

On the interaction of highly charged plates in an electrolyte: a correction

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(Received 1 October 1992; accepted 3 February 1993)

It is shown that the treatment of the interaction of electric double layers, as given by I. S. Sogami, T. Shinohara and M. V. Smalley (*Molec. Phys.*, 1990, **71**, 1251; 1992, **74**, 599; **76**, 1) contains errors and leads to incorrect results. These authors consider the interaction of parallel, identically charged plates with a surface potential that is independent of the distance between the plates. Surface charges are considered to be smeared out, and the electric field in the solution obeys the Poisson–Boltzmann equation. A weak attraction is found at large distances, and a strong repulsion at short distances. The authors stress that these results are in fundamental disagreement with results obtained in DLVO theory.

Two types of error are described. When the plates are brought closer together at constant surface potential, the absolute value of the surface charge decreases. The non-electric (chemical) part of the effect of this decrease on the free energy of the system is not taken into account and this omission results in the calculated attraction. Furthermore, in the calculation of the free energy of the system, the ions are considered to make a non-electric contribution to the free energy of the order of $-20kT$ per ion in 0.001 M solution. Unfortunately, the authors count fewer ions when the plates are close together, than when they are far apart, and this results in a wholly artificial calculated repulsion. When these errors are eliminated, the treatment as set up by the three authors reproduces the classical results, in particular a repulsion for all distances.

1. Introduction

Three papers by Smalley and Sogami, Shinohara and Smalley have appeared recently and are cited as I [1], II [2] and III [3]. In these papers, a theoretical treatment is given of the interaction between the electric double layers carried by two parallel plates, immersed in an electrolyte solution. The interaction is found to be weakly attractive at large separations and strongly repulsive at medium and small separations. The treatments are based on smeared out surface charges and on the Poisson–Boltzmann equation for the electric potential in the solution. The authors stress that the attractive part of the interaction is new and qualitatively at variance with the double layer treatment in DLVO theory. Moreover, the repulsion at short distances is much stronger than that according to DLVO data. The DLVO (Derjaguin–Landau–Verwey–Overbeek) theory [4, 5 a, b] explains the stability of lyophobic colloids, as based on interparticle forces, due to overlapping electric double layers and van der Waals attractions.

Unfortunately, the results obtained in these three papers are incorrect. In the present paper the errors are pointed out in detail, and it is shown how they can be eliminated.

First, it is worth remarking that Langmuir [6] showed in 1938 that, when two

identical double layers, e.g. on parallel plates, start to overlap, the resulting force between the plates is essentially a repulsion. The proof is transparent. For simplicity, let us consider only 1 : 1 electrolytes. In the symmetry plane between the plates there is no electric field, but the potential (ϕ_m) is finite, and it has the same sign as the surface potential (ϕ_s), if the potential far away from the surfaces is taken as zero. In the symmetry plane the counterion concentration is increased by a factor $\exp(+|e\phi_m/kT|)$ as compared to the bulk concentration at $\phi = 0$ and the coion concentration is decreased by a factor $\exp(-|e\phi_m/kT|)$. Since $\exp(+y) + \exp(-y) > 2$, the ion concentration at the symmetry plane is larger than in the bulk and thus the hydrostatic pressure there (Langmuir puts it equal to the osmotic pressure) is larger than the pressure in the bulk solution, far away from any double layers. Mechanical equilibrium in the liquid requires that the difference between the hydrostatic pressure (due to the excess ionic concentration) and Maxwell's stresses (due to the electric field in the double layer) has the same value everywhere between the plates, and therefore the net resulting pressure on the inside surfaces of the plates is equal to the hydrostatic pressure in the symmetry plane, where the Maxwell stress is absent. The same reasoning applies to the liquid outside the plates, from their surfaces to infinity and thus the net pressure on the outside surfaces is equal to the bulk pressure.

In the case of ideal behaviour of the ions in the solution (in agreement with the use of the Poisson–Boltzmann relation), the pressure difference between the two sides of a plate is equal to $n_0kT(\exp(+|e\phi_m/kT|) + \exp(-|e\phi_m/kT|) - 2)$, which is always positive, and thus the plates repel one another. In the above expression n_0 is the concentration of the 1 : 1 electrolyte far from the plates, where $\phi = 0$, k is the Boltzmann constant, T the temperature, and e the elementary charge.

