The counterion-release interaction

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Abstract
The case of two oppositely charged planar surfaces interacting across a salt
solution is reconsidered to explain why the release of counterions from the
slit between the plates can lead to an attractive contribution to the effective
interaction between the plates. We estimate the order of magnitude of the
effective inter-plate potential by first considering a Gouy–Chapman layer
in front of a single charged plate. The Gouy–Chapman problem is fully
characterized by just one parameter, the dimensionless surface charge parameter
s. Considering the number of ions in the double layer as a function of s, we can
identify two regimes: one in which the electro-neutrality of the double layer is
ensured through the exchange of co- and counterions, and another, at large s,
where counterions are to be recruited from the reservoir for the system to remain
electro-neutral. The counterion-release force plays a major role only for plates
with surface parameters that belong to the second regime. Having at hand the
results from the single-plate case we are then able to give a simple interpretation
of the counterion-release interaction. The counterion-release force is dominant
for systems with large s and at large distances. At small distances, when all extra
ions have left the slit between the plates, the release mechanism ceases to work
and the two plates attract each other due to an trivial electrostatic attraction.

1. Introduction

Whenever two oppositely charged objects in solution approach each other, their effective
interaction will have a contribution resulting from the release of ions. Since the double layers
associated with the objects are also oppositely charged, the two double layers will start to
dissolve each other when their distance becomes small enough for them to overlap. Then,
fixed charges on the objects begin to partially neutralize each other. Accordingly, mobile
ions of the double layers are no longer needed to screen the fixed charges. They can leave
the system and return to the bulk ion reservoir. This release of ions can lead to a substantial
reduction of the grand potential energy of the system. This energy contribution is known as
'counterion-release interaction'.

The notion of a counterion-release energy appeared in the literature for the first time in 1976 when deHaseth, Lohman and Record used it to explain the salt dependence of the binding constant K of a protein–DNA binding reaction [1, 2]. Since then, and especially in recent years, the counterion-release interaction has received much attention. It has been discussed in the context of biological macroion association in solution (e.g. binding of proteins to DNA [3–6]), as an important driving force in assembly of polyelectrolyte–surfactant complexes [7] and, more specifically, in cationic lipid–DNA complexes [8–20] (for a more general introduction see [21]) and in the theory of polyelectrolyte adsorption [22–27]. More examples include the interaction of two oppositely charged colloids [28] or membranes [29], and of polyelectrolyte stars [30], the problem of protein binding to polyelectrolyte brushes [31–34], but also curvature effects of charged lipid bilayers induced by the counterion release [35]. Recently a paper appeared where, for the first time, the counterion release seems to have been observed directly [36].

In two previous papers [23, 20], we examined how the release of counterions affects the adsorption behaviour of DNA molecules on oppositely charged membranes and studied the different terms contributing to the total grand potential energy as a function of the DNA–membrane distance. The present work now uses a very simple model system (in fact, the simplest possible) to give a detailed explanation for the deeper reason of the counterion-release force. We focus on the case of two oppositely charged planes which interact across a salt solution. This is an old problem [37] which has been treated in some length, for instance, in [38], but it has never served as a test case to explore the counterion-release force. We start by first outlining the problem we here wish to address.

2. Description of the problem

Consider two parallel, infinitely extended and oppositely charged plates which interact across a salt solution. The salt solution in between the two plates is assumed to be coupled to a reservoir of a 1:1 electrolyte in which the concentration of the positive and negative microions is fixed to the value c_s. The solvent is characterized by the Bjerrum length $\lambda_B = \beta e^2/\epsilon$, where e is the elementary charge, ϵ the dielectric constant of the solvent and $\beta = 1/kT$ the inverse thermal energy. The inverse Debye length κ, characterizing the salt solution, is then given by

$$\kappa^2 = 8\pi \lambda_B c_s. \tag{1}$$

As for the two plates, it suffices to know the surface charge density σ (given in units of e). For simplicity, we here consider a pair of exactly oppositely charged plates, that is, one plate carries the surface charge density $\sigma_1 = \sigma$ and the other the surface charge density $\sigma_2 = -\sigma$ ('antisymmetric' pair). The more general case of two plates with a charge mismatch has been treated by Lau and Pincus [39]. σ is assumed to be a positive quantity, $\sigma > 0$, and is equal to Z/A where Z is the total number of fixed charges on the plate and A the area.

