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Revisiting the Poisson–Boltzmann theory: Charge surfaces, multivalent ions and inter-plate forces

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ABSTRACT

The Poisson–Boltzmann (PB) theory is extensively used to gain insight on charged colloids and biological systems as well as to elucidate fundamental properties of intermolecular forces. Many works have been devoted in the past to study PB-related features and to confirm them experimentally. In this work we explore the properties of inter-plate forces in terms of different boundary conditions. We treat the cases of constant surface charge, constant surface potential and mixed boundaries. The interplay between electrostatic interactions, attractive counter-ion release, and repulsive van 't Hoff contribution is discussed separately for each case. Finally, we discuss how the crossover between attractive and repulsive interactions for constant surface charge case is influenced by the presence of multivalent counter-ions, where it is shown that the range of the attractive interaction grows with the valency.

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1. Introduction

The first applications of Poisson–Boltzmann (PB) theory date back to the beginning of the 20th century, with the pioneering works of Gouy and Chapman [1,2], which dealt with the counter-ion cloud formed in the vicinity of charged plates. A decade later, Debye and Hückel [3] worked out a theory for electrolyte solutions, based on the linear PB theory. Since then, PB theory has been extensively used for many basic and applied purposes, such as the seminal DLVO theory [4,5] that explains the stability of colloidal suspensions.

Nowadays, PB theory is a benchmark tool for a variety of experimental and industrial applications [5,6], in which it is being used to interpret experimental data quantitatively. It is a vital ingredient in any attempt to explain intermolecular forces and interactions between charged macromolecules, particles and surfaces.

However, the theory has some drawbacks, which have been studied during the last decades. Some of the refinements are related to the mean-field limitations of the theory, which does not account correctly for correlations and fluctuations [7,8]. Other modifications take into account additional interactions, such as steric effects [9,10] and hydration interaction [11]. All these refinements are motivated by a number of cases where the PB theory fails to explain experimental observations. For example, the theory misses some important features when treating multivalent ions and highly charged objects.

Nevertheless, as the collection of problems that one can treat with the PB theory is very broad in its scope and range, we aim in the present work to further explore several PB-related cases. We focus on two main aspects. In Section 2, the force between two charged plates is discussed as function of boundary type. In Section 3, we extend the discussion to multivalent ions and discuss their effect on the crossover from attractive to repulsive pressure.

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2. PB equation

Consider a two-plate system occupying the space between two planar surfaces located at $y = 0$ and at $y = D$ (y is the coordinate perpendicular to the plates). The system is coupled to a bulk reservoir of salt concentration n_b , assumed here to be monovalent, $z = 1$. The PB equation, describing the electrostatic potential and the ionic distributions in between the plates, reads

$$\frac{d^2\psi}{dy^2} = \frac{8\pi en_b}{\varepsilon} \sinh\left(\frac{e\psi}{k_B T}\right), \quad (1)$$

where e is the electron charge, ε the solvent dielectric constant, k_B the Boltzmann constant, and T is the temperature. By defining a dimensionless potential $\phi \equiv e\psi/k_B T$, the PB equation is written in a dimensionless form:

$$\frac{d^2\phi}{dx^2} = \sinh\phi, \quad (2)$$

where $x = \kappa y$ is the dimensionless coordinate, rescaled by the inverse Debye screening length κ^{-1} , defined by $\kappa^2 = 8\pi e^2 n_b / \varepsilon k_B T$.

Next, the boundary conditions on the plates can be defined in a general manner. The boundary condition at $y = 0$ and $y = d$ are given by

$$f_0(\phi(0), \phi'(0)) = 0 \quad \text{and} \quad f_d(\phi(d), \phi'(d)) = 0, \quad (3)$$

where $d \equiv \kappa D$ is the dimensionless inter-plate spacing. The functions f_0 and f_d are chosen with respect to the surface properties. This choice determines the nature of the interaction between the plates as is elaborated below.