Derjaguin [4], Bergmann, Löw-Beer and Zocher [7] and Verwey and Overbeek [5b] used variants on the same theme and all come to the same conclusion, a repulsive force or pressure, quantitatively identical to Langmuir's value. Knowledge of these early results should have made anybody suspicious of an attraction calculated for basically the same model.

Let there be no misunderstanding: that the above value for the repulsion implies ideal behaviour of the ions in the solution, as in Van't Hoff's value for the osmotic pressure and in the Poisson–Boltzmann equation. When correlation in the mutual position of the ions is taken into account, this introduces an attractive component in the interaction which may, e.g. for bivalent counterions, be stronger than the just calculated repulsion, and lead to a net attraction between the plates [8–12]. Attractions found in this way occur at high ionic concentrations (e.g. molar), with bi- or higher valent counterions and at small distances (order of 1 nm) between the surfaces, whereas Sogami, Shinohara and Smalley, who did not use this refinement, calculated attractions for small ionic concentrations (e.g. millimolar) for monovalent counterions and relatively large distances (e.g. 20 nm).

In paper I, Smalley applies the Sogami and Ise [13] approach to double layer interaction for the case of a number of parallel plates. By manipulating the difference between Helmholtz and Gibbs free energies, Sogami and Ise find an attraction for long distance interaction, and so does Smalley. It might suffice here to refer to my criticism [14] of Sogami's and Ise's work, which will also apply to paper I. However, Smalley has added a derivation of his own, showing that

$$\Delta G = \Delta F + \Delta E, \quad (1)$$

where ΔG , ΔF and ΔE are increments of, respectively, the Gibbs free energy, the Helmholtz free energy and the energy of double layer systems. In his derivation of equation (1), Smalley argues that the work $P\Delta V$ (P = pressure, V = volume) done by the system must be equal to the change in electrostatic energy ΔE in the double layers, and with $P\Delta V = \Delta E$ he finds equation (1) via $\Delta G = \Delta E + P\Delta V - T\Delta S$. The correct expression should have been $P\Delta V = -\Delta F$, work done by the system at constant P and T decreases the *free* energy and thus $\Delta G = 0$, as it should be at equilibrium at constant P and T .

It is much more interesting to consider papers II and III, in which an apparently valid method is used—no discussion about the difference between F and G —but which still lead to incorrect results.

2. Model of the system, electric potentials and concentrations of ions in it

As sketched in figure 1, two infinite parallel plates with uniform surface charges and infinitesimal thickness are considered to be immersed in a 1:1 electrolyte with infinite volume. x is the coordinate normal to the plate surfaces. It has its origin midway between the plates, which are located at $x = -l$ and at $x = +l$. Their distance apart $d = 2l$. The mean local electric potential is $\phi(x)$. A dimensionless potential $\Phi(x) = e\phi(x)/kT$ is introduced, which obeys the Poisson–Boltzmann

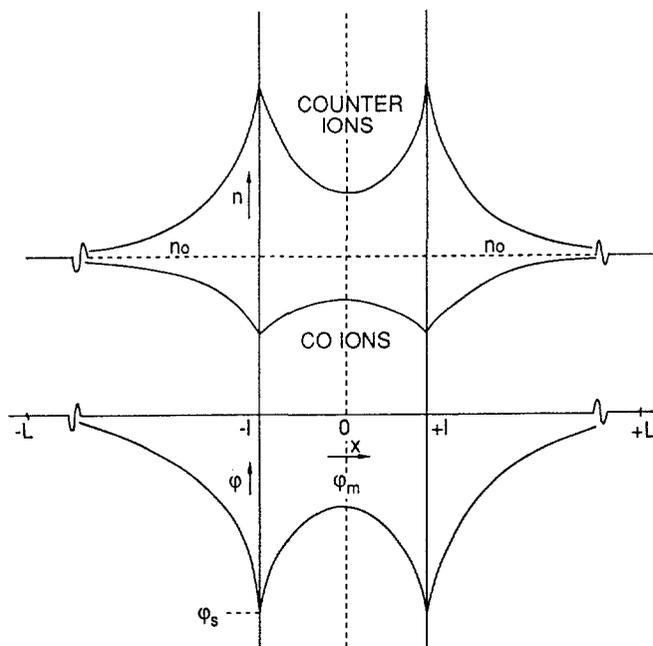


Figure 1. The model. Two parallel infinite plates at $+l$ and $-l$, bathed in a 1:1 electrolyte solution of concentration n_0 . The x coordinate is perpendicular to the plates and has its origin midway between them. The surface potential of the plates is ϕ_s (negative), the potential at $x = 0$ is ϕ_m . The course of the potential is sketched in the lower part of the figure. The coordinates $+L$ and $-L$ are far out of the influence of the double layers. In the upper part of the figure the local concentrations of counterions (+) and coions (–) are sketched.

