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RESEARCH ARTICLE

Poisson-Boltzmann for oppositely charged bodies: an explicit derivation

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The interaction between two parallel charged plates in ionic solution is a general starting point for studying colloidal complexes. An intuitive expression of the pressure exerted on the plates is usually proposed, which includes an electrostatic plus an osmotic contribution. We present here an explicit and self-consistent derivation of this formula in the only framework of the Poisson-Boltzmann theory. We also show that, depending on external constraints, the correct thermodynamic potential can differ from the usual PB free energy. For asymmetric, oppositely charged plates, the resulting expression predicts a non trivial equilibrium position with the plates separated by a finite distance. The depth of this energy minimum is decisive for the stability of the complex. It is therefore crucial to obtain its explicit dependence on the plates charge densities and on the ion concentration. It happens that analytic expressions for the position and depth of the energy minimum have been derived in 1975 by Ohshima [Ohshima H., *Colloid and Polymer Sci.* **253**, 150-157 (1975)] but, surprisingly, these important results seem to be overlooked today. We retrieve these expressions in a simpler formalism, more familiar to the physics community, and give a physical interpretation of the observed behavior.

Keywords: Poisson-Boltzmann theory, parallel plates, oppositely charged, colloid complex, energy profile.

1. Introduction

Poisson-Boltzmann theory is a statistical mean field theory that characterizes coarse-grained quantities such as the average particle distribution function and the electrostatic potential together with thermodynamic variables in systems composed of many charged and point like particles at thermal equilibrium. Despite the technical advances in the dilute and strong coupling regime [1–3], the statistical modeling of real solutions – often in an *intermediate* regime – is still an open problem [4]. The PB approximation remains a good reference theory for describing the essential features of electrolyte solutions at thermal equilibrium. It allows to model plasmas in the equilibrium regime, colloidal suspensions through the famous Cell Model [5], or polyelectrolytes in solution. Moreover, the increasing interest for the biological mechanisms at the sub-cellular scale leads the community to deal with the electrostatic interaction of biological objects in solution, as for the case of protein-protein interaction [6], protein-DNA interaction [7], DNA-membrane interaction [8], etc.

In the case where one is interested in the effective interaction between two charged bodies surrounded by mobile charges, it is frequently useful, given the difficulty of the equations that have to be solved, to rely on a one dimensional problem to capture the physics of the system [9]. This essentially amounts to focus on the

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1 interaction between two parallel charged plates in solution. Besides, approximated
2 methods have been developed in the past century to correct the 1D problem as to
3 take into account the geometric effects in the interaction of two mesoscopic bodies,
4 thus increasing all the more the interest of one dimensional models [10–14].

5 In general, the main quantities to be derived in the one dimensional case are (i)
6 an expression for the free energy of the system in the framework of the Poisson-
7 Boltzmann approximation, (ii) a differential equation for the mean electrostatic
8 potential and, in order to evaluate the actual interaction between the two plates,
9 (iii) an explicit expression for the pressure exerted on each surface.

10 Various derivations of the Poisson-Boltzmann approximation actually exist. A
11 good review of many ways to obtain the Poisson-Boltzmann equation has been
12 presented by Lau [15] including a saddle point approximation in a path integral
13 formulation (see also [4]). Less straightforward derivations are also available via
14 the Density Functional Theory (DFT)[16–18] or exact equations hierarchy [19].
15 Finally a less formal procedure has been proposed by Deserno *et al.*, in the field of
16 colloid physics, to obtain mean field quantities for charged systems [5].

17 Most presentations, despite their different approaches, lead to a same formula
18 for the pressure, which amounts to the sum of a purely electrostatic plus a purely
19 osmotic contribution. One merit of the Poisson-Boltzmann approximation is indeed
20 that this formula exactly matches the boundary-density theorem at the Wigner-
21 Seitz cell boundary [20] as well as the contact value theorem on the charged plates
22 [21]. The first question addressed in this paper is thus whether or not this intuitive
23 expression for the inter-plate pressure can be directly and exactly derived from
24 the Poisson-Boltzmann free energy, without need for additional arguments and
25 for any boundary conditions. After having introduced the system and its Poisson
26 Boltzmann free energy in Section 2, we derive in Section 3 the expected expression
27 for the pressure and show that a particular caution should be taken in the choice
28 of the right statistical ensemble when different “external” constraints are imposed
29 to the plates, as e.g. at constant potential or at constant charge conditions.

30 The pressure formula predicts the presence of a non trivial equilibrium distance
31 for plates of opposite and asymmetric charge densities. This has been shown in
32 the pioneering work of Parsegian and Gingell [9] who used the linear Debye-Hückel
33 theory in the case of high salt concentrations, and more recently, by Lau and Pincus
34 [22] in the framework of the nonlinear Poisson-Boltzmann equation restricted to
35 the case of no added salt.

36 The consequences of such an equilibrium on the effective behaviour of charged
37 bodies in solution can only be assessed by a study of the corresponding energy
38 profile, i.e. a comparison of the energy well depth to the thermal energy. If the
39 energy gain at the minimum is small with respect to $k_B T$, the two charged bod-
40 ies will not stabilize in the bound complex and will behave as in the absence of
41 electrostatic interaction. Quite surprisingly, this aspect of the problem is rarely
42 addressed in the contemporary literature. Some authors [23] discuss in details how
43 the equilibrium distance (the limit between attraction and repulsion) depends on
44 the plate charges and on the salt conditions, but do not address the question of the
45 depth of the free energy well. Nevertheless, very nice analytic expressions for both
46 the position and the energy values at the equilibrium position have been obtained
47 in 1975 by Ohshima [24]. The paper by Ohshima deals with the more complex case
48 of two parallel plates of given thickness and dielectric constant, thus leading to a
49 rather complex notation. Nonetheless, the important results of Ref. [24] are worth
50 being reproduced today at least in the more usual case of two charged surfaces, in
51 that they represent an exact and synthetic description of their interaction whatever
52 their charges and the ionic strength of the solution.
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In order to illustrate the system behavior in the simple but crucial case of monovalent solutions, in Section 4 we first solve explicitly the Poisson-Boltzmann problem and obtain the pressure and energy profiles. Then, we focus on the origin of the energy minimum and derive an expression for its position and depth in the framework of the Poisson-Boltzmann theory. We check the agreement between the analytic expression and the behaviour obtained by direct numerical integration of the Poisson-Boltzmann equation. Finally, we discuss the physical origin of the results by investigating the role of the different parameters, as the plate charges and the salt ions and counter-ions.

2. The Poisson-Boltzmann free energy of the two plates system

We are interested in the thermodynamic properties of a system composed of a fixed distribution of charges and of N point-like mobile ions in a solution at temperature T . The system is in contact with an infinite salt reservoir, so that the total number of ions N is not fixed. The valence, mass, position and momentum of the single ion indexed by “ i ” are denoted by z_i , m_i , r_i and p_i , respectively. For a given N , the Hamiltonian of the system can be written as follows:

$$H(\{\mathbf{r}\}, \{\mathbf{p}\}) = H_{kin} + H_{pot} = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i=1}^N z_i e \phi(\mathbf{r}_i) + \frac{1}{2} \int e \sigma(\mathbf{r}) \phi(\mathbf{r}) d^3 r \quad (1)$$

where σ is the fixed volumic charge distribution in unit of the elementary charge e and $\epsilon = \epsilon_0 \epsilon_r$ is the dielectric constant of the solvent. The function $\phi(\mathbf{r})$ is the electrostatic potential,

$$\phi(\mathbf{r}) \equiv \sum_{j=1}^N \frac{z_j e}{4\pi\epsilon|\mathbf{r} - \mathbf{r}_j|} + \int \frac{\sigma(\mathbf{r}') e}{4\pi\epsilon|\mathbf{r} - \mathbf{r}'|} d^3 r' = \sum_{\alpha=1}^p \int \frac{e z_\alpha n_\alpha(\mathbf{r}')}{4\pi\epsilon|\mathbf{r} - \mathbf{r}'|} d^3 r' + \int \frac{\sigma(\mathbf{r}') e}{4\pi\epsilon|\mathbf{r} - \mathbf{r}'|} d^3 r', \quad (2)$$

where we introduced the number and ion density of the species α , respectively N_α and $n_\alpha(\mathbf{r}) \equiv \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_i)$, with $\sum_{\alpha=1}^p N_\alpha = N$.

We now specify the geometry of our system. We consider two semi-infinite plane surfaces, uniformly charged and separated by a distance L with the electrolyte solution between them. The surfaces are positioned respectively at $x = 0$ and $x = L$. Each surface separates the solution from a plate of thickness d and dielectric constant ϵ_p (see Figure 1).

If the plates are conductors ($\epsilon_p = \infty$), the electric field inside the plates is zero. Similarly, for dielectric plates of infinite thickness ($d = \infty$), the electric field vanishes in the dielectric, thanks to the electroneutrality of the whole system (charged surfaces plus solution). We can therefore reasonably assume that, for thick enough plates, the same conditions hold, as indeed observed either analytically [25] or numerically [26, 27] (The case of thin plates should be treated differently, as discussed in [25–27]). In all these cases, the contribution to the system free energy of the region inside each plate vanishes. Furthermore, as we will see, the contribution of the solution beyond the outer faces of the two plates can be easily evaluated. In the following, we will therefore limit our system to the region between the two facing

surfaces. In order to take into account properly the boundaries at $x = 0$ and $x = L$ we introduce a parameter h for the calculations and then take the limit for $h \rightarrow 0$.

The fixed charge distribution in our geometry is then

$$\sigma(x) = \sigma_0\delta(x) + \sigma_L\delta(x - L) \quad (3)$$

where σ_0 and σ_L correspond to the surface charge densities of the two plates. Only the x coordinate is relevant due to the translation invariance along the z and y directions. In the following, we will focus on the volume delimited by a given finite surface A of the two facing plates.