What we seek to calculate here is the total interaction energy V between the plates per fixed charge Z, or, alternatively, per area A, as a function of the distance L between the plates. We will show that the interaction is not entirely given by the trivial electrostatic attraction between oppositely charged plates, but also by an entropic contribution related to the release of counterions from the slit between both plates. The interaction is attractive for all distances L (this is not the case if $\sigma_1 \neq -\sigma_2$ [40, 29]). The exact form of $V(L)$ will be analysed later; we first focus on the total energy difference ΔV between two plates at contact, $V(0)$, and at infinite distance from each other, $V(\infty)$. We take the energy at $L = 0$ as the reference point of our calculation ($V(0) = 0$). In reality, the situation at $L = 0$ is rather complicated from the physical point of view, and our model is certainly not fit to adequately describe this situation.

But it is not this limit that we are interested in. Concentrating on the effect the ions have on the interaction between the plates, the situation at $L = 0$ is for us characterized just by the fact that there are no microions left in the slit between the plates. At $L \to \infty$, on the other hand, the plates do not interact as their charges are perfectly screened by a layer of electrolyte ions. The diffusive ion layer close to the negative surface is positively charged, with a net charge that exactly cancels the net charge of the fixed plate charges, and vice versa for the positive surface. Except for the polarity, the planar double layers are identical for both plates; identical also is the total free energy (more precisely, 'grand-potential energy') stored in each double layer. This energy for a single plate is denoted by Ω_{SP}; it is always positive. It is clear then that $\Delta V / Z = V(\infty)/Z$ is given just by $2\Omega_{SP}/Z$. In order to evaluate Ω_{SP}, we have to study the well-known Gouy–Chapman problem of just one charged plate in contact with an electrolyte solution. From that we obtain ΔV and can then return to the interaction of two plates.

Hence: allowing two oppositely charged plates to come together from infinite separation to contact, one gains back twice the energy stored in a Gouy–Chapman double layer. In other words, to understand the deeper physical reason for the attraction between two oppositely charged surfaces in a salt solution, the best way to proceed is to analyse in what form the energy is stored in the Gouy–Chapman double layer of a single isolated plate.

3. The Gouy–Chapman self-energy of a single plate

We here recall the basic ideas of the Gouy–Chapman theory, a good account of which can be found in [41]. Of central interest in the following is the electrostatic mean-field potential ψ which we here write in its dimensionless form by multiplying it by $e\beta$. $\phi(x) = e\beta\psi(x)$ depends on the distance x ($x > 0$) from the plate, assumed to be located here at $x = 0$. The densities of the positive ($n_+(x)$) and negative microions ($n_-(x)$) differ from their bulk value c_s near the plates. Adopting the mean-field Poisson–Boltzmann approach one finds

$$n_{\pm}(x) = c_s e^{\mp \phi(x)} \tag{2}$$

so that the ion net charge density is $e(n_+ - n_-) = -2ec_s \sinh \phi$ and the ion particle density reads $n_+ + n_- = 2c_s \cosh \phi$. Combining equation (2) with Poisson's equation leads to the Poisson–Boltzmann equation

$$\phi''(x) = \kappa^2 \sinh \phi(x) \tag{3}$$

with κ^2 from equation (1). The electric field at the surface of the plate is known, $-\phi'(0) = 4\pi\lambda_B\sigma$. Also known is the field at $x \to \infty$ which must be zero in an electro-neutral system; therefore, $\phi'(\infty) = 0$. In addition we set $\phi(\infty) = 0$. We rescale all lengths of the problem by $1/\kappa$ according to $y = \kappa x$ and arrive at the following Gouy–Chapman boundary value problem:

$$\phi''(y) = \sinh \phi(y), \qquad \phi'(0) = -2s, \qquad \phi'(\infty) = 0. \tag{4}$$

The PB equation depends now only on the dimensionless parameter

$$s := \frac{2\pi\lambda_B\sigma}{\kappa}, \tag{5}$$

which we denote in the following as the 'surface parameter'. The boundary value problem has the solution [41]

$$\tanh(\phi(y)/4) = e^{-y}\tanh(\phi(0)/4), \qquad \sinh(\phi(0)/2) = s. \tag{6}$$

With that expression for ϕ one can now evaluate equation (2) to obtain the ion profiles.

Let us next write down the thermodynamic potential. We consider a (T, V, μ_s), i.e. a grand-canonical, ensemble with V the volume, T the temperature and μ_s the chemical potential

of the salt ions, fixed here through the salt concentration ($\beta\mu_s = \log \Lambda^3 c_s$ with Λ the thermal wavelength). The thermodynamic potential of this ensemble is the grand-canonical potential

$$\Omega(T, V, \mu_s) = U - TS - \mu_s N \tag{7}$$

with the internal energy U, the entropy S and the total number of microions N. All quantities, U, S, Ω and N, are understood to be related to a reference state taken here to be the electrolyte system with an uncharged plate ($s \to 0$). So N, for example, should be better called the 'excess' number of ions, as it is the number of ions in the system when the plate is charged minus the ion number when it is uncharged. It is obtained from integrating the ion particle density