equation

$$\frac{d^2\Phi(x)}{dx^2} = \kappa^2 \sinh \Phi(x), \quad (2)$$

where the Debye length $1/\kappa$ is equal to

$$\frac{1}{\kappa} = (\epsilon\epsilon_0 kT/2n_0e^2)^{1/2} \quad (3)$$

with ϵ as the dielectric constant of the solution, and ϵ_0 the permittivity of vacuum. The dimensionless potential in the solution near the plate surfaces (at $\pm l \pm 0$) is Φ_s (chosen negative) and is considered to be independent of the distance between the plates, not necessarily independent of the electrolyte concentration. This *constancy* of Φ_s is an essential factor in the whole treatment.

The surface charge density on the outside surfaces of the plates is Z_0e , related to the potential gradient by

$$\pm Z_0e = \frac{\epsilon\epsilon_0 kT}{e} \left(\frac{d\Phi}{dx} \right)_{x=\mp(l+0)}, \quad (4)$$

and it is independent of the distance between the plates.

On the inside surfaces the surface charge density Z_1e , is in general different from Z_0e and it obeys

$$\pm Z_1e = \frac{\epsilon\epsilon_0 kT}{e} \left(\frac{d\Phi}{dx} \right)_{x=\pm(l-0)}. \quad (5)$$

Z_0 and Z_1 have the sign of the surface charge.

Solution of the Poisson–Boltzmann equation between the two plates leads to elliptic integrals. This complication is avoided in paper II by neglecting the coion contribution to the charge density completely. However, in paper III the complete Poisson–Boltzmann equation is used. Since this is the only important difference between papers II and III, the discussion will be limited now to paper III.

In that paper the authors give the well known solutions of the Poisson–Boltzmann equation between the plates and outside the plates. We cite here the result of the first integration between the plates, leading to

$$\frac{d\Phi(x)}{d(\kappa x)} = \pm(2 \cosh \Phi(x) - 2 \cosh \Phi_m)^{1/2}, \quad (6)$$

where Φ_m stands for $\Phi(x=0)$, the dimensionless potential midway between the plates. A second integration results in

$$\kappa d = 2 \int_{\Phi_s}^{\Phi_m} \frac{d\Phi}{(2 \cosh \Phi - 2 \cosh \Phi_m)^{1/2}}. \quad (7)$$

The integral can be transformed into an elliptic integral and it gives a relation between Φ_m and the distance d between the plates.

The authors then proceed to calculate the total number of counterions (chosen positive, since the surface charge and potential have been chosen negative) and coions per unit cross-sectional area between the plates (N_{i+} and N_{i-}) and outside the plates (N_{o+} and N_{o-}) from $x = \pm l$ to $x = \pm L$, where L is chosen so large as to be far outside the influence of the double layers.

The expressions obtained are, written here in slightly different notation,

$$N_{o+}(L) = 2 \int_l^L \frac{n_0 \exp(-\Phi) d\Phi}{\kappa d\Phi/d(\kappa x)} = 2n_0 \left\{ L - l + \frac{2}{\kappa} (\exp(-\Phi_s/2) - 1) \right\} \quad (8)$$

and

$$N_{o-}(L) = 2n_0 \left\{ L - l + \frac{2}{\kappa} (\exp(+\Phi_s/2) - 1) \right\}. \quad (9)$$