In the presence of an ion reservoir the natural statistical ensemble is the grand canonical one. In this condition, the mean number of ions included between the two surfaces at equilibrium is of course a function of the plate separation L . Nevertheless, for a given plate separation, the grand canonical mean value $\langle N_\alpha \rangle(L)$ is fixed. This allows us to work, at given L , in the canonical ensemble, i.e. at fixed N_α , provided N_α is opportunely chosen, i.e. $N_\alpha = \langle N_\alpha \rangle$. This ensures indeed the statistical equivalence between the two ensembles at the thermodynamic limit.

Then, we can obtain the free energy of the system from the system partition function Z , as $F \equiv -k_B T \ln Z$. The kinetic part Z_{kin} can be easily calculated [28] and reads $Z_{kin} = \prod_{\alpha=1}^p (\Lambda_\alpha^{-3N_\alpha} / N_\alpha!)$, where $\Lambda_\alpha \equiv h (2\pi m_\alpha k_B T)^{-1/2}$ is the de Broglie thermal wavelength. The potential part of the partition function is not that simple to compute, because the electrostatic part of the Hamiltonian is a function of the position of all ions and cannot reduce to a product of uncorrelated functions. The simplest method to solve the problem is to rely on a mean field approximation. The Gibbs-Bogoliubov inequality allows one to find an upper bound for the free energy from an average of the Hamiltonian with a trial distribution $P_0(\mathbf{x})$ plus a Shannon type entropy built from the same distribution $P_0(\mathbf{x})$ [5]. For a given surface A , one gets therefore the following expression for the free energy functional per unit surface – that is the Poisson Boltzmann free energy functional:

$$\begin{aligned} \frac{F_{PB}[\{n^0\}]}{A} = \lim_{h \rightarrow 0} \frac{1}{2} \int_{-h}^{L+h} \rho^0(x) \phi^0(x) dx \\ + k_B T \sum_{\alpha=1}^p \int_{-h}^{L+h} \{n_\alpha^0(x) (\ln(\Lambda_\alpha^3 n_\alpha^0(x)) - 1)\} dx, \end{aligned} \quad (4)$$

where we have introduced $n_\alpha^0(x) \equiv N_\alpha P_0(x)$ following the normalization relation $N_\alpha \equiv A \int n_\alpha^0(x) dx$, and the global charge density ρ^0 defined by

$$\rho^0(x) = \sum_{\alpha=1}^p z_\alpha e n_\alpha^0(x) + e\sigma(x). \quad (5)$$

We recognize, in the first term of this functional, the electrostatic part of the energy of the system, while the second term corresponds to the entropic contribution of an ideal gas of ions.

We have therefore to minimize the functional $F_{PB}[\{n^0\}]/A$ with respect to the relevant functions n_α^0 . Moreover, the minimization should be performed under the condition

$$A \int_{-h}^{L+h} n_\alpha^0(x) dx = \langle N_\alpha \rangle, \quad (6)$$

this leading to define a new energy functional per unit area,

$$f_{PB} = \frac{F_{PB}[\{n^0\}]}{A} - \lim_{h \rightarrow 0} \sum_{\alpha=1}^p \mu_{\alpha} \int_{-h}^{L+h} n_{\alpha}^0(x) dx \quad (7)$$

where μ_{α} is a Lagrange multiplier and the integral equals N_{α}/A .

The minimization leads to the following relation between the *mean field* ion distributions \bar{n}_{α} minimizing f_{PB} and the corresponding mean field potential $\bar{\phi}(x)$:

$$\bar{n}_{\alpha}(x) = \Lambda_{\alpha}^{-3} e^{\beta \mu_{\alpha}} e^{-\beta e z_{\alpha} \bar{\phi}(x)}. \quad (8)$$

The reader will recognize in this result an explicit expression of the Boltzmann law, here rigorously re-obtained in the framework of the mean field approach.

The previous Equation still requires a closure relationship in order to determine the μ_{α} parameters. This can be obtained by replacing $\bar{n}_{\alpha}(x)$ from Equation (8) into Equation (6). Then, by performing the usual derivation of the mean values $\langle N_{\alpha} \rangle$ in the grand canonical ensemble, one can show that the ensemble equivalence is ensured by identifying the Lagrange multiplier μ_{α} to the chemical potential of ions of type α in the salt reservoir, i.e. $\mu_{\alpha} = k_B T \ln(n_{b,\alpha} \Lambda_{\alpha}^3)$ (where $n_{b,\alpha} = N_{\alpha}/V$ is the ion concentration).

Together with Equation (2), giving the electric field as a function of the charge distribution in the system, the previous Equation (8) constitute the solution of the problem. Equation (8) allows to obtain a simpler expression for the potential $\bar{\phi}(x)$ in terms of the free and fixed charge distributions in the system. Recalling that the electric potential and the charge density are linked by the Poisson equation, i.e.

$$\Delta \phi^0(\mathbf{r}) = -\frac{\rho^0(\mathbf{r})}{\epsilon} \quad (9)$$

and combining with Equation (8), we obtain indeed an ordinary differential equation for the adimensional mean field potential $\bar{\psi}(x) = \beta e \bar{\phi}(x)$. The resulting *Poisson-Boltzmann* (PB) equation reads in our one-dimensional case:

$$\frac{d^2 \bar{\psi}(x)}{dx^2} = -4\pi \ell_B \sum_{\alpha=1}^p z_{\alpha} \bar{n}_{\alpha}(x), \quad x \in \lim_{h \rightarrow 0} [+h, L-h] \quad (10)$$

with the boundary conditions

$$\begin{aligned} \lim_{h \rightarrow 0} \frac{d\bar{\psi}}{dx} \Big|_{+h} &= -4\pi \ell_B \sigma_0, \\ \lim_{h \rightarrow 0} \frac{d\bar{\psi}}{dx} \Big|_{L-h} &= 4\pi \ell_B \sigma_L. \end{aligned} \quad (11)$$

where $\ell_B \equiv e^2/4\pi\epsilon k_B T$ denotes the Bjerrum length and where we used electroneutrality of the considered system to get the boundary condition.

Before going on, we should note that it is possible to get a constant of motion C by multiplying (10) by $\frac{d\bar{\psi}}{dx}$ and then integrating in the $[+h, L-h]$ range. One gets

$$\frac{1}{2} \left(\frac{d\bar{\psi}}{dx} \right)^2 - 4\pi \ell_B \sum_{\alpha=1}^p \bar{n}_{\alpha}(x) = C. \quad (12)$$

This result will have a crucial role in the definition of the pressure between the two plates as we will see in the next section.

In order to compute a general expression for the pressure from a thermodynamic definition, we have now to evaluate the PB functional free energy at $n_\alpha^0(x) = \bar{n}_\alpha(x)$. The result, written in an equivalent but more practical form, will be identified with the system free energy. Indeed, at the $h \rightarrow 0$ limit, the integrals of any non diverging function in the two external regions vanish. Thus, after an integration by parts for the electrostatic contribution, we obtain for the PB free energy expressed in terms of the adimensional field $\bar{\psi}$:

$$\beta f_{PB}[\{\bar{n}\}, \sigma] = \lim_{h \rightarrow 0} \left\{ \frac{1}{8\pi\ell_B} \int_{+h}^{L-h} \left(\frac{d\bar{\psi}}{dx} \right)^2 dx + \sum_{\alpha=1}^p \int_{+h}^{L-h} \bar{n}_\alpha(x) [\ln(\Lambda_\alpha^3 \bar{n}_\alpha) - 1 - \beta\mu_\alpha] dx \right\}, \quad (13)$$

where we used Eqs. (11).

3. Determination of the pressure

We can now address the problem of finding an explicit expression for the pressure Π on the plates, according to the Poisson-Boltzmann theory. In the case of two *constant* charged densities on the plates, i.e. two plates whose charge densities are fixed once for ever, the plates self energy is independent of L and the usual derivation of the pressure from the free energy can therefore be used:

$$\Pi \equiv -A \left. \frac{\partial f_{PB}[\{\bar{n}_\alpha\}]}{\partial V} \right|_{\sigma, \mu_\alpha} = - \left. \frac{\partial f_{PB}[\{\bar{n}_\alpha\}]}{\partial L} \right|_{\sigma, \mu_\alpha}. \quad (14)$$

To take into account the presence of the salt reservoir, we take the derivatives in the previous Equation at constant μ_α .

To facilitate the calculation, let introduce the adimensional variable $\xi = x/L$, [15] and define a rescaled electric field \mathcal{E} for the adimensional potential, $\mathcal{E} \equiv -\frac{\partial \bar{\psi}}{\partial x}$. We then get directly from (10)

$$\sum_{\alpha=1}^p z_\alpha \bar{n}_\alpha = \frac{1}{4\pi\ell_B} \frac{1}{L} \frac{\partial \mathcal{E}}{\partial \xi}. \quad (15)$$

The entropic part of (13) can be written as

$$s_{PB}[\{\bar{n}\}, \sigma] = \lim_{h \rightarrow 0} \int_{+h}^{1-h} \left(-\frac{\bar{\psi}}{4\pi\ell_B} \frac{1}{L} \frac{\partial \mathcal{E}}{\partial \xi} - \sum_{\alpha=1}^p \bar{n}_\alpha \right) L d\xi \quad (16)$$

by using Equation (8). We can now take the derivative of Equation (16) with

respect to L , and get

$$\frac{\partial}{\partial L} s_{PB}[\{\bar{n}_j\}, \sigma] = \lim_{h \rightarrow 0} \int_{+h}^{1-h} \left[-\frac{1}{4\pi\ell_B} \left(\frac{\partial \bar{\psi}}{\partial L} \frac{d\mathcal{E}}{d\xi} + \bar{\psi} \frac{\partial}{\partial L} \frac{\partial \mathcal{E}}{\partial \xi} \right) - L \frac{\partial}{\partial L} \left(\sum_{\alpha=1}^p \bar{n}_\alpha \right) - \left(\sum_{\alpha=1}^p \bar{n}_\alpha \right) \right] d\xi \quad (17)$$

