of the total micro-ions charge distribution in the cell).

From the knowledge of $F$, the definition of the thermodynamic potential $R$ (which variations correspond to the reversible work performed by an operator and thus define the osmotic pressure) requires the specification of the

### 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

$$\Omega\{\{n_{\alpha}\}\} = F\{\{n_{\alpha}\}\} - \sum_{\alpha} \mu_\alpha N_\alpha; \quad \left( N_\alpha = \int_{-h}^{h} n_{\alpha} dz \right),$$

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thermodynamic situation under consideration. In the canonical case with constant charge plates, \( R = F \) \[29\]. If on the other hand, the platelets are held at constant potential (e.g. by an external generator), \( R \) is the Legendre transform of \( F \) with respect to the surface charge \[29,30\], namely

\[
R = F(\sigma, h, T) - \sigma \frac{\partial F}{\partial \sigma} \bigg|_{h,T} = F(\sigma, h, T) - \sigma \psi_p (\sigma, h, T),
\]

where \( \psi_p = \psi(z = 0) \) denotes the surface potential. In the opposite case of a system in equilibrium with a salt reservoir, \( R = R_\sigma = \Omega(\{n_\alpha\}) = F - \sum \mu_\alpha \int_{-h}^{h} n_\alpha(z) \, dz \) at constant charge \( \sigma \)

\[
R = R_\psi = F - \sum \mu_\alpha \int_{-h}^{h} n_\alpha(z) \, dz - \sigma \frac{\partial F}{\partial \sigma} \bigg|_{h,T} = \psi_{p} \sum \mu_\alpha \delta N_\alpha - \sigma \psi_{p},
\]

In any case, the osmotic pressure is defined as

\[
\Pi = -\frac{1}{2} \frac{\partial R}{\partial h},
\]

where \( R \) 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 \( \Pi \) can consequently be disposed of.

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

\[
\delta F = \left[ f - \sum n_\alpha \frac{\partial f}{\partial n_\alpha} \right]_{z=h} 2\delta h + \sum \mu_\alpha \delta N_\alpha + \psi_{p} \delta \sigma,
\]

so that the osmotic pressure reads

\[
\Pi = \left[ -f + \sum n_\alpha \frac{\partial f}{\partial n_\alpha} \right]_{z=h},
\]

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 mid-plane between the membranes:

\[
\Pi = \pi(z = h) \quad \text{where} \quad \pi(z) = -f[\{n_\alpha\}(z)] + \sum n_\alpha(z) \frac{\partial f}{\partial n_\alpha}(z).
\]

C. Stability analysis

When the stack is in osmotic equilibrium with a salt reservoir, the comparison of \( \Pi \) obtained in section II B with the pressure exerted by the reservoir quantifies the tendency towards swelling (\( \Pi > \Pi_{\text{res}} \)) or collapse (\( \Pi < \Pi_{\text{res}} \)). 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 \( \Pi \) is extremal in the reservoir, and that this extremum is a minimum under fairly general conditions. We first analyze the \( \psi \) dependence of the pressure \( \pi \), defined by \( \pi(\psi) = \pi(z) \) where \( \psi = \psi(z) \) is the solution of Poisson’s equation \[4\]. From Eq. \[11\] we have

\[
\frac{\partial \pi}{\partial \psi} = \sum \alpha n_\alpha \frac{\partial}{\partial \psi} \left( \frac{\partial f}{\partial n_\alpha} \right),
\]

that can be recast making use of the stationary condition \[3\]
\[ \frac{\partial \pi}{\partial \psi} = - \sum_{\alpha=1}^{N} n_{\alpha} e_{\alpha} \]

(13)

\[ = - \rho_c(z) \quad \text{outside the plate} \quad (z \neq 0). \]

(14)

\( \pi \) thus goes through an extremum in the reservoir (\( \Pi_{\text{res}} \) by definition) where the charge density vanishes (unlike at the mid-plane \( z = h \) where \( \rho_c \neq 0 \)). Relation (14) together with Poisson’s equation implies that the local stress introduced in (11) fulfills the mechanical equilibrium condition for the fluid of microions:

\[ \pi(z) = - \frac{\varepsilon}{8\pi} \left( \frac{\partial \psi}{\partial z} \right)^2 = \Pi, \]