Expressions (8) and (9) show clearly the background contributions $2n_0(L-l)$ on the outside of the two plates and the positive adsorption of the counterions (remember that ϕ_s has been chosen negative) and the negative adsorption of the coions. For the space between the plates

$$N_{i+}(l) = -2Z_i + 2n_0 l \exp(-\Phi_m) - \frac{4n_0}{\kappa} \exp\left(-\frac{\Phi_m}{2}\right) \int_{\phi=\sin^{-1} \exp((\Phi_s-\Phi_m)/2)}^{\pi/2} (1 - \exp(2\Phi_m) \sin^2 \phi)^{1/2} d\phi \quad (10)$$

and

$$N_{i-}(l) = +2Z_i + N_{i+}(l) = 2n_0 l \exp(-\Phi_m) - \frac{4n_0}{\kappa} \exp\left(\frac{-\Phi_m}{2}\right) \int_{\phi=\sin^{-1} \exp((\Phi_s-\Phi_m)/2)}^{\pi/2} (1 - \exp(2\Phi_m) \sin^2 \phi)^{1/2} d\phi \quad (11)$$

where N_o and N_i are positive numbers per unit area.

The integrals in expressions (10) and (11) are elliptic integrals of the second kind. These integrals are also written as:

$$\begin{aligned} & \int_{\phi=\sin^{-1} \exp((\Phi_s-\Phi_m)/2)}^{\pi/2} (1 - \exp(2\Phi_m) \sin^2 \phi)^{1/2} d\phi \\ & \equiv E(\pi/2, \exp \Phi_m) - E\left(\sin^{-1} \exp\left(\frac{\Phi_s - \Phi_m}{2}\right), \exp \Phi_m\right). \end{aligned} \quad (12)$$

So far the results of paper III are correct. The difficulties arise in the calculation of the free energy.

3. The Helmholtz free energy

In papers II and III, the Helmholtz free energy F of the system is divided into an electric part F^{el} and a non-electric part F° so that

$$F = F^{\circ} + F^{\text{el}} \quad (13)$$

The non-electric part is obtained by applying the formula for an ideal gas [15] to the small ions and, in the case of paper III, this leads to F_i° for the space per unit cross-section between the plates and to F_o° for the spaces outside the plates.

$$F_i^{\circ} = -kT \left[N_{i+} \left\{ 1 + \ln \frac{d}{N_{i+}} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2} \right\} + N_{i-} \left\{ 1 + \ln \frac{d}{N_{i-}} \left(\frac{2\pi m_- kT}{h^2} \right)^{3/2} \right\} \right] \quad (14)$$

and

$$\begin{aligned}
 F_o^0 &= -kT \left[N_{o+} \left\{ 1 + \ln \frac{2(L-l)}{N_{o+}} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2} \right\} \right. \\
 &\quad \left. + N_{o-} \left\{ 1 + \ln \frac{2(L-l)}{N_{o-}} \left(\frac{2\pi m_- kT}{h^2} \right)^{3/2} \right\} \right] \\
 &= +2n_0 dkT \left\{ 1 + \ln \frac{1}{n_0} \left(\frac{2\pi(m_+ m_-)^{1/2} kT}{h^2} \right)^{3/2} \right\} + \text{terms that do not depend on } d,
 \end{aligned} \tag{15}$$

where m_+ and m_- are the masses of a cation and an anion, respectively, and h is Planck's constant.

This procedure amounts to assigning to each ion of mass m_i in a solution of concentration n_i a non-electric contribution to its chemical potential μ_i of

$$\mu_i^0 = -kT \ln \left(\frac{2\pi m_i kT}{h^2} \right)^{3/2} + kT \ln n_i, \tag{16}$$

and to each solvent molecule a non-electric contribution to its chemical potential μ_w of

$$\mu_w^0 = -kT \sum_i \frac{n_i}{n_w} \tag{17}$$

in a solution containing n_i solute molecules (ions) of type i and n_w solvent molecules.

It is implicit in equations (14–17) that the solute concentrations are small, i.e. $n_i \ll n_w$. We also point out here that the non-electric chemical potential of the ions $-kT \ln (2\pi m_i kT/h^2)^{3/2}/n_i$ has the large value of about $-20kT$ for $m_i \sim 50\text{g}/6 \times 10^{23}$ for a concentration n_i corresponding to 0.001 molar.

F^{el} is found by the use of a Debye and Hückel type imaginary charging process, starting with all ions in the solutions and all charge carriers on the surfaces uncharged, with the restriction that during the charging process Z_o , Z_i , $N_{o\pm}$ and $N_{i\pm}$ remain constant. F^{el} is then given as

$$F^{\text{el}} = \int_{e'=0}^{e'=e} \frac{2E^{\text{el}} de'}{e'} \tag{18}$$

where E^{el} is the energy per unit cross-section of the electric field at the charging state e' of the elementary charge e .