$$N = A \int_0^\infty dx \, (n_+ + n_- - 2c_s) \tag{8}$$

with $n_\pm(x)$ from equation (2). It is found, using equations (4) and (6), to be

$$N = 4N_0(\sqrt{s^2 + 1} - 1) \tag{9}$$

with

$$N_0 = \frac{Ac_s}{\kappa} = \frac{Z}{4s} \tag{10}$$

where the last step in equation (10) results from combining equations (1) and (5). N_0 is the number of anions or cations in the volume $A\kappa^{-1}$ of the bulk salt solution; this volume is roughly the volume of the ionic layer close to the charged surface. Then the excess number of ions in the double layer per fixed charge on the plate reads

$$N(s)/Z = \frac{\sqrt{s^2 + 1} - 1}{s}. \tag{11}$$

Similarly, we find the excess number of anions $N_-(s)$ and cations $N_+(s)$

$$N_\pm(s)/Z = \frac{A}{Z} \int_0^\infty dx \, (n_\pm - c_s) = \frac{\sqrt{s^2 + 1} - 1 \mp s}{2s} \tag{12}$$

which can by means of equation (11) be rewritten as

$$N_\pm(s)/Z = \tfrac{1}{2} N(s)/Z \mp \tfrac{1}{2}. \tag{13}$$

The internal energy is the sum of the electrostatic energy and the ideal gas contribution

$$\beta U = \frac{A}{8\pi\lambda_B} \int_0^\infty dx \, \phi'(x)^2 + \frac{3}{2} N \tag{14}$$

with N from equation (8). Evaluating this expression with the Gouy–Chapman solution leads to

$$\beta U(s)/Z = \frac{5}{2} \frac{N(s)}{Z} \tag{15}$$

with $N(s)/Z$ from equation (11), implying that the first term in equation (14), the total electrostatic energy, is just

$$\beta U_{elec}(s)/Z = \frac{N(s)}{Z}, \tag{16}$$

that is two-thirds of the second term. The corresponding expression for the entropy can be obtained starting from the entropy expression of an inhomogeneous ideal gas

$$\beta TS = -A \int_0^\infty dx \, \left\{ n_+(\log(n_+\Lambda^3) - \tfrac{5}{2}) + n_-(\log(n_-\Lambda^3) - \tfrac{5}{2}) - 2c_s(\log(c_s\Lambda^3) - \tfrac{5}{2}) \right\} \tag{17}$$

with $n_\pm(x)$ from equation (2). Again, as in equations (8) and (14), we subtracted the value of the reference system with an uncharged plate. Using equations (4) and (6), it is straightforward to show that

$$\beta T S(s)/Z = \frac{N(s)}{Z}\left(\frac{9}{2} - \beta\mu_s\right) - 2\,\mathrm{asinh}(s) \qquad (18)$$

with $\beta\mu_s = \log \Lambda^3 c_s$. Just a part of this entropy is relevant for the grand potential. This part we denote by S_p; it is

$$\beta T S_p(s)/Z = (\beta T S(s) + \beta\mu_s N(s))/Z = \tfrac{9}{2}N(s)/Z - 2\,\mathrm{asinh}(s). \qquad (19)$$

Since $\Omega = U - TS_p$ (equation (7)), one subtracts equation (19) from (14) to finally find

$$\beta\Omega(s)/Z = 2\,\mathrm{asinh}(s) - 2\frac{\sqrt{s^2 + 1} - 1}{s}. \qquad (20)$$

The same treatment, but carried out in the canonical ensemble, can be found in [41]. Equations (14) and (17) best characterize the Poisson–Boltzmann approach: it treats a salt solution under the influence of external charges as an inhomogeneous ideal gas of point charges interacting in a typical mean-field fashion. Note also that while the original problem depends on four parameters $(T, c_s, \sigma, \epsilon)$, the quantities Ω, U, S_p and N—when calculated per fixed charge—all depend on just one parameter, the surface parameter s. The entropy in equation (18), on the other hand, depends additionally on the chemical potential of the salt ions.