Using the solutions of the PB equation one can calculate global thermodynamic quantities that are accessible in experiments. In particular, it can be shown [12] that integrating once the PB equation gives the osmotic pressure, Π , in terms of the electrostatic potential and the electrostatic field, ϕ' :

$$\Pi = -\frac{1}{2} \left(\frac{d\phi}{dx}\right)^2 + \cosh\phi - 1. \quad (4)$$

Here the osmotic pressure is rescaled by $2k_B T n_b$, yielding the dimensionless osmotic pressure Π . Note that the pressure is homogeneous and has no dependence on the coordinate x . It is straightforward to calculate the free energy per unit area F (in dimensionless units):

$$F = -\int_{-\infty}^d dx \Pi(x). \quad (5)$$

Although not always accurate, it is instructive to solve the linear PB equation

$$\frac{d^2\phi}{dx^2} = \phi, \quad (6)$$

whose solution is given by $\phi = A \cosh x + B \sinh x$. The constants A and B are obtained by satisfying the boundary conditions

$$f_0(A, B) = 0, \quad (7)$$

$$f_d(A \cosh d + B \sinh d, A \sinh d + B \cosh d) = 0, \quad (8)$$

and are functions of the separation d . The osmotic pressure depends on these two constants:

$$\Pi = \frac{1}{2}A^2 - \frac{1}{2}B^2. \quad (9)$$

In the following we choose three different types of boundary, and discuss how these choices affect the nature of the interaction between the plates.

2.1. Two constant charge plates

In many physical setups, the surface charge density can be regarded to a very high accuracy as a constant. Therefore, many theoretical works have addressed this case in the past, solving it numerically [13–19] or analytically [20–24]. The functions f_0 and f_d are given by

$$f_0(\phi(0), \phi'(0)) = \phi'(0) + \sigma_0 \quad (10)$$

$$f_d(\phi(d), \phi'(d)) = \phi'(d) - \sigma_d, \quad (11)$$

where σ_0 and σ_d are the two rescaled (dimensionless) surface charge densities, $\sigma_0 \rightarrow 4\pi e\sigma_0/(\kappa\varepsilon k_B T)$ and $\sigma_d \rightarrow 4\pi e\sigma_d/(\kappa\varepsilon k_B T)$, respectively. Substituting them in Eqs. (7) and (8), we obtain $A = (\sigma_d + \sigma_0 \cosh d)/\sinh d$ and $B = -\sigma_0$. The pressure and the free energy, given by Eqs. (9) and (5), read

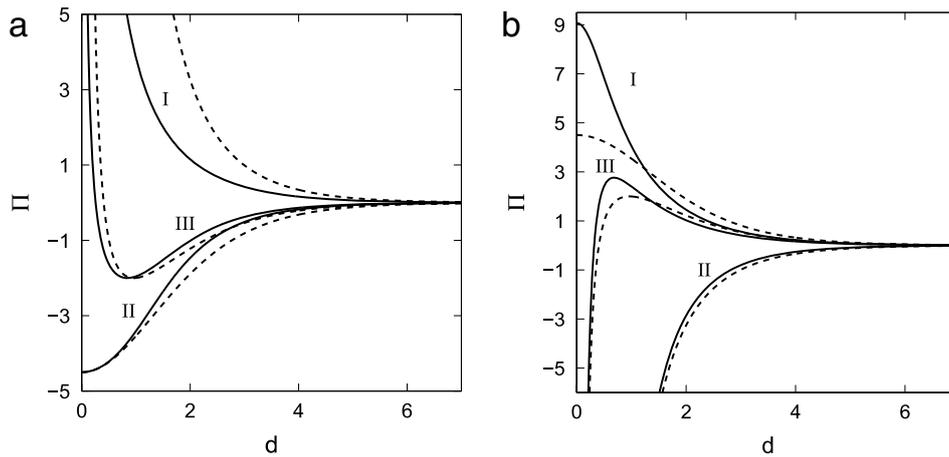


Fig. 1. Osmotic pressure Π as function of inter-plate separation, d . The solution to the linear (dashed) and non-linear (solid) PB equation are presented for constant surface charge case in (a) and constant surface potential in (b). Three profiles are shown for each case: I, II and III indicate the repulsive, attractive and a crossover profile, respectively. (a) The boundary conditions for profiles I, II and III are $\sigma_0 = \sigma_d = 3$, $\sigma_0 = -\sigma_d = 3$ and $\sigma_0 = -3\sigma_d/2 = 3$, respectively. (b) The boundary conditions for I, II and III are $\phi_0 = \phi_d = 3$, $\phi_0 = -\phi_d = 3$ and $\phi_0 = 3\phi_d/2 = 3$, respectively.