Finally, using again Equation (8) and recalling that \bar{n}_α are functions of $x = \xi L$, the derivative of the entropic term in the free energy, Equation (17), becomes

$$\lim_{h \rightarrow 0} \int_{+h}^{1-h} \left(-\frac{1}{4\pi\ell_B} \bar{\psi} \frac{\partial}{\partial L} \frac{\partial \mathcal{E}}{\partial \xi} - \sum_{\alpha=1}^p \bar{n}_\alpha \right) d\xi$$

In the same way, we calculate the partial derivative of the electrostatic part of Equation (13). Grouping the previous results and using Equation (12), one gets for the pressure:

$$\Pi = -\frac{k_B T}{4\pi\ell_B} C + \lim_{h \rightarrow 0} \frac{k_B T}{4\pi\ell_B} \left[\bar{\psi} \frac{\partial \mathcal{E}}{\partial L} \right]_{\xi=+h}^{\xi=1-h} \quad (18)$$

In the present case of constant charge densities on the plates, the electric field at the boundaries is independent of L and then the second term of Eq. (18) vanishes. The final expression for the pressure is therefore:

$$\Pi = -\frac{k_B T}{4\pi\ell_B} C = -\frac{k_B T}{8\pi\ell_B} \left(\frac{d\bar{\psi}}{dx} \right)^2 + k_B T \sum_{\alpha=1}^p \bar{n}_\alpha(x) \quad (19)$$

The latter result is quite intuitive since it represents the sum of the electrostatic stress and the osmotic pressure. It is indeed widely used in the literature. However, in the general case of *non constant* plate charge densities, the second term in Eq. (18) is a priori non zero. Such a term arises for instance when the potential on the plates is kept constant. **Consider for instance the case of the pressure between the two parallel plates of a capacitor.** If, for a given distance L between the plates and a given potential difference, we try to evaluate the pressure by differentiating the energy of the capacitor $CU^2/2$ with respect to L , then we get two different results whether the differentiation is done at constant charge or at constant potential. Of course the two derivations should give the same result since they refer to the same state of the system. The explanation of this apparent paradox is actually quite simple: when differentiating at fixed potential we include implicitly the energy supplied by the generator to keep the potential difference constant while varying L . Since this work only modifies the self energy of the plates and not their interaction, we have to subtract this part from the result. We retrieve in this way the correct result of the constant charge case [29].

In our case, one can easily realize that, at the boundaries, the expression $\bar{\psi} \partial \mathcal{E} / \partial L$ is equivalent to $\bar{\psi} \partial \sigma / \partial L$ and thus corresponds to the energy used to bring charges to the plates when varying the distance L . Then, the second term that arises in Eq.(18) is exactly the analogous of the generator term in the capacitor problem, and appears only because, using Gibbs terminology, we don't work in the correct

statistical ensemble. Indeed Eq.(14) represents a very useful and systematic procedure to get an expression for the pressure *provided* that the ensemble or equivalently the effective potential is chosen carefully. For instance, in the case of constant potential on the plates we have to make a functional Legendre transform to get the relevant thermodynamic potential:

$$g_{PB}[\{\bar{n}\}, \{\bar{\psi}\}_b] = f_{PB}[\{\bar{n}\}, \sigma] - \lim_{h \rightarrow 0} \int_{-h}^{L+h} \bar{\psi}(x) \sigma(x) dx \quad (20)$$

where $\{\bar{\psi}\}_b$ denotes the electrostatic potential at the boundaries. In this case Equation (14) must be replaced by:

$$\Pi \equiv - \left. \frac{\partial g_{PB}[\{\bar{n}_\alpha\}]}{\partial L} \right|_{\{\bar{\psi}\}_b} \quad (21)$$

Since the derivative of the additional term in g_{PB} exactly balances the second term of Equation (18), we finally retrieve the general result (19). For a different but equivalent discussion, see also Ref.[30].

4. Existence and characterization of the energy minimum for asymmetric charged plates

4.1. Zero pressure distance L_{min}

It can be interesting to illustrate the implications of Equation (19) for the case of two charged bodies in a 1:1 solution. The extension to a multivalent solution is straightforward¹, but the simpler case is more instructive. Let $n_{b,1} = n_{b,-1} = n_b$ be the bulk concentrations of the positive and negative monovalent ions.

First of all, we recall that our calculations apply to thick plates. Equation (19) has been obtained by minimizing the free energy of the region $x \in [0, L]$ and represents then the pressure due to the inhomogeneous electrolyte solution between the plates, which we call the inner pressure. A similar calculation can be performed for the solution beyond the outer face of each plate, leading to the outer pressure Π_{ext} . This pressure can be calculated in the same way as the inner pressure. Indeed, Equation (19) is valid as well in the outer part of the system. Thanks to the overall system electroneutrality, the electric field vanishes at infinity and then Equation (19) leads to $\Pi_{ext} = 2n_b k_B T$. The net force per unit surface exerted on each plate is given by the difference between the inner and the outer value of the pressure. We thus introduce the *excess* pressure P

$$\begin{aligned} P &= \Pi(x) - \Pi_{ext} = \\ &= -\frac{k_B T}{8\pi\ell_B} \left(\frac{d\bar{\psi}}{dx} \right)^2 + k_B T \sum_{\alpha} (\bar{n}_{\alpha}(x) - n_b) \end{aligned} \quad (22)$$

that vanishes when L increases toward infinity. The reservoir ions are here assumed to behave like an ideal gas, coherently with the mean field approximation.

¹Note however that the Poisson-Boltzmann approach is known to be less accurate in the case of multivalent salt solutions. It has been shown e.g. that a qualitatively different behavior can appear in the presence of divalent ions, as the attraction between equally charged plates [31].

Now, P is a function of L , that can be obtained by solving the PB Equation (10) for each $L \in]0; +\infty[$.

We then numerically analyse the sign of P as a function of L and of the plate charge ratios $r = \sigma_L/\sigma_0$. For $r > 0$ (charges of same sign) the plates always repel each other, which is a general consequence of the PB theory [9]. For the particular case $r = -1$ the interaction is instead always attractive. Interestingly, in the more general case of $r < 0$, and $r \neq -1$, there always exists one and only one *equilibrium distance* $L_{min}(r)$ between the plates for which we observe a transition between attraction and repulsion (i.e. a vanishing P). The transition occurs at a distance that depends on the charge densities of the plates, and a pronounced repulsion always appears at short distances, despite the fact that the plates are oppositely charged.

Such transitions were already predicted in linearized treatments of the problem [9] in 1972. More recently, the non linear case has been reconsidered [23], although an exact derivation of the transition distance as a function of the plates charges and salt concentration had already been obtained by Ohshima [24] in 1975.

Following the main lines of Ref. [24], it is possible to obtain an analytic expression for the equilibrium position explicitly dependent on the plate charge densities and on the salt concentration, for the case of a monovalent solution. We perform this calculation explicitly in Appendix A. We obtain the following expression for the position of the energy minimum L_{min} :

$$L_{min} = \lambda_D \left| \ln \left(\frac{|\sigma'_0|(2 + \sqrt{\sigma'_L{}^2 + 4})}{|\sigma'_L|(2 + \sqrt{\sigma'_0{}^2 + 4})} \right) \right| \quad (23)$$

where we have introduced the Debye length, $\lambda_D = 1/\sqrt{8\pi\ell_B n_b}$ and the adimensional charge densities $\sigma'_0 = 4\pi\ell_B\lambda_D\sigma_0$ and $\sigma'_L = 4\pi\ell_B\lambda_D\sigma_L$. A similar expression for the distance at which $P = 0$ is given in Ref. [23], Equation (9)¹.

In Figure 2 we compare the previous expression Equation (23) for L_{min} with the corresponding values directly obtained from the numerical solution of the PB equation, for different salt concentrations and charge density ratios. The minimum positions L_{min} are numerically estimated directly from the energy profiles. As expected, the formula of Equation (23) exactly agrees with the numerical results.

Two limiting regimes can now be considered. Let introduce the Gouy-Chapman lengths for both plates, $\lambda_0 = |1/2\pi\ell_B\sigma_0|$ and $\lambda_L = |1/2\pi\ell_B\sigma_L|$. In low salt conditions, one has $\lambda_D \gg \lambda_0$ and $\lambda_D \gg \lambda_L$ and, as a consequence, the position of the energy minimum is approximately given by

$$L_{min} \simeq 2\lambda_D \left| \frac{1}{|\sigma'_L|} - \frac{1}{|\sigma'_0|} \right| = |\lambda_L - \lambda_0| \quad (\text{low salt}), \quad (24)$$

In this limit, L_{min} becomes therefore independent of the salt concentration and is only a function of the plates charge densities, i.e. of the ratio r for the cases considered here since λ_0 is always kept fixed. In Figure 3, we report the local ion distribution in the inter-plate space as a function of x/L for a given choice of the plate charges and for different bulk ion concentrations n_b . At low salt (Figure 3 a), the concentration of the counter-ions of the most charged plate is much larger than

¹We noticed a difference of sign in the definition of the parameters γ_{\pm} of Ref. [23] with respect to our notation. This discrepancy arises from a different choice of the boundaries at which the pressure is evaluated, and has no consequences on the results, provided that the absolute value of the equilibrium distance $d (= L_{min})$ is taken in equation (9) of Ref. [23]. for the case where $\sigma_0 > \sigma_L$.

the salt concentration. In this case, the short range repulsion is therefore mainly due to the counter-ions of the most charged plate. We stress that the solid and dotted curves in Figure 2 also correspond to this low salt regime.