4. Analysis of the Gouy–Chapman self-energy

We have now all formulae at hand to understand the origin of the grand-potential energy it takes to build up a Gouy–Chapman double layer. Figure 1 shows $N_+(s)/Z$, $N_-(s)/Z$ and $N(s)/Z$ from equations (12) and (11). All three curves are step-like functions, going from +0.5 to 1 (N_-/Z, counterions), from -0.5 to 0 (N_+/Z, co-ions) and accordingly from zero to one in the case of $N(s)/Z$. The asymptotic behaviour of $N(s)/Z$ follows from equation (11) and is for $s \ll 1$ given by $N(s)/Z = s/2 + \mathcal{O}(s^3)$, while for $s \gg 1$ we find $N(s)/Z = 1 - s^{-1} + \mathcal{O}(s^{-2})$. Accordingly, equation (12) yields $N_\pm(s)/Z = \mp 1/2 + s/4 + \mathcal{O}(s^2)$ in the case $s \ll 1$ and $N_\pm(s)/Z = (1 \mp 1 - s^{-1})/2 + \mathcal{O}(s^{-2})$ for $s \gg 1$. We interpret this asymptotic behaviour as follows. Because $N_\pm(s)/Z \approx 1/2$ and $N(s)/Z \approx 0$ for $s \to 0$ every charge on the surface is neutralized by transferring 0.5 co-ions from the double layer into the reservoir, and replacing it by 0.5 counterions taken from the reservoir, while the total number of micro-ions in the double layer is not affected by this replacement. Due to this we call the $s \ll 1$ regime with $N(s)/Z \approx 0$ the 'replacement' regime. This replacement mechanism to neutralize a plate charge comes to a natural end when all co-ions in the double layer are replaced. Then $N_+/Z \approx 0$ which is the case if $s \to \infty$. Now, for $s \gg 1$, the plate charge is neutralized by taking one full counterion per fixed charge from the reservoir. Accordingly, the total number of ions in the double layer increases and $N(s)/Z \approx 1$. We therefore name this regime the 'recruitment' regime.

In figure 2, the entropy expressions in equations (18) (dashed curve) and (19) (solid curve) are plotted. The asymptotic expansion of the entropy follows from equation (18) and reads for $s \to 0$: $S(s)/Z = (1 - \beta\mu_s)s/4 + \mathcal{O}(s^3)$; in the case $s \to \infty$ we find $S(s)/Z = -2\ln(2s) + 9/2 - \beta\mu_s + \mathcal{O}(s^{-1})$. One observes in figure 2 an increase of $S(s)/Z$ for $s < 10$ which results from the $N(s)$ dependence of the first term in equation (18). Since $N(s)/Z \to 1$ for large s, this first term becomes constant and the second term in equation (18) becomes dominant, which goes like $-2\ln(2s)$ for large s, thus appearing as a straight line on
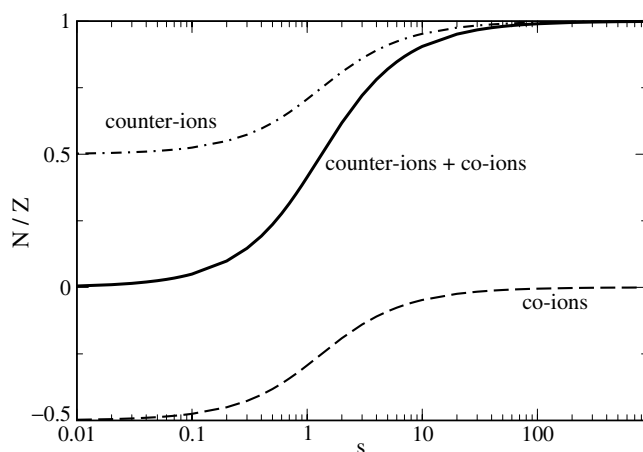
Figure 1. Number of co- and counterions (dashed and dashed–dotted curve) and the sum of both (solid curve) per fixed charge on the plate as a function of the dimensionless surface charge density s defined in equation (5).
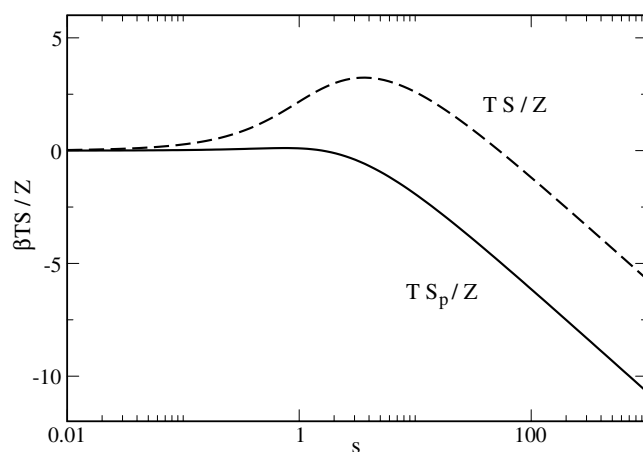

Figure 2. The entropy per fixed charge on the plate (dashed curve) as a function of the surface parameter s for $\beta\mu_s = -5$. The solid curve is the μ_s-independent part of the entropy (defined as S_p in equation (19)).