$$\Pi = \frac{2\sigma_0\sigma_d \cosh d + \sigma_0^2 + \sigma_d^2}{2 \sinh^2 d}, \tag{12}$$

$$F = \frac{2\sigma_0\sigma_d + (\sigma_0^2 + \sigma_d^2)e^{-d}}{2 \sinh d}. \tag{13}$$

no minus sign

For large separations ($d \gg 1$), the pressure decays exponentially $\Pi \simeq \sigma_0\sigma_d e^{-d}$, where the sign of the pressure is determined by the relative sign between σ_0 and σ_d [20]. For unlike charges ($\sigma_0 \cdot \sigma_d < 0$) the pressure is attractive ($\Pi > 0$), while like charges ($\sigma_0 \cdot \sigma_d > 0$) repel each other. For small separations there is no dependence on the sign of σ_0 and σ_d , and Π becomes purely repulsive: $\Pi = (\sigma_0 + \sigma_d)^2 / 2 \sinh^2 d > 0$, for entropic reasons (elaborated below). Thus, there is a crossover from attractive to repulsive pressure for unlike charges. There is one exception for this finding: when $\sigma_0 = -\sigma_d$, the pressure is purely attractive. For like charges, the pressure is monotonically positive, and the charges repel each other for all the separations.

The physical interpretation for this behavior is based on the interplay between two mechanisms as was previously discussed (e.g., see Ref. [24]). When the plates are brought closer, the neutralizing ionic clouds increasingly overlap. Since the ionic clouds have opposite signs, pairs of negative and positive counter-ions gain additional entropy by staying in the bulk instead of neutralizing the system, while the plates, in turn, neutralize each other. The closer the plates are, the larger is the ionic cloud overlap, and more counter-ions are released to the bulk, resulting in an attractive pressure. However, when the magnitude of the surface charges is dissimilar ($|\sigma_0| \neq |\sigma_d|$), a finite amount of counter-ions are forced to stay in between the plates to neutralize the excess of charge. The concentration of these neutralizing counter-ions grows when the separation is reduced, leading to a repulsive pressure (due to the van 't Hoff pressure of the counter-ions). For small separations ($d \rightarrow 0$), this repulsion diverges as $\Pi \sim 1/d$.

For the pure antisymmetric case, where $\sigma_0 = -\sigma_d$, only the counter-ion release mechanism is observed since no counter-ions are needed to neutralize the plates in small separations (there is no charge excess and the two plates completely neutralize each other). This is the origin of the pure attractive pressure in this case. On the other hand, when $\sigma_0 \cdot \sigma_d > 0$, only the repulsive pressure, caused by counter-ion neutralization, takes place since the clouds have similar signs, and there is no counter-ion release. We hence conclude that the crossover from attractive to repulsive pressure occurs only for unlike charges ($\sigma_0 \cdot \sigma_d < 0$) with asymmetric magnitudes, $|\sigma_0| \neq |\sigma_d|$.

In Fig. 1(a), three curves of pressure versus distance with constant surface charge boundaries are shown. In addition to the simple analytical results obtained for the linearized PB case, we solve the non-linear PB equation numerically. Both are presented in Fig. 1; the linear case as dashed lines and the non-linear case as solid lines. The comparison between the solid and dashed curves shows that the solution of the linear equation agrees qualitatively with the exact solution of the non-linear equation. The numerical deviations between the two are small for the chosen values of σ_0 and σ_d . However, for larger surface charges the deviations grow, and the linear solution is not sufficiently accurate anymore.