Inversely, at high salt, $\lambda_D \ll \lambda_0$ and $\lambda_D \ll \lambda_L$, and the equilibrium is

$$L_{min} \simeq \lambda_D \left| \ln \left| \frac{\sigma'_0}{\sigma'_L} \right| \right| = \lambda_D \left| \ln \left| \frac{\sigma_0}{\sigma_L} \right| \right| \quad (\text{high salt}). \quad (25)$$

In this limit the estimated equilibrium length L_{min} is then proportional to the Debye length, i.e. to $n_b^{-1/2}$. As shown in Figure 3 b, the short range repulsion is indeed essentially due to the salt ions whose osmotic effect is modulated by the charges on the plates. The dashed and dot-dashed curves in Figure 2 correspond to the high salt regime. In this high salt regime, a good approximated expression for the equilibrium position can also be obtained in the framework of the linearised PB equation, as expected. We checked indeed that the resulting expression [9] matches well the curves in Figure 2 for any ratios r at high salt concentrations (data not shown). Instead, the linear PB approximation cannot reproduce the observed behavior at low salt, whereas the expression of Equation (23) remains exact.

How the $P = 0$ condition should be interpreted in terms of electrostatic and osmotic contributions? The mechanism leading to an equilibrium position is not difficult to understand, starting from the expression of the excess pressure, Equation (22). As already observed, the pressure is proportional to the constant of motion C and is therefore constant in the inter-plate space $x \in [0, L]$. Let then consider the pressure P exerted on one plate, e.g. at $x = 0$. In this limit, the electrostatic term in Equation (22) simply reads $-k_B T \sigma_0^2 / 2$, and is therefore independent of L . On the contrary, the osmotic term depends on the ion concentration and is therefore a function of L . We then note that the expression for the ion density, Equation (8) can be rewritten in terms of the bulk concentrations and of the reduced potential as

$$\bar{n}_\alpha(x) = n_b e^{-z_\alpha \bar{\psi}(x)}. \quad (26)$$

The equilibrium condition $P = 0$, when calculated both on the left and right plates, can thus be written as a condition for the mean field potential at the boundaries that reads

$$\cosh \bar{\psi}_0(L_{eq}) = \frac{\pi \ell_B \sigma_0^2}{n_b} + 1. \quad (27)$$

$$\cosh \bar{\psi}_L(L_{eq}) = \frac{\pi \ell_B \sigma_L^2}{n_b} + 1. \quad (28)$$

where we introduced $\bar{\psi}_0(L) = \bar{\psi}(x = 0)$ and $\bar{\psi}_L(L) = \bar{\psi}(x = L) \forall L \in [0, \infty[$, and where L_{eq} is a distance between the plates for which $P = 0$.

From now on we will focus on the case of asymmetrically and oppositely charged plates, $r < 0$. In Figure 4 we compare the adimensional potential $\bar{\psi}_0(L)$ to the two roots $\pm \text{arccosh}(\pi \ell_B \sigma_0^2 / n_b + 1)$ of Equation (27). A trivial solution to Eqs. (27) and (28) corresponds to the limit $L \rightarrow \infty$, where $P = 0$ by construction. In this limit, and typically for $L \gg \lambda_0 + \lambda_L$, each plate charge is neutralized by its cloud of counterions as if the other plate didn't exist. At a large enough distance x from the plates, therefore, the ionic atmosphere behaves as an ideal gas and its pressure contribution $\Pi(x)$ exactly compensates the reservoir pressure Π_∞ . We also note

that, in this case, according to (26), the sign of $\bar{\psi}_0$ and $\bar{\psi}_L$ at infinity are opposite for oppositely charged plates.

Let now look for another, finite solution of Eqs. (27) and (28) leading to $L_{eq} = L_{min}$. For this case, we only have to determine the signs of $\bar{\psi}_0(L_{min})$ and $\bar{\psi}_L(L_{min})$. It is easy to see that the only possible solution is that the counterions of one plate prevail on *both* plates, so that $\bar{\psi}_0(L_{min})$ and $\bar{\psi}_L(L_{min})$ should have the same sign. It is the potential of the less charged plate that will change its sign at a given distance L between infinity and L_{min} . In Figure 4 we show indeed that the sign of the adimensional potential $\bar{\psi}_0$ changes for $r < -1$ whereas it remains the same when $r > -1$. The opposite arises for $\bar{\psi}_L$ (data not shown).

The physical interpretation of the observed equilibrium is thus straightforward. The most charged plate carries its cloud of condensed counterions when approaching the less charged one. The counterions of the less charged plate are more easily released in the bulk when the two ion clouds overlap. This process continues until the electroneutrality constraint precludes a further release of ions, this leading the ion concentration, and therefore the repulsive osmotic pressure, to increase. The equilibrium is then obtained at the distance L_{min} where electrostatic attraction and osmotic repulsion exactly balance.

4.2. Energy value E_{min} at the minimum

We have shown that the pressure always vanishes at a given inter-plate distance for oppositely, asymmetric charged plates. Nevertheless, if the presence of a vanishing pressure always corresponds in principle to an equilibrium position between the plates, it does not guarantee by itself that this equilibrium position will be stable enough to be relevant from a thermodynamic point of view. Indeed, in order to assess the real existence of a stable equilibrium, we need to estimate the corresponding energy gain. We stress again that, if the energy gain at the minimum is small with respect to $k_B T$, the two charged bodies will behave as in the absence of electrostatic interaction (the energy going to zero at large distances). On the contrary, a deep minimum will make the bodies stabilize at a non-zero equilibrium distance.

The explicit calculation of the whole function $P(L)$ allows us to evaluate the energy profile $E(L)$ and compare the depth of the potential well to the thermal energy $k_B T$. The energies per unit area are shown in Figure 5 (bottom), for the same charge densities as considered above. In order to use more natural units, energies are given in units of $k_B T / 100 \text{ nm}^2$. As expected, an energy minimum always exists for $r < 0$ and $r \neq -1$. Interestingly, while for $0 < r < 1$ the energy minimum depth shows a relevant dependence on the second plate charge density σ_L , this dependence disappears for $r < -1$ where the depth becomes constant.

A more systematic investigation of the energy minimum depth for varying charge densities and salt conditions is shown in Figure 6. The value of the energy per a unit area of 100 nm^2 for different ionic strengths is given as a function of the ratio of the plates charge densities r , again for σ_0 fixed at $-0.05 e/\text{nm}^2$. In low salt, the energy minimum depends on the ratio r and on the salt concentration, and it reaches its maximum value for $r = -1$, i.e. when the position of the minimum degenerates to $L = 0$. Energy depths are up to roughly $10 k_B T$ per 100 nm^2 . Figure 6 also confirms that the minimum depth becomes constant for $r < -1$, and coincides in this case with its (maximum) value at the singular value $r = -1$.

In his paper, Ohshima [24] also obtains an analytic expression for the energy at the minimum. An equivalent calculation, adapted to our formalism, is presented

in Appendix B. The final result reads

$$\beta E_{min} = 8n_b \lambda_D \left\{ \sqrt{|\sigma'_m|^2 + 4} - 2 - |\sigma'_m| \operatorname{arcsinh} \left| \frac{\sigma'_m}{2} \right| \right\}, \quad (29)$$

where σ'_m is the adimensional charge parameter related to the *smallest* plate charge density, i.e. $\sigma'_m = \min(\sigma'_0, \sigma'_L)$. In Figure 6 we compare the previous expression for the value of the energy depth with the results obtained by direct integration of the Poisson-Boltzmann equation. The two results show a perfect agreement. Together with Equation (23), the last result allows to a rapid and precise estimate of the equilibrium position and strength, and represent therefore a powerful tool in order to study the effective interaction between charged bodies in solution.

Nevertheless, we have to stress finally that Equation (29), as well as Figures 5 and 6, only give the energy *per unit area* (fixed to 100 nm^2 in the Figures). To obtain the total energy between two charged bodies in solution and compare it to the thermal energy, the surface and geometry of the bodies should be taken into account. This roughly amounts to multiply the energy by an *effective interaction area*, but the estimation of this area is not easy in that it depends on the bodies shape. Indeed, the variation of the interaction with the distance should be included in the calculation of the effective interaction area. A typical choice is the use of the Derjaguin approximation [32, 33], that calculates the interaction energy U between two curved surfaces by integrating the interaction energy per unit area between two flat plates $E(L)$ as

$$U \simeq \int_A E(L) dA \simeq f([R_1], [R_2]) \int_{D_{min}}^{\infty} E(L) dL, \quad (30)$$

where D_{min} is the distance of closest approach between the two curved surfaces, dA is the differential area of the surfaces facing each other, $[R_1]$ and $[R_2]$ represent the sets of principal radii of curvature of the surfaces 1 and 2, respectively, at the distance of closest approach, and $f([a1], [a2])$ is a function of the radii of curvature of the surfaces. A very rough estimate should consider that the interaction between the two surfaces becomes negligible when their distance becomes larger than the screening Debye length λ_D . In a 0.1 M solution, the Debye length is of the order of 1 nm. For the case of two spherical colloids of 100 nm diameter, (it varies from approximately 0.3 nm for an 1 M solution to 10 nm for 0.01 M). If the two spheres are in contact (i.e. for $L = 0$), a simple geometric construction (depicted schematically in Figure 7) allows to calculate the surface area on each sphere that is separate by less than a Debye length from the facing one, this leading to a surface of the order of 300 nm^2 (roughly 1 % of the whole sphere surface). As a consequence, the depth of the energy well would reach approximately $\sim 20 k_B T$ in these conditions, and be thus large enough to ensure the kinetic stability of the complex at ordinary thermal conditions. Note however, that the two spheres will *not* be in contact anymore at equilibrium, but at a distance close to L_{min} , which can vary from 0 to approximately 2 nm depending on the value of the ratio r . When this distance becomes comparable to λ_D , the interaction area decreases considerably. Therefore, the actual interaction surface will be in general reduced to a value that depends on the two lengths L_{min} and λ_D , and should be calculated case by case. Note that, in this sense, the shape of the two interacting bodies is bound to play a crucial role, in that it can modify considerably the distances between the facing surfaces and consequently the effective interaction area.

5. Summary and conclusion

In this paper we derived, within the genuine framework of the Poisson-Boltzmann approximation, the main quantities of interest for the interaction between two charged surfaces in solution.