The electric free energy per unit cross-section between the plates is then found to be

$$\begin{aligned}
 F_i^{\text{el}} &= \int_{e'=0}^{e'=e} \frac{de'}{e'} \int_{-l}^{+l} \frac{\epsilon\epsilon_0 k^2 T^2}{(e')^2} \left(\frac{d\Phi'(x)}{dx} \right)^2 dx = 2Z_i kT [1 + \Phi_s] - n_o kT \exp(-\Phi_m) \\
 &\quad \times \left[\frac{8 \exp(\Phi_m/2)}{\kappa} \left\{ E \left(\sin^{-1} \exp \frac{\Phi_s - \Phi_m}{2}, \exp \Phi_m \right) - E \left(\frac{\pi}{2}, \exp \Phi_m \right) \right\} \right. \\
 &\quad \left. + (1 - \exp(2\Phi_m))d \right] - N_{i+} kT \ln \frac{N_{i+}}{n_o d} - N_{i-} kT \ln \frac{N_{i-}}{n_o d}.
 \end{aligned} \tag{19}$$

It is not necessary to write out F_0^{el} , the electric free energy outside the plates since, if L is chosen large enough, F_0^{el} is independent of the distance between the plates and, thus, is of no importance for the interaction.

The authors of paper III (and similarly for paper II) combine the d dependent parts of F_i^{el} , F_i° and F_0° and consider their sum minus the analogous value for $d \rightarrow \infty$ as the free energy of interaction per unit area. Unfortunately, this is wrong. The error has two facets.

First, the total number of cations and anions in the solutions between $-L$ and $+L$ depends on the distance d between the plates. This can be checked by calculation from the N 's given in equations (8–11), but it can also be made evident in a more qualitative way. When the plates are far apart, the total ion content is $4n_0L$ plus 4 times the positive adsorption of counterions per unit area, minus 4 times the negative adsorption of coions. When the plates are (nearly) in contact the double layers between the plates have disappeared and the total ion content is $4n_0L$ plus (or minus) only 2 times the adsorptions per unit area. In bringing the plates closer together, counterions of two double layers are lost and a smaller number of coions are 'created' in the system. The loss of counterions which each contribute $\approx -20kT$ to F° is the main cause of the calculated repulsion. It should be obvious, however, that these ions are not really lost or created, but simply added to or taken from the 'infinite' amount of solution far from the double layers.

Second, the surface potential ϕ_s can remain constant only if the surface charge density $|Z_i e|$ decreases with decreasing distance d . This can be effected by desorption of ions carrying the surface charge or by the adsorption of counterions or by a combination of these processes. Thermodynamic equilibrium requires that the electrochemical potential $\tilde{\mu}_i = \mu_i + e_i \phi$ of the ions involved remains constant and, thus, for the counterions μ_i (adsorbed) $+ e_i \phi_s = \mu_i$ (solution at $\phi = 0$). The electric effect of the adsorbed ions is completely incorporated in F_i^{el} , but the non-electric (also called chemical) effect μ_i (adsorbed) $- \mu_i$ (solution) is not taken into account in the theory as given in papers II and III. For each counterion adsorbed, the free energy F of the system increases by μ_i (adsorbed) $- \mu_i$ (solution) $= -e_i \phi_s = +|e \phi_s|$. This increase in the free energy at a decrease of $|Z_i|$ and thus of d contributes a repulsion, which overcompensates the attraction at large separations as calculated in papers II and III.

So far the arguments presented here have been qualitative or semiquantitative. The following section shows that, after the theory is corrected for the above mentioned effects, it reproduces quantitatively the results as known for the interaction of double layers on parallel surfaces and, in particular, shows a repulsion for all distances.