2.2. Two constant surface potentials

The functions f_0 and f_d are given here by

$$f_0(\phi(0), \phi'(0)) = \phi(0) - \phi_0 \tag{14}$$

$$f_d(\phi(d), \phi'(d)) = \phi(d) - \phi_d, \tag{15}$$

where ϕ_0 and ϕ_d are dimensionless surface potentials. Obtaining the constants A and B from these two relations, $A = \phi_0$ and $B = (\phi_d - \phi_0 \cosh d) / \sinh d$, leads to the dimensionless osmotic pressure Π and free energy F :

$$\Pi = \frac{2\phi_0\phi_d \cosh d - \phi_0^2 - \phi_d^2}{2 \sinh^2 d}, \quad (16)$$

$$F = \frac{2\phi_0\phi_d - (\phi_0^2 + \phi_d^2)e^{-d}}{2 \sinh d}. \quad (17)$$

These expressions are almost identical to the constant surface charge case (except for the sign), and indeed, for large separations the relative sign of ϕ_0 and ϕ_d determines the pressure: $\Pi \simeq \phi_0\phi_d e^{-d}$, similarly to the large separation behavior of the constant charge case. However, for small separations, the pressure is different: $\Pi \simeq -(\phi_0 - \phi_d)^2 / 2 \sinh^2 d$, yielding a pure attractive pressure, except for $\phi_0 = \phi_d$. Unlike the constant charge case, in the constant potential case the counter-ion concentration remains constant near each plate, but the effective surface charge diverges when the plates are brought closer together. This results in a diverging electrostatic attraction that governs the pressure for small d .

Another remark about the constant potential case is that the crossover from repulsive to attractive pressure prevails only for like potentials ($\phi_0 \cdot \phi_d > 0$). For unlike potentials ($\phi_0 \cdot \phi_d < 0$) the pressure is purely attractive, while for the special symmetric case, $\phi_0 = \phi_d$, the pressure is purely repulsive.

In Fig. 1(b), we show three curves of pressure versus distance for three different surface potential values (attractive, repulsive and crossover). Note that the attractive profile diverges, while the repulsive one saturates and is different than the constant surface charge case, where the repulsive one diverges and the attractive one saturates. This is due to the different constraints that the boundaries apply on the ionic solution. Also note that the deviations of the exact non-linear PB solution from the linearized one are large for small inter-plate separations, due to the large overlap between the two induced counter-ion clouds.

2.3. The mixed case

The third case is a mixed boundary condition, where the plate at $y = 0$ has a constant potential while the one at $y = D$ has a constant charge. The functions f_0 and f_d are given by $f_0(\phi(0), \phi'(0)) = \phi(0) - \phi_0$ and $f_d(\phi(d), \phi'(d)) = \phi'(d) - \sigma_d$. Substituting the solution for ϕ in these two relations, the constants A and B are obtained: $A = \phi_0$ and $B = (\sigma_d - \phi_0 \sinh d) / \cosh d$. The pressure Π and the free energy F are given by

$$\Pi = \frac{2\phi_0\sigma_d \sinh d + \phi_0^2 - \sigma_d^2}{2 \cosh^2 d}, \quad (18)$$

$$F = \frac{2\phi_0\sigma_d + (\phi_0^2 - \sigma_d^2)e^{-d}}{2 \cosh d}. \quad (19)$$

For large separation the pressure behaves as $\Pi \simeq \phi_0\sigma_d e^{-d}$, similarly to the previous two cases where the nature of the pressure is determined by the relative sign ($\phi_0 \cdot \sigma_d$). The similarity between the three cases for large d is due to the decoupling between the plates, effectively leading to two isolated planes with no mutual effect on their surface potential or charge. On the other hand, examining the small separation limit, we obtain $\Pi \simeq (\phi_0^2 - \sigma_d^2) / 2 \cosh^2 d$ where the sign of the pressure depends on the magnitudes of ϕ_0 and σ_d , unlike the former cases. When $|\sigma_d| > |\phi_0|$, the pressure is attractive, while in the opposite case, $|\sigma_d| < |\phi_0|$, the plates repel each other. The competition between the counter-ion release, the charge neutralization, and constant ion density at the constant potential surface leads to this versatile behavior. Moreover, in contrast to the former cases, there is no divergence here at small separations, and the pressure saturates as $d \rightarrow 0$. Note the special case where $|\sigma_d| = |\phi_0|$ that leads to vanishing of the pressure as $d \rightarrow 0$.