Interestingly, such a rigorous derivation brings up an extended formula for the interplate pressure, formally differing from the usual expression (giving the sum of electrostatic and osmotic contributions) by an extra-term. While in the considered case of fixed charges boundary conditions, this additional term vanishes and we recover the standard expression for the pressure, the question arises whether it leads to a modified result when different boundary conditions are considered. We stressed that the Poisson-Boltzmann free energy is properly used as the reference thermodynamic potential *only* at fixed charges. To show how the choice of the thermodynamic potential depends on the boundary conditions, we explicitly solved the problem in the fixed potential case, and show how to recover the physical meaningful pressure in that case. These precisions on the interplay between boundary conditions and thermodynamic ensemble have been obtained here thanks to a detailed and deductive derivation from the very basis of the Poisson-Boltzmann approach. Let us stress once again that shortcutting the details of the mathematical derivation potentially leads to underappreciate the role of the boundary conditions.

We then explicitly solved the problem in the simple case of a 1:1 salt solution and observed a very rich behavior as a function of the ratio of the plates charge densities and of the salt concentration, with a non trivial equilibrium position arising in large intervals of these parameters. The distance at which the osmotic and electrostatic pressures are in equilibrium is finely tuned by the system parameters. Such equilibrium position can stabilize two asymmetrically charged bodies at a nonzero distance, provided that the corresponding free energy gain is large enough compared to the thermal noise. At a given temperature, the stability of the complex can therefore be assessed only by explicitly calculating the depth of the corresponding energy well. We obtained a readily available answer to this problem by deriving analytic expressions for the position and depth of the energy well, by a reactualized version of the overlooked derivation of Ohshima [24].

In order to compare the energy values with the thermal energy, an estimation of the interaction area is also necessary. As an example, we gave an estimation for the typical case of spherical colloids, and found that the interaction energy well is typically of the order of several $k_B T$, this leading to a quite deep minimum. This estimation is only a rough approximation because, for a given problem either in biological or colloidal systems, the behavior of the two interacting bodies is strongly dependent not only on salt conditions and on the bodies charge but also on their shape. Indeed, the shape could affect sensibly the extent of the interacting areas and the ion confinement, with relevant consequences on the interaction profile, as we recently discussed in the framework of DNA-protein interaction [34]. Interestingly, shape effects become also extremely important in the rapidly growing field of nanoparticles and colloidal building blocks synthesis [35]. More generally, the results presented herein could be of interest for the theoretical modeling of ionic colloidal crystals of oppositely charged particles recently obtained experimentally [36–38]. The formation of structures with packing density significantly lower than for close packing, and the large diversity of structures observed, should indeed strongly depend on the specific interaction potential between the colloidal particles. While these first studies have been based on simplified interaction models (linear PB with no osmotic pressure [36], pure Coulomb interaction [37]), the implementation of the more accurate interaction energy profile as described in our work

1 should substantially improve the description of such complex colloidal systems and
2 the prediction of the observed lattice structures.
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APPENDICES

A. Determination of the minimum position.

Starting from Equation (13) and taking into account the contribution of the surrounding ions as in Equation (22), one can obtain a suitable form for the *excess free energy* that will allow one to evaluate its amplitude at a given position x . We start by writing the excess free energy as

$$\begin{aligned} \beta\mathcal{F}_{PB}[\sigma, \{\bar{n}\}] &= \int_0^L \left[\frac{1}{8\pi\ell_B} \left(\frac{d\bar{\psi}}{dx} \right)^2 - \sum_{\alpha=1}^2 \bar{n}_\alpha(x) \right] dx \\ &+ 2n_b L + \sum_{\alpha=1}^2 \int_0^L \bar{n}_\alpha [-z_\alpha \bar{\psi}(x)] dx \end{aligned} \quad (\text{A1})$$

where the $2n_b L$ term arises from the Π_∞ contribution. Now, using (12) and (10) one finds:

$$\begin{aligned} \beta\mathcal{F}_{PB}[\sigma\{\bar{n}\}] &= 2n_b \left\{ \left(\frac{1}{2}C' + 1 \right) L + \int_0^L \bar{\psi}(x) \sinh \bar{\psi}(x) dx \right\} \\ &= 2n_b \left\{ \left(\frac{1}{2}C' + 1 \right) L + \lambda_D^2 \left[\bar{\psi}(x) \frac{d\bar{\psi}}{dx} \right]_0^L \right. \\ &\quad \left. - \lambda_D^2 \int_0^L \left(\frac{d\bar{\psi}}{dx} \right)^2 dx \right\} \end{aligned} \quad (\text{A2})$$

where we have introduced the Debye length, $\lambda_D = 1/\sqrt{8\pi\ell_B n_b}$, $C' = C/(4\pi\ell_B n_b)$ and we performed an integration by part for the last equation.

In order to calculate L_{min} , it is convenient to introduce the following adimensional parameters:

$$\eta = x/\lambda_D \quad (\text{A3})$$

$$\gamma(\eta) = \bar{\psi}(x) \quad (\text{A4})$$

$$\theta(\eta) = \frac{d\gamma}{d\eta}. \quad (\text{A5})$$

In terms of these variables, the Poisson-Boltzmann equation just writes

$$\frac{d\theta}{d\eta} = \sinh \gamma \quad (\text{A6})$$

with the boundary conditions

$$\begin{aligned} \theta(0) &= -\sigma'_0 = -4\pi\ell_B \lambda_D \sigma_0 \\ \theta(\eta_L) &= \sigma'_L = 4\pi\ell_B \lambda_D \sigma_L \end{aligned} \quad (\text{A7})$$

and the equivalent of Equation (12), giving the constant of motion for the system,

reads $\theta^2 = 2 \cosh \gamma + C'$. From this equation one gets

$$\begin{aligned} \frac{(\theta^2 - C')^2}{4} &= \cosh^2 \gamma = 1 + \sinh^2 \gamma \\ \frac{(\theta^2 - C')^2}{4} - 1 &= \left(\frac{d\theta}{d\eta} \right)^2 \\ \Rightarrow \left| \frac{d\eta}{d\theta} \right| &= \frac{1}{\sqrt{(\theta^2 - C')^2/4 - 1}} \end{aligned} \quad (\text{A8})$$

By integrating η from 0 to η_L , with $|d\eta| = d\eta$, we thus obtain

$$\int_{\theta(0)}^{\theta(\eta_L)} \left| \frac{d\eta}{d\theta} \right| d\theta = \int_0^{\eta_L} d\eta \frac{d\theta}{|d\theta|}.$$

We are interested here in the case of oppositely charged plates, where the energy minimum does exist. We have therefore to consider different cases. Let assume for the moment that $|\sigma'_0| > |\sigma'_L|$. If now $\sigma'_0 < 0$ and $\sigma'_L > 0$, then $\theta(0)$ and $\theta(\eta_L)$ have both positive values and $|d\theta| = -d\theta$. We then have

$$\eta_L = \int_{|\sigma'_L|}^{|\sigma'_0|} \left| \frac{d\eta}{d\theta} \right| d\theta \quad \sigma'_0 < 0, \quad \sigma'_L > 0. \quad (\text{A9})$$

On the other hand, if $\sigma'_0 > 0$ and $\sigma'_L < 0$, then $\theta(0)$ and $\theta(\eta_L)$ have both negative values and $|d\theta| = d\theta$. We thus obtain

$$\eta_L = - \int_{-|\sigma'_L|}^{-|\sigma'_0|} \left| \frac{d\eta}{d\theta} \right| d\theta \quad \sigma'_0 > 0, \quad \sigma'_L < 0. \quad (\text{A10})$$

Nevertheless, since $|d\eta/d\theta|$ is only a function of θ^2 we can make the change of variable $\Theta = -\theta$ in Eq.(A10) and retrieve the result (A9). Therefore, we always have

$$\eta_L = \int_{|\sigma'_L|}^{|\sigma'_0|} \frac{2}{\sqrt{(\theta^2 - C' + 2)(\theta^2 - C' - 2)}} d\theta \quad (\text{A11})$$

If now $L = L_{min}$, then $P = 0$, i.e. $\Pi = \Pi_\infty = 2k_B T n_b$, and therefore $C' = -2$. At the equilibrium position, Eq.(A11) becomes then

$$\eta_{L_{min}} = \int_{|\sigma'_L|}^{|\sigma'_0|} \frac{2}{\theta \sqrt{\theta^2 + 4}} d\theta = \int_{|\sigma'_L|/2}^{|\sigma'_0|/2} \frac{1}{\alpha \sqrt{\alpha^2 + 1}} d\theta$$

where we introduced $\alpha = \theta/2$. As a primitive function of $1/(x\sqrt{x^2+1})$ is $\ln(x/(1+\sqrt{x^2+1}))$, we get for the case $|\sigma'_0| > |\sigma'_L|$

$$\eta_{L_{min}} = \ln \left(\frac{|\sigma'_0|(2 + \sqrt{|\sigma'_L|^2 + 4})}{|\sigma'_L|(2 + \sqrt{|\sigma'_0|^2 + 4})} \right). \quad (\text{A12})$$

The extension to the opposite case of $|\sigma'_0| < |\sigma'_L|$ is straightforward, this leading to the following final formula for the position of the energy minimum $L_{min} =$

$\lambda_D \eta_{L_{min}}$:

$$L_{min} = \lambda_D \left| \ln \left(\frac{|\sigma'_0|(2 + \sqrt{\sigma'_L{}^2 + 4})}{|\sigma'_L|(2 + \sqrt{\sigma'_0{}^2 + 4})} \right) \right|.$$

B. Determination of the energy value at the minimum.

Following the main lines of the calculation presented in [24], we here look for an analytic expression for the energy at the minimum. In our framework, the interaction energy computed numerically directly from the integration of the excess pressure writes formally (by definition of the integration):

$$\beta E(L) = \beta(\mathcal{F}(L) - \mathcal{F}(\infty)) \quad (\text{B1})$$

where $\mathcal{F}(L)$ is given by (A2). By using the dimensionless parameters defined in the previous section, we have

$$\beta \mathcal{F} = \{(K(L) + J(L) - I(L))\} 2n_b \lambda_D, \quad (\text{B2})$$

with

$$K(L) = \left(\frac{1}{2}C' + 1\right)\eta_L,$$

$$J(L) = \left[\gamma(\eta)\theta(\eta)\right]_0^{\eta_L},$$

$$I(L) = \int_0^{\eta_L} \theta^2 d\eta.$$

We will now, first, calculate the three contributions to $\mathcal{F}(L_{min})$, and then the corresponding contributions to $\mathcal{F}(\infty)$.