a logarithmic scale. As a result of these two competing terms, the entropy has a maximum at intermediate s. The height of the maximum depends on the value of μ_s (which is usually a negative quantity). The entropy is an extensive variable that trivially increases if the number of particles is increased. In going from S to S_p of equation (19) we extract the μ_s-independent part of the entropy that is thus independent of the properties of the reservoir (in a canonical description S_p is the entropy). S_p has the same asymptotic behaviour as $S(s)/Z$ but without the terms $\sim \beta\mu_s$ and is dominated almost entirely by the term $-2\,\mathrm{asinh}(s)$. Figure 2 (solid curve) shows that the maximum has almost vanished and that S_p is small for $s < 1$ and becomes negative for $s > 1$. It is not a coincidence that these two regimes match the replacement and recruitment regimes identified in figure 1: as the entropy is insensitive to the sign of the charge, a simple replacement of a co-ion by a counterion can not affect the entropy. In other
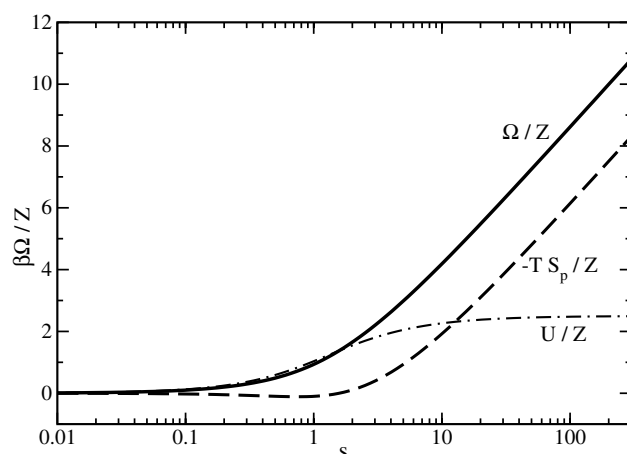
Figure 3. Grand-potential energy $\Omega = U - T S_p$ of a Gouy–Chapman double layer per fixed charge as a function of the surface parameter s, and its two components, the internal energy U and the entropic contribution $-T S_p = -(T S + \mu_s N)$.

words, the s range where S_p is almost zero just identifies the replacement regime in which the electro-neutrality of the double layer is ensured through the exchange of co- and counterions. On the other hand, in the recruitment regime at large s, counterions must be inserted into the double layer, the total number of ions per volume increases and, accordingly, the volume per ion shrinks. This of course has an effect on the entropy. Indeed, for $s \to \infty$, both $\beta T S(s)$ and $\beta T S_p(s)$ behave like $-Z \ln(2s)$, and since $2s = Z/(2A\kappa^{-1}c_s)$ (equation (10)) and $Z \to N_-$ for $s \to \infty$, we find $-\beta T S_p(s) \sim N_- \log(n/c_s)$ with $n = N_-/(2A\kappa^{-1})$. n is the mean particle density in the double layer and $N_- \log(n/c_s)$ is the difference of an ideal gas entropy at a density n and a density c_s. This supports our interpretation that at large s the entropy is negative just because of the shrinking volume per ion.

The negative of $T S_p/Z$ is plotted as dashed curve in figure 3. Adding the internal energy, equation (15) (dashed–dotted curve in figure 3), one obtains the grand-potential energy, equation (20), plotted in figure 3 as a solid curve. It is clear from equation (15) that the U/Z saturates at $5/2$; see figure 3. Therefore, at large s, Ω is dominated by the entropic term S_p, and here, in particular, by the term $\mathrm{asinh}(s)$. For $s \ll 1$, $\beta\Omega/Z \approx 2N/Z$ of which $\frac{5}{2}N/Z$ comes from the internal energy ($\frac{3}{2}N/Z$ ideal gas, N/Z electrostatics) and $-\frac{1}{2}N/Z$ from $-\beta T S_p/Z$. This means that, in the replacement regime, the grand potential is almost entirely given by the internal energy, because, as we have seen, the entropic contribution S_p, being not affected by an ion replacement, is very small. At $s \gg 1$, counterions are to be recruited from the reservoir, the mean ion density in the double layer increases, S_p decreases and the grand-potential energy becomes dominated by entropy (at $s = 10$ the term $-T S_p$ contributes 50% of Ω, at $s = 100$ already about 75%).

5. The physical origin of the counterion-release force

If one indeed replaced the correct curve of $N(s)/Z$ in figure 1 by a step function ($N/Z = 0$ for $s < 1$, and $N/Z = 1$ for $s \geqslant 1$) and applied this to the grand-potential energy, one would find that $\beta\Omega$ is zero if $s < 1$, and $2Z(\ln(2s) - 1)$ if $s \gg 1$. The latter energy is purely entropic and results from the fact that with increasing s the volume per ion in the double layer shrinks. Having this in mind, one can now understand the physical reason for the counterion-release force.