(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 \( \pi \) can be obtained by introducing the Hessian matrix \( N \times N \)

\[ H_{\alpha\beta} = \frac{\partial^2 f}{\partial n_\alpha \partial n_\beta} \]

(16)

that obeys the relation

\[ \sum_{\beta=1}^{N} H_{\alpha\beta} \frac{\partial n_\beta}{\partial \psi} = - e_\alpha \]

(17)

as can be seen from Eq. (4). We thus have

\[ \frac{\partial^2 \pi}{\partial \psi^2} = \sum_{\alpha\beta} H_{\alpha\beta} \frac{\partial n_\alpha}{\partial \psi} \frac{\partial n_\beta}{\partial \psi}, \]

(18)

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

\( \Pi > \Pi_{\text{res}} \).

In spite of the differences outlined at the beginning of section II between the pair potential and the multi-body 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 \( e \to 0 \) (at fixed valency \( e_{\alpha}/e \)), we obtain a locally neutral mixture where the total free energy functional reduces to the contribution \( f \). The thermodynamic stability criterion of this neutral mixture implies the positive definiteness of the matrix \( H_{\alpha\beta} \) that is independent on \( e \).

- **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 micro-species described by the same density \( f \). The thermodynamic stability condition of the full functional (1) involves the 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 towards 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 micro-species. Indeed, from the computation of the free energy variation detailed in section 13, the effective force can be written

\[ F_z = -\frac{1}{2} \frac{\delta R}{\delta h} = \Pi_{\text{in}} - \Pi_{\text{out}}. \]  

(19)

From the vanishing of the electric field at \( z = 0 \) and \( |z| \to \infty \), we have \( \Pi_{\text{in}} = \pi(z = 0) \) and \( \Pi_{\text{out}} = \pi(|z| \to \infty) \). For \( |z| \to \infty \), the charge density vanishes so that \( \Pi_{\text{out}} \) equals the osmotic pressure in the salt reservoir under consideration. The argument of section 13 indicates that \( \Pi_{\text{in}} > \Pi_{\text{out}} \) and that the interactions are repulsive under the assumption of positive definiteness for the stability matrix \( \partial^2 f/\partial z^2 \). 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 [14,15] for the same system treated at the level of Poisson-Boltzmann. The work of Sogami et al. has already been criticized [16,17], 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 [14,15], introduced to describe the swelling behaviour of n-butyl-ammonium vermiculite gels.

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

\[ f(n_{\alpha}) = \beta^{-1} \sum_{\alpha=1}^N n_{\alpha} \left( \ln (n_{\alpha} \Lambda^3_{\alpha}) - 1 \right), \]  

(20)

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

\[ n_{\alpha}(z) = n_{\alpha}^0 \exp(-\beta e_{\alpha} \psi) \]  

(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 \( \psi \) is chosen to vanish for \( |z| \to \infty \), so that \( n_{\alpha}^0 \) is the density of species \( \alpha \) far from the plates with a corresponding chemical potential

\[ \mu_{\alpha} = kT \ln (n_{\alpha}^0 \Lambda^3_{\alpha}). \]  

(22)

As a result of the global electroneutrality condition, it can be checked that the final free energy [expression (23) below] is independent on an arbitrary shift of the potential \( \psi \) [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:

\[ F = \mathcal{F}(\{n_{\alpha}\}) = \psi p_{\alpha} \frac{1}{8\pi} \int_{-\infty}^{\infty} \left( \frac{\partial \phi}{\partial z} \right)^2 dz + \sum_{\alpha} N_{\alpha} (\mu_{\alpha} - kT) \]  

\[ = \psi p_{\alpha} + \int_{-\infty}^{\infty} \Pi dz + \sum_{\alpha} N_{\alpha} (\mu_{\alpha} - 2kT), \]  