Let start by calculating $I(L_{min})$. From the definition, we have

$$\begin{aligned} I(L_{min}) &= \int_0^{\eta_{L_{min}}} \theta^2 \left(\frac{d\eta}{d\theta}\right) d\theta = - \int_{|\sigma'_0|}^{|\sigma'_L|} \theta^2 \left|\frac{d\eta}{d\theta}\right| d\theta \\ &= \int_{|\sigma'_L|}^{|\sigma'_0|} \frac{2\theta}{\theta^2 + 4} d\theta \\ &= 2(\sqrt{|\sigma'_0|^2 + 4} - \sqrt{|\sigma'_L|^2 + 4}) \end{aligned} \quad (\text{B3})$$

where we used the fact that, on the $[0, \eta_L]$ range, $d\eta/d\theta = -|d\eta/d\theta|$.

To calculate $J(L_{min})$ we recall that when $L = L_{min}$ we have $\cosh \gamma(0) = \sigma'_0{}^2/2 + 1$. By using the relation $(\cosh x - 1)/2 = \sinh^2(x/2)$, we then get $\sinh^2 \gamma(0)/2 = \sigma'_0{}^2/4$, and thus

$$\left|\sinh \frac{\gamma(0)}{2}\right| = \frac{1}{2}|\sigma'_0| \quad (\text{B4})$$

In the same way we have

$$\left| \sinh \frac{\gamma(\eta_{L_{min}})}{2} \right| = \frac{1}{2} |\sigma'_L|. \quad (\text{B5})$$

We can now easily calculate $J(L_{min})$ starting from

$$\begin{aligned} J(L_{min}) &= \gamma(\eta_{L_{min}}) \theta(\eta_{L_{min}}) - \gamma(0) \theta(0) \\ &= \gamma(\eta_{L_{min}}) |\sigma'_L| + \gamma(0) \sigma'_0. \end{aligned}$$

Now, at L_{min} , $\gamma(\eta_{L_{min}})$ and $\gamma(0)$ have the same sign, which is governed by the most charged plate. Let again focus on the case where $\sigma'_0 < 0$ and $|\sigma'_0| > |\sigma'_L|$, as used in our illustrations. In this case, the sign of $\gamma(\eta_{L_{min}})$ and $\gamma(0)$ is the same as the sign of σ'_0 (cf. Figure 4), this leading to

$$J(L_{min}) = -2 |\sigma'_L| \operatorname{arcsinh} \left| \frac{\sigma'_L}{2} \right| - 2 |\sigma'_0| \operatorname{arcsinh} \left| \frac{\sigma'_0}{2} \right| \quad (\text{B6})$$

We easily obtain that $K(L_{min}) = 0$ since $C' = -2$ for $L = L_{min}$.

The overall result for $\mathcal{F}(L_{min})$ reads therefore

$$\begin{aligned} \beta \mathcal{F}(L_{min}) &= 4n_b \lambda_D \left\{ -|\sigma'_L| \operatorname{arcsinh} \left| \frac{\sigma'_L}{2} \right| \right. \\ &\quad \left. - |\sigma'_0| \operatorname{arcsinh} \left| \frac{\sigma'_0}{2} \right| - (\sqrt{|\sigma'_0|^2 + 4} - \sqrt{|\sigma'_L|^2 + 4}) \right\}. \end{aligned} \quad (\text{B7})$$

Let now calculate $\mathcal{F}(\infty)$. We have to be quite cautious to compute $I(\infty)$. Indeed, we have

$$I(\infty) = \lim_{\eta_L \rightarrow \infty} \int_0^{\eta_L} \theta^2 \left(\frac{d\eta}{d\theta} d\theta \right),$$

and the point is that $d\eta/d\theta$ has not the same sign all over the range $[0, \infty[$. Actually because of the infinite distance between the two plates, each plate tends to behave as a single plate in this limit, and thus there exists a distance for which $\theta = 0$. So, θ will be initially equal to $|\sigma'_0|$, then decrease to zero and increase again to $|\sigma'_L|$. We have therefore:

$$\begin{aligned} I(\infty) &= - \int_{|\sigma'_0|}^0 \theta^2 \left| \frac{d\eta}{d\theta} \right| d\theta + \int_0^{|\sigma'_L|} \theta^2 \left| \frac{d\eta}{d\theta} \right| d\theta \\ &= - \left[2\sqrt{\theta^2 + 4} \right]_{|\sigma'_0|}^0 + \left[2\sqrt{\theta^2 + 4} \right]_0^{|\sigma'_L|} \\ &= -8 + 2\sqrt{|\sigma'_0|^2 + 4} + 2\sqrt{|\sigma'_L|^2 + 4}. \end{aligned} \quad (\text{B8})$$

Besides, we have for $J(\infty)$:

$$\begin{aligned} J(\infty) &= \gamma(\infty) |\sigma'_L| - \gamma(0) |\sigma'_0| \\ &= 2 |\sigma'_L| \operatorname{arcsinh} \left| \frac{\sigma'_L}{2} \right| - 2 |\sigma'_0| \operatorname{arcsinh} \left| \frac{\sigma'_0}{2} \right| \end{aligned} \quad (\text{B9})$$

1 because it's only the reduced potential γ corresponding to the plate with the lowest
 2 charge (in absolute value) that changes its sign between L_{min} and L_{∞} (cf. again
 3 Figure 4).

4 When there is an infinite distance between the plates we also have $C' = -2$
 5 (intuitively because there is no more interaction between the plates) and thus
 6 $K(\infty) = 0$. We then have:

$$7 \quad \beta\mathcal{F}(\infty) = 4n_b\lambda_D \left\{ |\sigma'_L| \operatorname{arcsinh} \left| \frac{\sigma'_L}{2} \right| \right. \\
 8 \quad \left. - |\sigma'_0| \operatorname{arcsinh} \left| \frac{\sigma'_0}{2} \right| - (-4 + \sqrt{|\sigma'_0|^2 + 4} + \sqrt{|\sigma'_L|^2 + 4}) \right\}. \quad (\text{B10})$$

9 From the evaluation of Equation (B1) at $L = L_{min}$, we get then finally the
 10 following expression for the energy at the minimum in the case when $\sigma'_0 < 0$ and
 11 $|\sigma'_0| > |\sigma'_L|$:

$$12 \quad \beta E_{min} = 8n_b\lambda_D \left\{ \sqrt{|\sigma'_L|^2 + 4} - 2 - |\sigma'_L| \operatorname{arcsinh} \left| \frac{\sigma'_L}{2} \right| \right\}. \quad (\text{B11})$$

13 On the other hand, one can easily be convinced that inverting the roles of $|\sigma'_0|$
 14 and $|\sigma'_L|$ leads to the same expression as Equation (B11) where $|\sigma'_0|$ and $|\sigma'_L|$ are
 15 inverted. Therefore, the very general result writes (Equation (29))

$$16 \quad \beta E_{min} = 8n_b\lambda_D \left\{ \sqrt{|\sigma'_m|^2 + 4} - 2 - |\sigma'_m| \operatorname{arcsinh} \left| \frac{\sigma'_m}{2} \right| \right\}, \quad (\text{B12})$$

17 where σ'_m is related to the *smallest* plate charge density, i.e. $|\sigma'_m| = \min(|\sigma'_0|, |\sigma'_L|)$.