The grand-potential energy in equation (20) is half of the total energy one gains when de-charging two oppositely charged plates by transferring them from $L = \infty$ to 0. For two plates with $s < 1$, this energy gain is relatively small; it comes mainly from the internal energy; entropy plays hardly any role. If $s > 1$, the energy is large, electrostatics and the internal energy are less significant, and entropy (more precisely, the μ_s-independent part of the entropy) dominates the energy. On de-charging the plates, ions are released from the double layer, the volume per ion of the released ions increases and the system thus gains entropy S_p. As there are many micro-ions, this is an enormous energy ($\Omega \sim Z!$). From this it becomes clear that the name 'counterion-release' force is in principle justified only for systems with a large value of s (either highly charged or having a low ionic strength) because only then (in the 'recruitment' regime) does the release of ions have an energetic effect. One also recognizes that the electrostatic attraction—which one would naively think to be dominant—is in fact rather small when compared to the entropic attraction induced by the released ions. Even in the replacement regime where the counterion release effect is not effective, the electrostatics just contributes 50% of the attraction. In the replacement regime where $N(s)/Z \approx 1$ the electrostatics is just $1\ kT$ per fixed charge on the plate (see equation (16)). This has to be compared to the values of $\beta\Omega/Z$ in figure 3!

Let us consider for a moment the Debye–Hückel limiting case in which $|\phi(x)| < 1$ so that the right-hand side of equation (4) can be expanded up to linear order. The solution to (4) is $\phi(x) = 2se^{-\kappa x}$, the densities read $n_\pm(x) = c_s(1 \mp 2se^{-\kappa x})$ and we find for N_+/Z and N_-/Z, defined in equation (12), just $\mp\frac{1}{2}$. Thus, $N/Z = 0$. In words: in the Debye–Hückel limit, one is confined to the replacement regime; the total number of ions in the double layer is always the same. Entropy thus should not play a role. Indeed, inserting equations (8), (14) and (17) in equation (7) and using equation (2) and $\log(c_s\Lambda^3) = \beta\mu_s$, one finds after an integration by parts

$$\beta\Omega = \frac{Z}{2}\phi(0) + Ac_s \int_0^\infty \mathrm{d}x\, \big(\phi(x)\sinh\phi(x) - 2(\cosh\phi(x) - 1)\big) \tag{21}$$

which reduces to

$$\beta\Omega = \frac{Z}{2}\phi(0) \tag{22}$$

if $|\phi(x)| < 1$ everywhere. This is just the electrostatic energy of the fixed charges in the mean-field potential. These remarks show that neither an ion release nor an attraction connected with this release can be understood in terms of a linear theory; the attraction resulting from the release of ions is a phenomenon arising solely from the non-linearity of the Poisson–Boltzmann equation.

6. Counterion-release attraction

For the single-plate problem we have derived Ω_{SP}, and have thus a value for the order of magnitude of the counterion-release attraction, $\Delta V/Z = V(\infty)/Z = 2\Omega_{SP}/Z$. To calculate the full interaction potential $V(\kappa L)$ between the antisymmetric pair of plates at distance κL, one has to solve numerically the problem

$$\phi''(y) = \sinh\phi(y), \qquad \phi'(0) = -2s, \qquad \phi'(\kappa L) = -2s \tag{23}$$

and use this in the equations (8), (14) and (17) to obtain the quantities N, U and S, and from them the quantities Ω and S_p as defined in the previous section. In (8), (14) and (17) one has to integrate from zero to κL. All functions are now κL-dependent. Of course, for $\kappa L \to \infty$, all functions have values that are just twice the value calculated in the one-plate problem of the
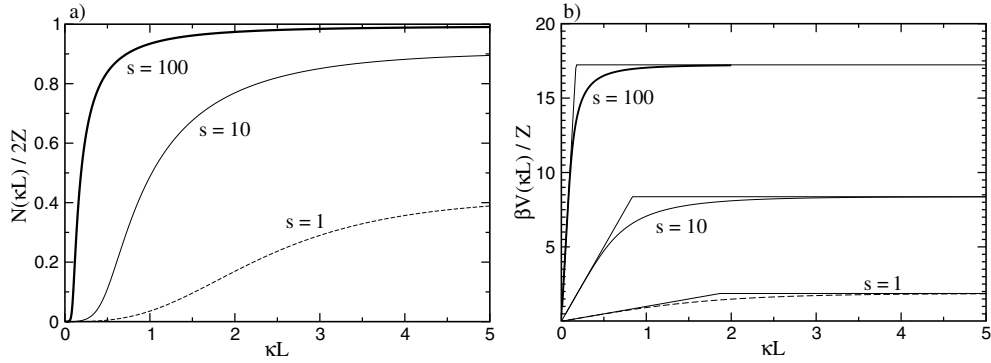
Figure 4. (a) Total number of microions per fixed charge between two oppositely charged plates as a function of the plate distance κL, for three values of the surface parameter s. (b) The interaction potential $V(\kappa L)$ between two oppositely charged plates, obtained from the numerical solution of equation (23). Dashed curves for $s = 1$; thin solid curves for $s = 10$; thick solid curves for $s = 100$. Also given are predictions for $V(\kappa L)$ as obtained from a simple approximative formula, equation (24).