(23)

where Eq. [13] and the ideal equation of state for \( \pi(z) \) have been used in going from the first to second line. Note that it is understood that the osmotic term \( \Pi \) in (23) takes the value \( \Pi_{\text{in}} \) (resp. \( \Pi_{\text{out}} \)) for \( |z| < h \) (resp. \( |z| > h \)). Strictly speaking, expression (23) diverges (if salt is added to the electrolyte, some of the quantities \( N_{\alpha} \) 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 [1] for a review of the standard solutions, including the present geometry), \( F \) may be computed from equation (23). Following this route, we readily recover the Helmholtz free energy obtained by Sogami et al. by means of a charging process. In Equation (23), \( \sigma = \sigma_{\text{in}} + \sigma_{\text{out}} \) stands for the total surface charge on a platelet, including both the different inner (\( \sigma_{\text{in}} \) from \( z = h^- \)) and outer (\( \sigma_{\text{out}} \) from \( z = h^+ \)) contributions, denoted respectively \( Z_i \) and \( Z_o \) in [14,15].

In the model of [14,15], the electrostatic potential is imposed to be continuous throughout the system and the surface potential \( \psi_p \) is independent on 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 \( n_{\alpha}^0 \) 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 $R_\psi$ defined in Eq. (1) should be used in computing the force whereas $F$ has been considered in [13,14]. The definition of the model imposes that when $h$ changes at fixed $\psi_p$, $Z_o$ 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

$$R_\psi = F_{in} + F_{out} - \sum_\alpha \mu_\alpha \int_{-\infty}^{\infty} n_\alpha(z) \, dz - \sigma_{in} \psi_p,$$

(24)

whereas $F = F_{in} + F_{out}$ has been considered in [14]. Omission of the chemical potential terms $\mu_\alpha n_\alpha$ in the right hand-side of Eq. (24) leads the force computed in [14] to depend on the masses (through the lengths $\Lambda_\alpha$), which is impossible in an equilibrium statistical mechanics theory, as already pointed out in [11]. With the aid of the relations given in [14] (e.g. Eqs (63), (64) and (65) valid in the case of counter-ion dominance between the plates), an explicit computation of the force $F_z = -\partial R_\psi / \partial (2h)$ yields the standard expression

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

(25)

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

(26)

where the continuity of the co- and counter-ion charge density across the membrane (resulting from the imposed continuity of the potential) has been used in going from (23) to (25). The compatibility of Eq. (25) with (19) is transparent. In terms of the variables used in [14], where $\Phi(0)$ denotes the reduced potential at mid-distance between the plates, we get

$$F_z = \frac{2\pi}{\varepsilon} e^2 (Z_o^2 - Z_i^2) = 4n_0 kT \sinh \left[ \Phi(0) \frac{2}{kT} \right] \geq 0,$$

(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 $\sigma_{in}$ are outer $\sigma_{out}$ surface charges are held constant, the effective force is still given by (25). This translates into the Legendre identity

$$\frac{\partial R_\psi}{\partial h}_{\psi_p, \sigma_{out}} = \frac{\partial}{\partial h} \left[ R_\psi - \psi_p \frac{\partial R_\psi}{\partial \psi_p} \right]_{\sigma_{in}, \sigma_{out}} = \frac{\partial (R_\psi + \sigma_{in} \psi_p)}{\partial h}_{\sigma_{in}, \sigma_{out}}$$

(28)

that can be considered as a test for the consistency of the thermodynamic potential used. In the limit of counter-ion dominance between the plates investigated in [14], the identity (28) can be checked explicitly with the thermodynamic potential $R_\psi$ used here.

**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 behaviour 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 [14]. 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 [14].

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 $F$ is necessarily mean-field like:

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

(29)

with a $\delta$-correlated short range part. This shortcoming may be circumvented by the inclusion of non-local terms in the theory, e.g. in the spirit of the weighted density approximation [33,34]. However, we expect the local formalism considered here to be instructive for inter-plate separations much larger than the ionic size.
References [10–12] proved that the effective interactions between a pair of like-charged colloids immersed with counter-ions and salt in a confining cylinder of infinite extension [see Figure 1(a)] 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 1(b), in the specific case of Neumann boundary conditions on the surface $\Sigma$ (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 sub-cell cylinder of length $h$, with again Neumann boundary conditions [the right half part of the cylinder, indicated by a dotted rectangle in Fig. 1(b)]. We assume the effective force acting on colloid 1 repulsive ($F_z^1 \geq 0$). 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. 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 $h \to \infty$). The hypothesis of infinite length is thus a key ingredient of the proofs in Refs. [10–12]. It is moreover worthwhile to note that numerical solutions of the non-linear Poisson-Boltzmann equation for finite-size disc-like clay platelets confined in a finite length Wigner-Seitz cylinder, show repulsive effective pair forces when the distance between the clay particles is smaller than the half length $h$ of the cylinder [35].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Illustrative side view of the cell models considered. Mirror symmetry with respect to the mid-plane $z = 0$ between the two colloids is enforced (this requirement is an important ingredient in the proofs [10–12]).}
\end{figure}