References

- [1] Kung W. and Lau A. W. C. *Charged plates beyond mean field: One loop corrections by salt density Fluctuations* cond-mat/0603191 preprint (2006)
- [2] Borukhov I., Andelman D. and Orland H. *Steric Effects in Electrolytes: A Modified Poisson-Boltzmann Equation* Phys. Rev. Lett. **79** 435 (1997)
- [3] Borukhov I., Andelman D. and Orland H. *Adsorption of Large Ions from an Electrolyte Solution: A Modified Poisson-Boltzmann Equation* Electrochimica Acta **46** 221 (2000)
- [4] Netz R. R. and Orland H. *Beyond Poisson Boltzmann: Fluctuations effects and correlation functions* Eur. Phys. J. E, **1**, 203-214 (2000)
- [5] Deserno M. et al. *Cell model and Poisson Boltzmann theory: a brief introduction* in Proceedings of the NATO Advanced Study Institute on Electrostatic Effects in Soft Matter and Biophysics, edited by C. Holm, P. Kélicheff and R. Podgornik (Kluwer, Dordrecht, 2001)
- [6] Tang, C., Iwahara, J. and Clore, G. M. *Visualization of transient encounter complexes in protein protein association* Nature **444** 383-386 (2006)
- [7] von Hippel, H. *Diffusion driven mechanism of protein translocation on nucleic acids. III. The E. coli lac repressor-operator interaction: kinetic measurements and conclusions* Biochemistry **20** 6961-6977 (2007)
- [8] Sens P. and Joanny J.-F. *Counterion Release and Electrostatic Adsorption* Phys. Rev. Lett. **84** 4862-4865 (2000)
- [9] Parsegian V. and Gingell D. *On the electrostatic interaction across a salt solution between two bodies bearing unequal charges* Biophys. J. **12** 1192-1204 (1972)
- [10] Verwey E. J. W. and Overbeek J. TH. G. *Theory of the stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948)
- [11] Bhattacharjee S., Elimelech M. and Borkovec M. *DLVO Interaction between Colloidal Particles: Beyond Derjaguin's Approximation* CROATICA CHEMICA ACTA CCACAA **71** 883-903 (1998)
- [12] Bhattacharjee S. and Elimelech M. *Surface Element Integration: A novel Technique for Evaluation of DLVO Interaction between a particle and a flat plate* Journ. Coll. and Inter. Sci. **193**, 273-285 (1997)
- [13] Tamashiro M. N. and Schiessel H. *Where the linearized Poisson-Boltzmann cell model fails: the planar case as a prototype study* Phys. Rev. E, **68**, 066106 (2003)
- [14] Zypman F. R. *Exact expressions for colloidal plane-particle interaction forces and energies with applications to atomic force microscopy* J. Phys. Condens. Matter **18** 2795-2803 (2006)
- [15] Lau A. W.-C. *Fluctuation and correlations effects in electrostatics of Highly-Charged Surfaces* PhD Thesis (Oct. 2000)
- [16] Hansen J.-P. and McDonald I. R. *Theory of Simple Liquids* (Academic Press, London, Third Edition, 2006)
- [17] Denton A. R. *Electroneutrality and phase behavior of colloidal suspensions* Phys. Rev. E **76** 051401 (2007)
- [18] Zoetekouw B. and van Roij R. *Volume terms for charged colloids: a grand-canonical treatment* Phys. Rev. E **73** 021403 (2006)
- [19] Carnie S. L. and Torrie G. M. *The Statistical Mechanics of the Electrical Double Layer* Adv. Chem. Phys. **56** 141 (1984)
- [20] Marcus R. A. *Calculation of Thermodynamic Properties of Polyelectrolytes* J. Chem. Phys. **23** 1057 (1955)
- [21] Wennerström H., Jönsson B. and Linse P. *The cell model for polyelectrolyte systems* J. Chem. Phys. **76** 4665 (1982)
- [22] Lau A. and Pincus P. *Binding of oppositely charged membranes and membrane reorganization* Eur. Phys. J. B **10** 175 (1999)
- [23] Ben-Yaakov D., Burak Y., Andelman D. and Safran S. A. *Electrostatic interactions of asymmetrically charged membranes* Europhys. Lett., **79** 48002 (2007)
- [24] Ohshima H. *Diffuse double layer interaction between two parallel plates with constant surface charge density in an electrolyte solution III: Potential energy of double layer interaction* Colloid and Polymer Sci. **253** 150-157 (1975)
- [25] Ohshima H. *Diffuse double layer interaction between two parallel plates with constant surface charge density in an electrolyte solution II: the interaction between dissimilar plates* Colloid and Polymer Sci. **252** 257-267 (1974)
- [26] Torres A., van Roij R. and Téllez G. *Finite thickness and charge relaxation in double-layer interactions* Colloid Interface Sci. **301** 176-183 (2006)
- [27] Torres A. and van Roij R. *Finite-Thickness-Enhanced Attractions for Oppositely Charged Membranes and Colloidal Platelets* Langmuir **24** 1110-1119 (2008)
- [28] Huang K. *Statistical Mechanics* (Wiley, New-York, Second Edition, 1987)
- [29] Feynman R. P., Leighton R. B. and Sand M. *The Feynman Lectures on Physics, Volume 2* (Addison-Wesley, Pearson PLC, 2006)
- [30] Trizac E. *Electrostatically Swollen Lamellar Stacks and Adiabatic Pair Potential Charged Platelike Colloids in an Electrolyte* Langmuir **17** 4793-4798 (2001)
- [31] Bohinc K., Iglic, A. and May S. *Interaction between macroions mediated by divalent rod-like ions* Europhys. Lett. **68** 494-500 (2004)
- [32] Derjaguin B. V. *Untersuchungen über die Reibung und Adhusion* Kolloid-Z. **69** 155 (1934)
- [33] White L. R. *On the Deryaguin approximation for the interaction of macrobodies* J. Colloid Interface Sci. **95** 286 (1983)
- [34] Dahirel et al. *Non-specific DNA-protein interaction: Why proteins can diffuse along DNA* arXiv:0902.2708v1 (2009)
- [35] Glozer S. C. and Solomon M. J. *Anisotropy of building blocks and their assembly into complex structures* Nature Materials **6** 557-562 (2007)
- [36] Leunissen M. E. et al *Ionic colloidal crystals of oppositely charged particles* Nature **437** 235-240 (2005)

- 1 [37] Bartlett P. and Campbell A. I. *Three dimensional binary superlattices of oppositely charged colloids*
2 Phys. Rev. Lett. **95** 128302 (2005)
3 [38] Shevchenko E. V. et al *Structural diversity in binary nanoparticle superlattices* Nature **439** 55-59
4 (2006)
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Figure caption

FIG. 1: A schematic view of the system considered throughout the paper. The two semi-infinite planes of charge density σ_0 and σ_L , positioned respectively at $x = 0$ and $x = L$, are immersed in the ionic solution. An ion reservoir freely exchanges ions with the system.

FIG. 2: Comparison between the estimation for the position of the energy minimum of Equation (23) (solid lines) and the values of L_{min} obtained on the basis of the direct resolution of the Poisson-Boltzmann model (points). We chose $\sigma_0 = -0.05 e/nm^2$. Lengths are given in nm, and as functions of the ratio $r = \sigma_L/\sigma_0$, for different salt concentrations: 0.001 M (asterisks), 0.01 M (circles), 0.1 M (squares), 1 M (diamonds).

FIG. 3: Positive (solid line) and negative (dashed line) ion distributions in the inter-plate space, at the equilibrium distance $L = L_{min}$, for the case of two charged plates with charge densities $\sigma_0 = -0.05 e/nm^2$ and $\sigma_L = 0.1 e/nm^2$, and for two different salt concentrations n_b : 0.001 M (low salt, **a**) and 1 M (high salt, **b**). The thick grey line indicates the value of the bulk ion concentration n_b .

FIG. 4: The adimensional mean field potential at $x = 0$, $\bar{\psi}(0)$, as a function of the inter-plate distance L (nm) and for the same ionic strength and charge density ratios of Figure 5. The two horizontal lines correspond to the two roots $\pm \operatorname{arccosh}(\pi \ell_B \sigma_0^2 / n_b + 1)$ of the left plate equilibrium condition, Equation (27). The circles emphasize the non trivial solutions leading to an equilibrium position.

FIG. 5: The interaction energy per unit surface E ($k_B T/100 \text{ nm}^2$) for the interaction of a plate of charge density $\sigma_0 = -0.05 e/nm^2$ at $x = 0$ with different plates of charge densities σ_L , as a function of the distance L (nm) between them. The ratio $r = \sigma_L/\sigma_0$ between the densities varies from -2 to 1 according to the figure legend. The plates are immersed in a 0.1 M monovalent solution.

FIG. 6: Comparison between the estimation of the energy minimum of Equation (29) (solid lines) and the values of the energy at the minimum position L_{min} obtained by direct integration of the Poisson-Boltzmann model, for different salt concentrations: 0.001 M (asterisks), 0.01 M (circles), 0.1 M (squares), 1 M (diamonds). We have used again $\sigma_0 = -0.05 e/nm^2$. In order to use more natural units, energies are given in units of $k_B T/100 \text{ nm}^2$.

FIG. 7: Sketch for the calculation of the interacting area for the case of two identical spheres. The area of each dashed spherical surface is $S = \frac{\pi}{4}(d^2 + 4h^2)$.

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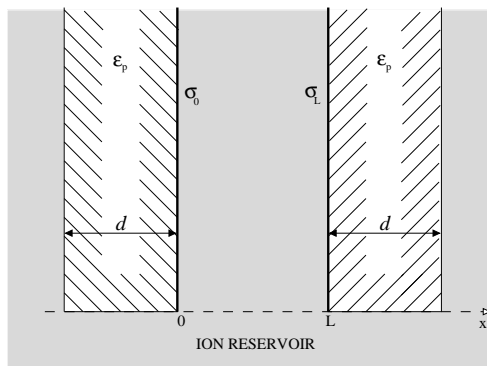