After this paper had been submitted for publication, the referees brought a paper by Levine and Hall [16] to my attention, in which paper II was criticized and a correct treatment of the case without coions between the plates was offered. Levine and Hall use a model slightly different from that of Sogami, Shinohara and Smalley. They use a finite (as opposed to infinitely large) system, require explicitly that the total numbers of cations and anions in the system are independent of the plate separation, they accept that the concentration far from the plates varies slightly with the plate separation, and they argue that in the calculation of the force between the plates it is the *surface charge*, that has to be kept *constant*, rather than the *surface potential*, thus avoiding the difficulties inherent in the free energy of adsorption of a variable number of surface ions. They still find a repulsion at small separation and an attraction at larger separation, but they argue that the model with no coions between the plates is no longer applicable at these larger separations.

The present author's corrected theory stays as close as possible to Sogami *et al.*'s model and, as already mentioned above, finds a repulsion for all distances.

4. Corrected theory

The model has to be completed by an indication of the mechanism allowing the surface charge to be changed. Taking the example of n-butylammonium vermiculite, given in paper III, dissociation of counterions from the originally neutral surface has been chosen. With this choice the number N_{i-} of free coions per unit cross-sectional area between the plates is equal to

$$N_{i-} = n_0d + 2\Gamma_{\text{co}}(d) = n_0d - 2|\Gamma_{\text{co}}(d)|, \quad (20)$$

where Γ_j is the Gibbs adsorption per unit area of species j . The number N_{i+} of free counterions per unit cross-section between the plates is

$$N_{i+} = N_{i-} - 2Z_i = n_0d + 2\Gamma_{\text{counter}}(d) = n_0d + 2\Gamma_{\text{co}}(d) - 2Z_i. \quad (21)$$

The number of adsorbed counterions per unit cross-section between the plates is

$$\frac{\text{No. of adsorbed counterions}}{\text{Unit cross-section}} = 2(Z_i - Z_o) = 2|Z_o - Z_i|. \quad (22)$$

The total number of counterions (free + adsorbed) per unit cross-section between the plates is

$$\frac{\text{Total no. of counterions}}{\text{Unit cross-section}} = N_{i+} + 2Z_i - 2Z_o = N_{i-} - 2Z_o. \quad (23)$$

In view of the large negative values of the standard chemical potentials of the ions, we have to avoid a situation in which the total number of ions considered depends on d . We therefore choose the total number of coions per unit area (both between and outside the plates) equal to C_- and that of the counterions to C_+ , where

$$C_+ = C_- - 4Z_o \quad (24)$$

For N_{i+} and N_{i-} we continue to use the values of equations (11) and (12). But $N_{o+}(L)$ and $N_{o-}(L)$ of equations (8) and (9) have to be replaced by

$$N_{o+}(\text{new}) = C_+ - N_{i+} - 2(Z_i - Z_o) = N_{o-}(\text{new}) - 2Z_o \quad (25)$$

and

$$N_{o-}(\text{new}) = C_- - N_{i-}. \quad (26)$$

For the Helmholtz free energy we can take F_i^o and F_i^{el} exactly as in paper III, and thus use equations (14) and (19). The relevant contribution of F_0^o , however, is different from the d dependent part of equation (15). We have to consider that in forming the layer d between the plates N_{i-} anions and cations have been taken from the outside solution at a concentration n_o and $(N_{i+} - N_{i-})$ cations have been generated by dissociation from the surfaces. The solvent (water) in the layer d comes from an essentially equally thick layer in the outside solution. Thus we write for F_0^o

$F_0^o =$ Constant minus free energy lost from the outside solution in building the layer d

$$\begin{aligned} &= C - F_0^o(d) \\ &= C - \left\{ -2N_{i-}kT \ln \left(\frac{2\pi(m_+m_-)^{1/2}kT}{h^2} \right)^{3/2} + 2N_{i-}kT \ln n_o - 2n_0dkT \right\}. \quad (27) \end{aligned}$$

In addition to the three contributions from equations (14), (19) and (27) we have to add a fourth contribution from the $2|Z_o - Z_i|$ adsorbed counterions, taking into account their standard chemical potential, just as for the other counterions, and the non-electric work of adsorption, $-e\phi_s = |e\phi_s|$. Thus

$$F_{\text{ads}} = -2kT|Z_o - Z_i| \ln \frac{1}{n_0} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2} + 2kT|Z_o - Z_i| \cdot |\Phi_s|. \quad (28)$$