\section*{APPENDIX B:}

It will be shown that upon modifying the distance between the plates ($h \to h + \delta h$), 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, Equation (1) and the symmetry $z \leftrightarrow -z$, we have

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

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

$$
\frac{1}{2} \int_{-h}^{h} \delta (\rho_c \psi) \, dz = \int_{-h}^{h} \psi \delta \rho_c \, dz + \int_{h}^{h+\delta h} \rho_c \psi \, dz \tag{B2}
$$

$$
= \int_{-h}^{h} \psi \delta \rho_c \, dz + \sum_{\alpha=1}^{N} \int_{h}^{h+\delta h} n_\alpha \left( \mu_\alpha - \frac{\partial f}{\partial n_\alpha} \right) \, dz. \tag{B3}
$$
The stationary condition (4) was used in going from (B2) to (B3). Similarly, with $N_\alpha = \int_{-h}^{h} n_\alpha dz$ and since $\rho_c$ reduces to the microions charge distribution $\sum_\alpha e_\alpha n_\alpha$ outside the platelets (in particular between $h$ and $h + \delta h$)

$$\int_{-h}^{h} \delta f dz = \sum_{\alpha=1}^{N} \int_{-h}^{h} (\mu_\alpha - e_\alpha \psi) \delta n_\alpha dz = \sum_{\alpha=1}^{N} \mu_\alpha \left( \delta N_\alpha - 2 \int_{h}^{h+\delta h} n_\alpha dz \right) - \int_{-h}^{h} \psi \delta \rho_c dz + \psi(z = 0) \delta \sigma.$$ (B4)

Gathering results, we obtain equation (9).

[1] G.M. Kepler and S. Fraden, Phys. Rev. Lett. 1994, 73, 356; M.D. Carbajal-Tinoco, F. Castro-Román and J.L. Arauz-Lara, Phys. Rev. E 1996, 53, 3745; A.M. Larsen and D.G. Grier, Nature 1997, 385, 230; J.C. Crocker and D.G. Grier, Phys. Rev. Lett. 1996, 77, 1897.

[2] N. Gronbech-Jensen, K.M. Beardmore and P. Pincus, Physica A 1998, 261, 74; E. Allahyarov, I. D’Amico and H. Löwen, Phys. Rev. E 1999, 60, 3199; D. Goulding and J.-P. Hansen, Europhys. Lett. 1999, 46, 407; P. Linse and V. Lobaskin, Phys. Rev. Lett. 1999, 83, 4208; J.J. Gray, B. Chiang and R.T. Bonecaze, Nature 1999, 402, 750; J.J. Arenzon, J.F. Stilck and Y. Levin, Eur. Phys. J. B 1999, 1, 79.

[3] R. van Roij, J.P. Hansen and M. Dijkstra, Phys. Rev. E. 1999, 59, 2010.

[4] P.B. Warren, J. Chem. Phys. 2000, 112, 4683.

[5] T.M. Squires and M.P. Brenner, Phys. Rev. Lett. 2000, 85, 4976; I.V. Ivlev, cond-mat/0012212.

[6] H. van Olphen, “Clay Colloid Chemistry” (John Wiley, New York, 1977).

[7] M. Dubois, T. Zemb, L. Belloni, A. Delville, P. Levitz and R. Setton, J. Chem. Phys. 1992, 75, 944.

[8] G. Gouy, J. Phys. 1910, 9, 457; D.L. Chapman, Phil. Mag. 1913, 25, 475.