In this section we have demonstrated how versatile the electrostatic pressure between two plates can be in the framework of the PB theory. We note that the three cases treated here have the simplest boundary conditions one can consider. In physical realizations, one should often take also into account the charge regulation mechanisms [25], where the surface properties are determined by additional surface parameters such as the ionic dissociation degree. In these cases the functions f_0 and f_d have a more complex form, that describes the relation between ϕ and ϕ' at $x = 0$ or $x = d$ due to surface activity.

3. Attraction to repulsion crossover with multivalent salts

We consider a two-plate system with unlike charges, $\sigma_0 < 0$ and $\sigma_d > 0$, in the presence of an ionic solution with multivalent salt. First we treat the case of a symmetric salt ($z:z$) and then consider mixtures of two salts: a symmetric monovalent salt (1:1) combined with an asymmetric multivalent salt (1: z).

3.1. Multivalent symmetric salt ($z : z$)

In this case the dimensionless PB equation of Eq. (2) is generalized and reads

$$\frac{d^2\phi}{dx^2} = z \sinh(z\phi) \tag{20}$$

where z is the ionic valency. The boundary conditions at $x = 0$ and d are given by

$$f_0(\phi(0), \phi'(0)) = \phi'(0) + \sigma_0 \quad \text{and} \quad f_d(\phi(d), \phi'(d)) = \phi'(d) - \sigma_d. \tag{21}$$

In this form the equation is almost identical to the monovalent salt case Eq. (2). Therefore, the attraction to repulsion condition of the monovalent case (as was discussed in Ref. [24]) can be used:

$$\Pi = \begin{cases} < 0 & e^{-\sqrt{z}d} < \gamma_0/\gamma_d < e^{\sqrt{z}d} \quad \text{and} \quad \sigma_0 \cdot \sigma_d < 0 \\ > 0 & \text{otherwise} \end{cases} \tag{22}$$

where $\gamma_{0,d} = \sqrt{(2\sqrt{z}/\sigma_{0,d})^2 + 1} - |2\sqrt{z}/\sigma_{0,d}|$.

3.2. Mixtures of electrolytes

Next we consider a binary salt mixture. The first is an asymmetric salt (1:z) for which the bulk concentrations of the multivalent cations and monovalent anions are n_b^z and zn_b^z , respectively. The second is a monovalent salt (1:1) for which the bulk concentration is n_b . The dimensionless PB equation now reads

$$\frac{d^2\phi}{dx^2} = \sinh\phi - \frac{z\alpha}{2}(e^{-z\phi} - e^\phi) \tag{23}$$

where $\alpha = n_b^z/n_b$ is the ratio between the bulk densities of the multivalent and monovalent cations. This equation depends explicitly on the parameters α and z , while all the other physical parameters are taken into account by the dimensionless boundary conditions (Eq. (21)). The first integration of this equation gives the dimensionless pressure in between the plates:

$$\Pi_{\text{in}} = -\frac{1}{2}\phi'^2 + \cosh\phi + \frac{\alpha}{2}e^{-z\phi} + \frac{z\alpha}{2}e^\phi. \tag{24}$$

The pressure in the outer region is calculated by taking $\phi = \phi' = 0$:

$$\Pi_{\text{out}} = 1 + \frac{\alpha}{2} + \frac{z\alpha}{2}. \tag{25}$$

In order to calculate the attraction/repulsion crossover line we examine the point in the parameter space where the net pressure on the plates $\Pi = \Pi_{\text{in}} - \Pi_{\text{out}}$ vanishes, yielding the following relation between ϕ and ϕ' :

$$\phi' = \sqrt{2(\cosh\phi - 1) + \alpha(e^{-z\phi} - 1) + z\alpha(e^\phi - 1)}. \tag{26}$$

By solving this first-order differential equation, the boundary line between attraction and repulsion regions in the $(d, |\sigma_d/\sigma_0|)$ plane can be obtained.