Adding the contributions from equations (14), (19) and (28) and the d dependent part of equation (27) we find for the free energy of the layer between the two plates:

$$\begin{aligned} F_{\text{corrected}} = & -kT \left[N_{i+} \left\{ 1 + \ln \frac{d}{N_{i+}} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2} \right\} + N_{i-} \left\{ 1 + \ln \frac{d}{N_{i-}} \left(\frac{2\pi m_- kT}{h^2} \right)^{3/2} \right\} \right] \\ & + 2Z_i kT [1 + \Phi_s] - n_0 kT \exp(-\Phi_m) \times \left[\frac{8 \exp(\Phi_m/2)}{\kappa} \right. \\ & \times \left\{ E \left(\sin^{-1} \exp \frac{\Phi_s - \Phi_m}{2}, \exp \Phi_m \right) - E(\pi/2, \exp \Phi_m) \right\} \\ & \left. + (1 - \exp(2\Phi_m))d \right] - N_{i+} kT \ln \frac{N_{i+}}{n_0 d} - N_{i-} kT \ln \frac{N_{i-}}{n_0 d} + 2N_{i-} kT \ln \frac{1}{n_0} \\ & \times \left(\frac{2\pi(m_+ m_-)^{1/2} kT}{h^2} \right)^{3/2} + 2n_0 dkT + 2kT(Z_o - Z_i)\Phi_s + 2(Z_o - Z_i)kT \\ & \times \ln \frac{1}{n_0} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2}. \quad (29) \end{aligned}$$

With the help of equation (21), $N_{i+} = N_{i-} - 2Z_i$, relations (10) and (11) for N_{i+} and N_{i-} , and the combination of equations (5) and (6), leading to

$$Z_i = -\frac{2n_0}{\kappa} (2 \cosh \Phi_s - 2 \cosh \Phi_m)^{1/2}, \quad (30)$$

$F_{\text{corrected}}$ can be transformed into:

$$\begin{aligned} F_{\text{corrected}} = & 2kTZ_o \left(\ln \frac{1}{n_0} \left(\frac{2\pi m_+ kT}{h^2} \right)^{3/2} + \Phi_s \right) - n_0 dkT (3 \exp(-\Phi_m) - 2 - \exp(\Phi_m)) \\ & - \frac{8n_0 kT}{\kappa} (2 \cosh \Phi_s - 2 \cosh \Phi_m)^{1/2} + \frac{16n_0 kT}{\kappa} \exp(-\Phi_m/2) \\ & \times \int_{\phi = \sin^{-1} \exp(\Phi_s - \Phi_m)/2}^{\pi/2} (1 - \exp(2\Phi_m) \sin^2 \phi)^{1/2} d\phi. \quad (31) \end{aligned}$$

This is equal to exactly twice the expression derived by Verwey and Overbeek [5 b, p. 81; see also [17], p. 253], except for the first term, proportional to $2kTZ_o$, which is due to the fact that $2|Z_o|$ counterions are provided by the two surfaces facing the layer d . The factor two comes in because in [5 b] the free energy is calculated for half the layer d and in this paper for the full layer.

It is not easy to see at a glance that $F_{\text{corrected}}$ as given in equation (29) represents a repulsion at all distances, but $(\partial F_{\text{corrected}}/\partial d)_{\Phi_s}$ is easily found and is negative for all distances [5 b], p. 91).

Now this was quite a complicated way of deriving an expression for the free energy of two overlapping double layers. Much simpler derivations are possible, but here it was our purpose to show that the method proposed by Sogami, Shinohara and Smalley, if worked out correctly, leads to the correct and well known value for this free energy.

5. Conclusion

The attraction found between parallel plates, covered with identical double layers, is not a consequence of the model but is due to the omission of the condition for thermodynamic equilibrium between surface charge carriers and ions of the same type in the solution. In the example chosen, it is the equilibrium between counterions bound to the surface, that decrease the surface charge, and free counterions. The repulsion found at medium and short distances is incorrect, due to allowing ions to enter or leave the system, when the interplate distance is changed. A correct calculation of the free energy of the model used by Sogami, Shinohara and Smalley leads to known results and, in particular, to a repulsion for all distances between the plates.

I am grateful to Dr M. V. Smalley for providing me with preprints of papers II and III and for an interesting exchange of letters. I thank Professor H. N. W. Lekkerkerker for his constant interest, Ms Toni Vos for typing the manuscript, and Mr. J. den Boesterd for preparing the figure.

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