previous section. Figure 4(a) shows $N(\kappa L)$ per fixed charge as a function of the distance for three different values of the surface parameter. For each s, the value at $\kappa L = 5$ is the same as one can find in figure 1 for this s, implying that at this distance the $\kappa L \to \infty$ limit is already reached. The figure demonstrates how on reducing κL, ions are released from the slit between the plates. Figure 4(b) show the interaction potential $V(\kappa L) = \Omega(\kappa L)$, evaluated using the solution of equation (23). Since at small distances $N(\kappa L)$ becomes invariably zero, one is allowed in this region to ignore the micro-ions and may assume the electric field to have the constant value $2\kappa s$ (capacitor in dielectric medium). One finds $\beta V(\kappa L)/Z = s\kappa L$. A rough approximation for $V(\kappa L)$ then is

$$\beta V(\kappa L)/Z = \begin{cases} \kappa s L & \kappa L < \beta V(\infty)/s \\ \beta V(\infty) & \kappa L > \beta V(\infty)/s \end{cases} \qquad (24)$$

with

$$\beta V(\infty)/Z = 4 \operatorname{asinh}(s) - 4\frac{\sqrt{s^2 + 1} - 1}{s}. \qquad (25)$$

$V(\kappa L)/Z$, approximated by this simple formula, is also plotted in figure 4(b). Figure 5(a) shows $V(\kappa L)/Z$ for $s = 100$ and the two parts that it consists of, $U(\kappa L)$ and $-T S_p(\kappa L)$. $-T S_p(\kappa L)$ has almost the same form as $N(\kappa L)/N(\infty)$ in figure 4(a); for small distances ($\kappa L < 0.05$) all ions have left the slit, and $S_p = 0$: entropy then ceases to have an effect on the effective plate interaction which is now governed exclusively by $U(\kappa L)$.

We define dimensionless forces in the following way:

$$f_\Omega(\kappa L) = -\frac{\partial}{\partial(\kappa L)}\beta\Omega(\kappa L)/Z$$

$$f_S(\kappa L) = -\frac{\partial}{\partial(\kappa L)}\beta(-T S_p(\kappa L))/Z \qquad (26)$$