In the limit of low salt densities, one can assume that the concentration of the multivalent counter-ions is much larger than that of the monovalent ones due to entropy considerations. Hence, we can solve the counter-ions only equation, and derive a similar condition for the low salt limit as was derived in Ref. [24]:

$$\left| \frac{1}{|\sigma_0|} - \frac{1}{\sigma_d} \right| < \frac{1}{\sigma^*}, \tag{27}$$

where $\sigma^* = \epsilon k_B T / 2\pi e D$ is a characteristic charge surface density that depends on D . This condition has no dependence on the salt concentration, so the multivalent and monovalent cases have the same behavior in this limit.

In Fig. 2(a), we show the effect of adding multivalent salt to the solution. It is evident from the plot that the attraction region grows with adding multivalent salt. In Fig. 2(b), the effect of increasing the valency of the multivalent cations is examined. In the plot it can be seen that the attraction region is increased for higher valencies. It is interesting to note that the crossover distance d scales inversely with the valency for constant asymmetry ratio $|\sigma_d/\sigma_0|$.

4. Summary

In this work we have explored a variety of PB theory results. In particular, we have focused on several types of charge boundaries that affect the nature of the pressure between two plates, as well as how multivalent ions influence the crossover between attractive and repulsive inter-plate pressure.

It is evident from this work that solutions of the linear PB equation can serve as a qualitative tool for understanding the interaction. However, when interpreting experimental data, one should solve the non-linear PB theory in order to have better numerical accuracy, especially for small inter-plate separation, d .

Finally, we would like to stress that the surfaces cannot always be regarded as having either a constant surface charge or potential. In quite a number of experimental setups the surface properties depend explicitly on the inter-plate separation. For example, the degree of dissociation of surface charge groups can vary with d . In order to take this effect into account one should use boundary conditions that are determined self-consistently as a function of separation [25].

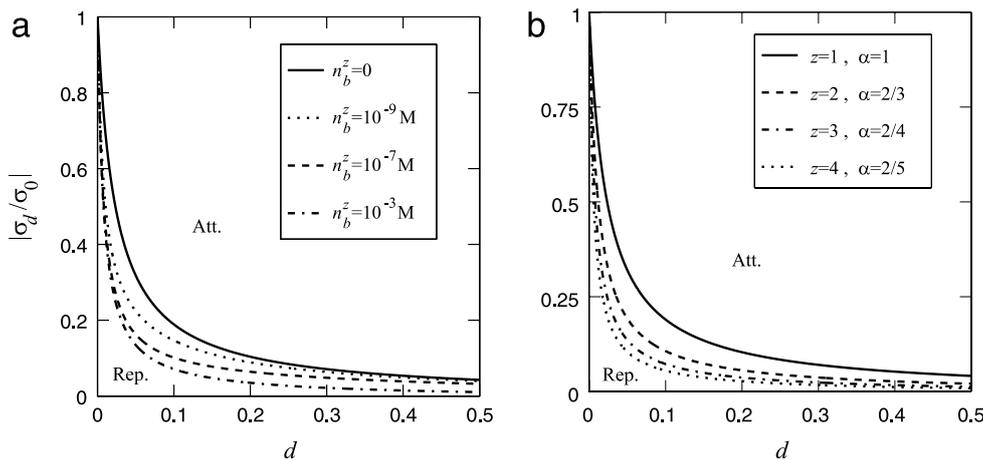


Fig. 2. Crossover between attraction and repulsion for binary salt mixtures. (a) Different values of the multivalent cation concentration n_b^z (see box). The monovalent salt concentration is $n_b = 10^{-3}$ M and the negative surface charge density is $\sigma_0 = -e/100 \text{ \AA}^{-2}$. The valency of the cations is $z = +3$. (b) Varying the multivalent cation valency, z . The negative surface charge density σ_0 is the same as in (a). The overall ion bulk concentration, $n_t = 2n_b + (1+z)\alpha n_b = 4n_b$, is kept constant for all the curves, yielding a constant reference pressure in the outer region.

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