Figure 1. F. Paillusson et al

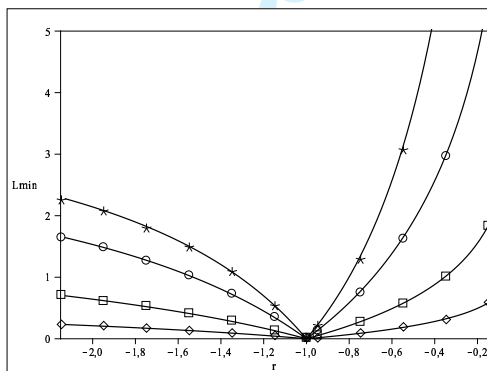


Figure 2. F. Paillusson et al

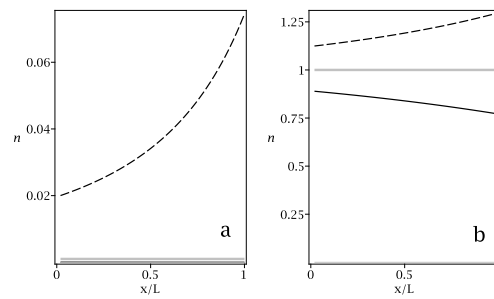


Figure 3. F. Paillusson et al

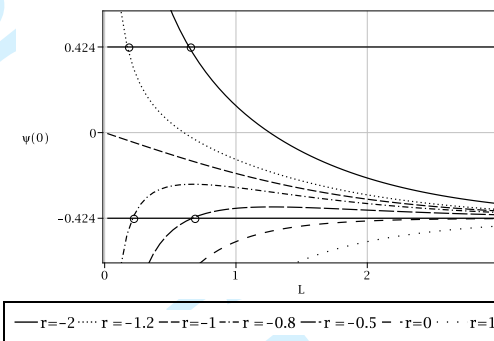


Figure 4. F. Paillusson et al

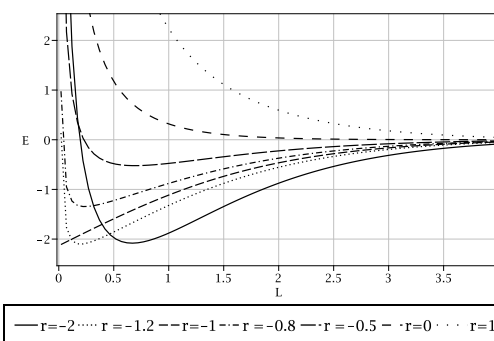


Figure 5. F. Paillusson et al

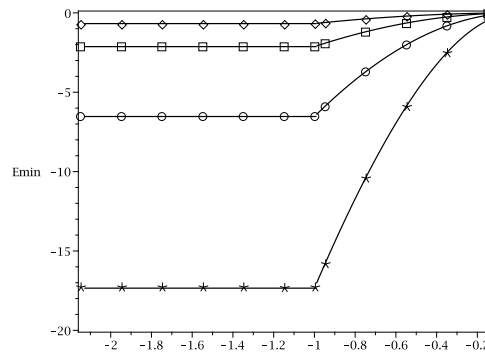


Figure 6. F. Paillusson et al

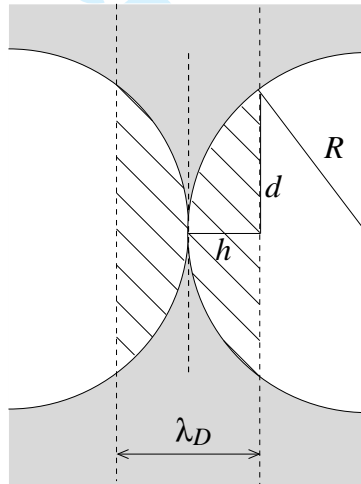


Figure 7. F. Paillusson et al

NEW APPENDIX

We propose to the Editor and the referees this new appendix to our paper *Poisson-Boltzmann for oppositely charged bodies: an explicit derivation*. We let them judge on the opportunity of adding it to our manuscript.

A. DETERMINATION OF THE POISSON BOLTZMANN FREE ENERGY.

Gibbs-Bogoliubov inequality

Consider a physical system in contact with a thermostat at temperature T . One can thus work in the canonical ensemble, where the probability \mathcal{P}_λ for the system to be in a microscopic state λ at energy H_λ is given by the Boltzmann law: $\mathcal{P}_\lambda \equiv Z^{-1} e^{-\beta H_\lambda}$ where $\beta \equiv (k_B T)^{-1}$ and the partition function Z defined as usual:

$$Z \equiv \sum_{\{\lambda\}} e^{-\beta H_\lambda}. \quad (A1)$$

Note that the previous general definition of Z should be rewritten, in the case of a continuous energy as an integral over the system conjugate variables. Nevertheless, we will use here the notation of Eq. (A1) for the sake of simplicity.

By introducing a yet unspecified distribution of probability for the microscopic states, $\mathcal{P}_0(\lambda)$, we can write:

$$Z = \sum_{\{\lambda\}} e^{-\beta H_\lambda} \mathcal{P}_0(\lambda) e^{-\ln \mathcal{P}_0(\lambda)} = \langle e^{-\beta H - \ln \mathcal{P}_0(\lambda)} \rangle_0 \quad (A2)$$

where $\langle \dots \rangle_0$ indicates a statistical averaging over the distribution \mathcal{P}_0 .

Using the definition of the free energy given in the main text, we get the following expression for the free energy:

$$F = -k_B T \ln \left(\langle e^{-\beta H - \ln \mathcal{P}_0(\lambda)} \rangle_0 \right). \quad (A3)$$

By using the well known relation $\langle \ln X \rangle \leq \ln \langle X \rangle$ (valid for any random variable X) one obtains the inequality

$$F \leq -k_B T \langle \ln \{ e^{-\beta H - \ln \mathcal{P}_0(\lambda)} \} \rangle_0$$

which can be written finally

$$F \leq \langle H \rangle_0 - T S_0 \quad (A4)$$

where

$$S_0 \equiv -k_B \sum_{\{\lambda\}} \mathcal{P}_0(\lambda) \ln \mathcal{P}_0(\lambda) \quad (A5)$$

is the corresponding entropy term.

Eq.s (A4) and (A5) constitute the so called Gibbs-Bogoliubov inequality which is always valid in the canonical ensemble.

The potential term

In order to calculate the free energy contribution arising from the potential terms in the partition function we will make a mean field approximation by applying the Gibbs-Bogoliubov inequality (A4) to Z_{pot} . Let $\mathcal{P}_0(\lambda)$ be the corresponding position probability of independent particles satisfying the two relations:

$$\mathcal{P}_0(\{\mathbf{r}\}) \equiv P_0(\mathbf{r}_1) P_0(\mathbf{r}_2) \dots P_0(\mathbf{r}_N) \quad (A6)$$

$$\int d^3 r_i P_0(\mathbf{r}_i) = 1 \quad (A7)$$

$\forall i \in \{1, \dots, N\}$. The introduction of $\mathcal{P}_0(\{\mathbf{r}\})$ leads to a statistical averaged description of the charge distribution:

$$n_\alpha^0(\mathbf{r}) \equiv N_\alpha P_0(\mathbf{r}). \quad (A8)$$

Note that $n_\alpha^0(\mathbf{r})$ has to be distinguished from the actual ion density $n_\alpha(\mathbf{r})$ previously defined. More explicitly, one can write $n_\alpha(\mathbf{r}) = n_\alpha^0(\mathbf{r}) + \delta n_\alpha(\mathbf{r})$.

Let first calculate $\langle H_{pot} \rangle_0$. By using the defined H_{pot} and (A6) we obtain

$$\begin{aligned} \langle H_{pot} \rangle_0 &= \frac{1}{2} \sum_{\alpha=1}^p z_\alpha e \sum_{i=1}^{N_\alpha} \int \dots \int \phi(\mathbf{r}_i) \prod_{i=1}^N P_0(\mathbf{r}_i) d^3 r_i \\ &+ \frac{1}{2} \int e \sigma(\mathbf{r}) \phi(\mathbf{r}) d^3 r \end{aligned} \quad (A9)$$

where we used the fact that $\int e \sigma(\mathbf{r}) \phi(\mathbf{r}) d^3 r$ does not depend on $r_1 \dots r_N$. By using the normalization Eq. (A7) and introducing the ion distributions $n_\alpha^0(\mathbf{r})$, Eq. (A9) can be written as:

$$\langle H_{pot} \rangle_0 = \frac{1}{2} \int e \sigma(\mathbf{r}) \phi(\mathbf{r}) d^3 r + \frac{1}{2} \sum_{\alpha=1}^p z_\alpha e \int n_\alpha^0(\mathbf{r}) \phi(\mathbf{r}) d^3 r. \quad (A10)$$

To be coherent with the statistical approach just introduced, we have to functionally expand the electric potential as a functional of $n_\alpha(\mathbf{r})$. One gets:

$$\phi[n_\alpha] = \phi[n_\alpha^0] + \int \left. \frac{\delta \phi}{\delta n_\alpha(\mathbf{r}')} \right|_{n_\alpha^0} \delta n_\alpha(\mathbf{r}') d^3 r' + O((\delta n_\alpha)^2). \quad (A11)$$

In the following, we will note

$$\phi^0(\mathbf{r}) \equiv \phi[n_\alpha^0](\mathbf{r}) \quad (A12)$$

the mean field electric potential. Neglecting terms of order higher than zero in Eq. (A10), i.e. in the framework of the mean field approximation, we finally get an expression of the averaged potential term as a functional of $\phi^0(\mathbf{r})$:

$$\langle H_{pot} \rangle_0 = \frac{1}{2} \int e \sigma(\mathbf{r}) \phi^0(\mathbf{r}) d^3 r + \frac{1}{2} \sum_{\alpha=1}^p z_\alpha e \int n_\alpha^0(\mathbf{r}) \phi^0(\mathbf{r}) d^3 r \quad (A13)$$

The Poisson-Boltzmann free energy

Once having obtained $\langle H_{pot} \rangle_0$, we need to calculate the corresponding S_0 , the entropic contribution arising from the position degrees of freedom. The calculation is straightforward. Using equations (A6) and (A8), S_0 becomes

$$S_0 = -k_B \sum_{\alpha=1}^p \int n_\alpha^0(\mathbf{r}) \ln P_0(\mathbf{r}) d^3 r. \quad (A14)$$

We are now able to write $Z = Z_{kinetic} \cdot Z_{pot}$, hence the Gibbs free energy $F = -k_B T \ln Z_{pot} - k_B T \ln Z_{kin}$. The application of the Gibbs-Bogoliubov inequality then leads to $F \leq \langle H_{pot} \rangle_0 - T S_{pos}^0 - k_B \ln Z_{kin}$. By using Eq.s (A2), (A13) and (A14), we get from the previous inequality:

$$F \lesssim F_{PB}$$

Where F_{PB} is the *Poisson-Boltzmann functional free energy* that can be written as:

$$\begin{aligned} F_{PB}[\{n^0\}] &\equiv \frac{1}{2} \int \left(e \sigma(\mathbf{r}) \phi^0(\mathbf{r}) + \sum_{\alpha=1}^p z_\alpha e n_\alpha^0(\mathbf{r}) \phi^0(\mathbf{r}) \right) d^3 r \\ &+ k_B T \sum_{\alpha=1}^p \int n_\alpha^0(\mathbf{r}) \left(\ln (\Lambda_\alpha^3 n_\alpha^0(\mathbf{r})) - 1 \right) d^3 r \end{aligned}$$

where we used the Stirling approximation to approximate the kinetic term of Eq. (A2) and the normalization relation $N_\alpha \equiv \int n_\alpha^0(\mathbf{r}) d^3 r$.