[9] D. Andelman in “Membranes, their Structure and Conformation”, edited by R. Lipowsky and E. Sackmann (Elsevier, Amsterdam 1996).

[10] J.C. Neu, Phys. Rev. Lett. 1999, 82, 1072.

[11] J.E. Sader and D.Y. Chan, J. Colloid Interface Sci. 1999, 213, 268; J.E. Sader and D.Y. Chan, Langmuir 2000, 16, 324.

[12] E. Trizac, Phys. Rev. E 2000, 62, R1465.

[13] Y. Burak and D. Andelman, J. Chem. Phys. 2001, 114, 3271.

[14] I.S. Sogami, T. Shinohara and M.V. Smalley, Molec. Phys. 1991, 74, 599.

[15] I.S. Sogami, T. Shinohara and M.V. Smalley, Molec. Phys. 1992, 76, 1.

[16] S. Levine and D.G. Hall, Langmuir 1992, 8, 1090.

[17] R. Ettelaie, Langmuir 1993, 9, 1888.

[18] J.T.G. Overbeek, Molec. Phys. 1993, 80, 685.

[19] E. Ruckenstein, Adv. Colloid Interface Sci. 1998, 75, 169.

[20] M.V. Smalley and I.S. Sogami, Molec. Phys. 1995, 85, 869; M.V. Smalley, Langmuir 1995, 11, 1813; M.V. Smalley in “Ordering and phase transition in charged colloids”, edited by A.K. Akora and B.V.R Tata (VCH, 1996).

[21] E. Trizac and J.L. Raimbault, Phys. Rev. E 1999, 60, 6530. In this article, equation (14) [and therefore (16)] are 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 micro-ions is taken into account via the Modified Poisson-Boltzmann theory put forward in [22], a similar conclusion cannot be reached for the situation of complete confinement (finite length of the confining cylinder). Appendix A provides a simple counter-example showing that effective attraction can result from complete lateral confinement. The above error has been corrected in the more general analysis of Ref. [22].

[22] For a review article, see J.-P. Hansen and H. Löwen, Annu. Rev. Phys. Chem. 2000, 51, 209.

[23] M.J. Stevens and M.O. Robbins, Europhys. Lett. 1990, 12, 81.

[24] H. Löwen, J.-P. Hansen and P.A. Madden, J. Chem. Phys. 1993, 98, 3275.

[25] M.C. Barbosa, M. Deserno and C. Holm, Europhys. Lett. 2000, 52, 80.

[26] For a review, see J.-P. Hansen and E. Smarrigiasi, in “Monte Carlo and Molecular Dynamics of Condensed Matter Systems”, edited by K. Binder and G. Ciccotti (SIF, Bologna, 1996), or R. Evans, in “Fundamentals of Inhomogeneous Fluids”, edited by D. Henderson (Marcel Dekker, New York, 1992).

[27] M. Eigen and E. Wicke, J. Phys. Chem. 1954, 58, 702; V. Kralj-Iglič and A. Iglič, J. Phys. II France 1996, 6, 477; I. Borukhov, D. Andelman and H. Orland, Phys. Rev. Lett. 1997, 79, 435 and Electrochimica Acta 2000, 46, 221.

[28] L. Lue, N. Zoeller and D. Blankschtein, Langmuir 1999, 15, 3726.

[29] L.D. Landau and E.M. Lifschitz, “Electrodynamics of continuous media” (Pergamon Press, Oxford, 1984).

[30] H.B. Callen, “Thermodynamics” (John Wiley, New York, 1960).

[31] R. Kjellander and D.J. Mitchell, Molec. Phys. 1997, 91, 173.

[32] R.A. Marcus, J. Chem. Phys. 1955, 23, 1057; E. Trizac and J.-P. Hansen, Phys. Rev. E 1997, 56, 3137.

[33] A. Diehl, M.N. Tamashiro, M.C. Barbosa and Y. Levin, Physica A 1999, 274, 433.

[34] R.D. Groot, J. Chem. Phys. 1991, 95, 9191.

[35] R.J.F Leote de Carvalho, E. Trizac and J.-P. Hansen, Phys. Rev. E 2000, 61, 1634.