$$f_U(L) = -\frac{\partial}{\partial(\kappa L)}\beta U(\kappa L)/Z.$$

Of course, $f_\Omega(\kappa L) = f_U(\kappa L) + f_S(\kappa L)$. The three force curves, for $s = 1$, 10 and 100, are shown in figures 5(b)–(d). The total force is always attractive with a range from $\kappa L \approx 0.25$
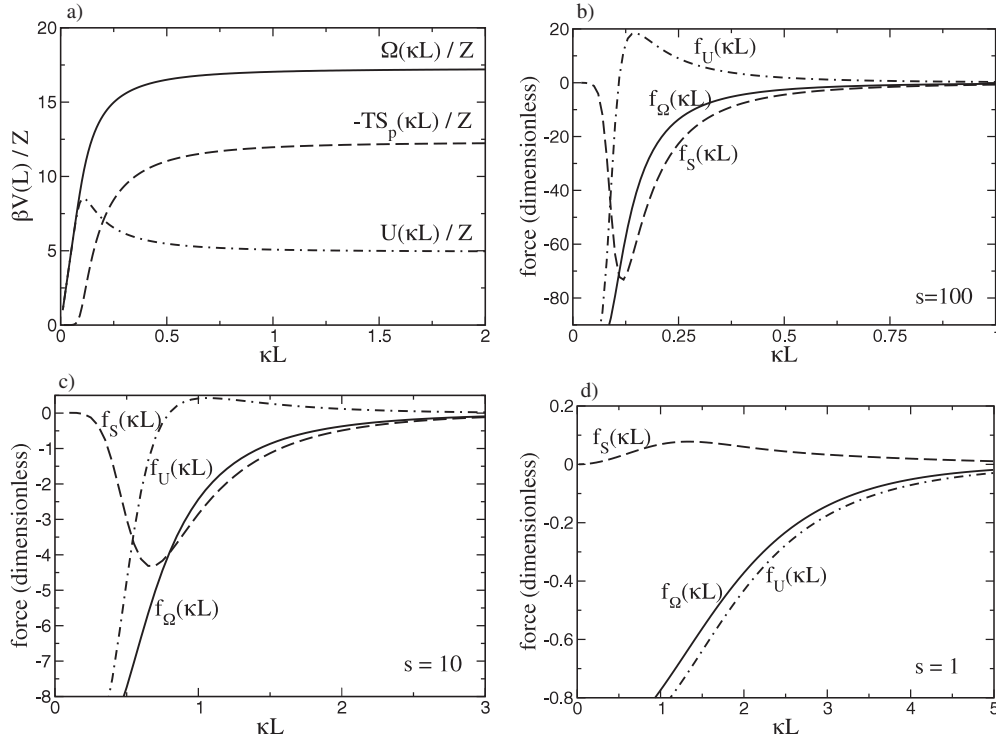
Figure 5. (a) The internal energy $U(\kappa L)$, the entropic contribution $-TS_p(\kappa L)$, and the sum of both, the interaction potential $V(\kappa L) = \Omega(\kappa L) = U(\kappa L) - TS_p(\kappa L)$, as a function of the distance κL ($s = 100$). (b)–(d) Inter-plate force as a function of the distance for $s = 1$, 10 and 100. The dimensionless forces $f_\Omega(\kappa L)$, $f_S(\kappa L)$ and $f_U(\kappa L)$ are defined in equation (26). $f_\Omega(\kappa L) = f_U(\kappa L) + f_S(\kappa L)$.

($s = 100$) to $\kappa L \approx 5$ ($s = 1$). For $s = 100$ and 10, the total force at larger distances is dominated by the entropic force $f_S(\kappa L)$. Interestingly, the force $f_U(\kappa L)$, derived from the internal energy (including, in particular, the electrostatic energy) is repulsive (!) in this distance regime. This best characterizes the importance of the release forces: two oppositely charged plates would repel each other, without the attraction produced by the release of counterions. At shorter distances $f_S(\kappa L)$ becomes weaker and $f_U(\kappa L)$ at the same time becomes attractive, until for $\kappa L \to 0$ the total attraction is purely electrostatic in nature. The trivial case of a purely electrostatic attraction at all distances is shown in figure 5(d) for $s = 1$. $f_U(\kappa L)$ is always attractive and dominates the interaction while $f_S(\kappa L)$ can practically be ignored. This curve could be calculated within Debye–Hückel theory. Note that there is a factor of 100 between the forces for $s = 1$ and those for $s = 100$. Note also that these are the forces per fixed charge (on one plate). To compute total forces one has to multiply these numbers by Z, and since $s \sim Z$ the difference between the total forces will be even larger. This once more underlines the importance of the counterion-release force.

7. Conclusion

The purpose of this paper is to explain why the release of ions in the slit between two oppositely charged plates leads to an attractive force between the plates. To estimate the order of magnitude of the effective interaction potential we computed the amount of grand-potential energy stored in a Gouy–Chapman layer in front of a single charged plate. It just depends on the dimensionless

surface parameter s. Considering the number of ions in the double layer as a function of s, we could identify two regimes: the 'replacement' and the 'recruitment' regime. The entropy S_p is almost zero in the replacement regime in which the electro-neutrality of the double layer is ensured through the exchange of co- and counterions. At large s, counterions are recruited from the reservoir, so the volume per ion in the double layer shrinks. This affects the entropy. It is this energy (of entropic origin) that one gains back if the counterions are released on bringing two oppositely charged plates together. Ions have less free volume in the double layer than they have in the reservoir. This fact explains the energy behind the counterion-release force.

The counterion-release force is dominant for systems with large s and at large distances when it is capable of overcoming a repulsive interaction resulting from the internal energy. At small distances when all extra ions have left the slit between the plates, it ceases to work. Then the two plates attract each other due to an electrostatic attraction. The parameter s is of crucial importance to estimate whether or not a counterion-release force is active in a given system. As a rule of thumb, it is important only if s is much larger than one. This is a regime where the non-linearity of the Poisson–Boltzmann equation is essential. Thus the occurrence of a release force is a phenomenon which is naturally related to non-linear screening. It is known that for highly charged surfaces the mean-field description of the problem fails. Nevertheless, we believe that the mechanism of the counterion release described in this paper also remains valid in the regime where the Poisson–Boltzmann approach is no longer justifiable.

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