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On the Repulsive Interaction Between Strongly Overlapping Double Layers of Charge-regulated Surfaces☆

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ABSTRACT

The Donnan equilibrium is employed to evaluate the entropic repulsion between two charged plates that feature charge regulation and are in equilibrium with a reservoir solution of monovalent salt. This approach represents the zero-field limit of the Poisson–Boltzmann equation, valid for strongly overlapping electrical double layers. We show that this scenario features an intrinsic length scale, which serves as the unscreened pendant of the Debye length for strongly overlapping double layers. In general, the scaling of the disjoining pressure with inter-plate distance is dependent on the boundary conditions (constant charge, constant potential, or charge regulation). Surprisingly, here we find for sufficiently low potentials the same inverse-square decay as for constant charge surfaces. We test the validity of the zero-field limit by comparison with self-consistent field lattice computations that invoke the full Poisson equation for finitely sized ions between two charge-regulated plates.

The electrical double-layer repulsion between two charged surfaces in equilibrium with a salt reservoir is conventionally [1–10] evaluated under the assumption that surfaces are sufficiently far apart such that their double-layers only weakly interact. This so-called 'weak-overlap approximation' [4] implies that the electrical potential in the mid-plane between the two surfaces is small (though surface potentials, nevertheless, may be high). Within this weak-overlap approximation, the Poisson–Boltzmann (PB) equation eventually yields osmotic disjoining pressures that decay exponentially; the typical decay length being the Debye screening length κ^{-1} which measures the thickness of a diffuse electrical double-layer in solution. Together with Van der Waals attractions, one arrives at the exponentially screened, classical DLVO potential [1–4], which is applicable to dilute colloidal fluids in which the average colloid–colloid distance is (much) larger than κ^{-1}.

When distances between charged surfaces are comparable to or less than κ^{-1} such that double-layers strongly overlap and the weak-overlap approximation breaks down, one must resort to more complicated solutions containing elliptic functions [11] or to numerical solutions. For low surface potentials with plates in close proximity and in presence of background salt, analytical approximations exist featuring a peculiar inverse square decay of the disjoining pressure with the inter-plate separation [11]. To the best of our knowledge, however, these approximations are only known for the boundary condition of *constant* surface charge [11–13], but not for surfaces featuring charge regulation, even though these boundary conditions in general do not lead to the same scaling behavior of the disjoining pressure [14]. It should be mentioned that an inverse square decay is also known for the salt-free (counter-ion only) limit at *large* separations, even in case of charge regulation [11,15].

Here we demonstrate a relatively straightforward and analytical treatment of the disjoining pressure between strongly overlapping flat double-layers featuring charge regulation on the basis of the Donnan equilibrium. This method exploits the circumstance that, on approach of two charged plates, absolute values of the potential in the electrolyte solution between the plates rise, but potential *gradients* on average become smaller. Thus to analyze repulsions between plates at a distance comparable to the Debye length, the limit of a weak electric field has to be considered [13] rather than the limit of a high potential [1,2]. From the weak-field point of view, the simplest starting point is obviously the case where the electric field is zero everywhere, i.e., the ions in the inter-plate electrolyte solution are homogeneously distributed in a constant electrical potential, also known as the Donnan potential [16,17].

Zero-field disjoining pressures as function of the Donnan potential

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are derived as follows. Consider two parallel plates separated by an electrolyte solution S in thermodynamic equilibrium with a large reservoir containing a constant number density ρ_s of salt molecules of fully dissociated 1–1 electrolyte. The electrical potential in S, relative to the potential in the reservoir, equals the constant Donnan potential $\overline{\Psi}$, where the bar indicates the zero-field assumption. The ions in S are homogeneously distributed in zero electric field, with average densities given by the Boltzmann distributions for ideal ions:

$$\overline{\rho}_{\pm} = \rho_s \exp(\mp\bar{u}), \quad \text{where } \bar{u} \equiv \frac{e\overline{\Psi}}{k_{BT}}. \tag{1}$$

Here $\bar{u}$ represents the dimensionless Donnan potential, e is the elementary charge, and k_BT is the thermal energy. The excess ion density $\Delta\rho$ in S relative to the ion density in the reservoir is $\Delta\rho \equiv \overline{\rho}_+ + \overline{\rho}_- - 2\rho_s$, which can be combined with Eq. (1) to yield $\Delta\rho = 2\rho_s(\cosh\bar{u} - 1)$. For ideal ions obeying Van 't Hoff's law, the disjoining pressure equals $\Delta\Pi_d = \Delta\rho k_BT$, which in terms of the Donnan potential reads

$$\frac{\Delta\Pi_d}{2\rho_s k_B T} = \cosh\bar{u} - 1. \tag{2}$$

Here pressures are scaled on the osmotic pressure $2\rho_s k_BT$ of the salt reservoir. Since $\cosh\bar{u} > 1$, the ion density in S always exceeds the reservoir ion density so charged plates always spontaneously separate ('disjoin'). Eq. (2) is exact for homogeneously distributed, ideal ions, and is independent of the extent of surface charge regulation. The inter-plate Donnan potential $\bar{u}$ in Eq. (2) follows from the charge density on the surfaces and the electro-neutrality condition, which we will consider next.

Suppose the surfaces have a number of sites per unit area σ_{tot} that each may release a mono-valent positive counter-ion into solution; a practical example, addressed later, are the protons released by the dissociating hydroxyl groups from a silica surface. When σ denotes the density of dissociated, negatively charged sites and $\overline{\rho}_+$ the density of counter-ions in S, the dissociation equilibrium constant is given by $K = (\sigma\overline{\rho}_+)/(\sigma_{tot} - \sigma)$. On substitution of the cation Boltzmann distribution from Eq. (1) the degree of dissociation σ/σ_{tot} follows as

$$\frac{\sigma}{\sigma_{tot}} = \frac{K}{K + \overline{\rho}_+} = \frac{k}{k + \exp(-\bar{u})}, \tag{3}$$

where we introduced the dimensionless equilibrium constant

$$k \equiv K/\rho_s. \tag{4}$$

When the plates move apart, the charge density σ increases according to Eq. (3) and approaches the maximum value

$$\sigma_{max} = \sigma_{tot}\frac{k}{1+k}, \tag{5}$$

achieved for the case of zero Donnan potential for a single free plate.

Next we employ the electro-neutrality condition $\overline{\rho}_+ h = \overline{\rho}_- h + 2\sigma$, for two negatively charged plates at inter-plate distance h, to find on substitution of σ from Eq. (3):

$$\frac{\overline{\rho}_+ - \overline{\rho}_-}{2\rho_s} = \frac{1+k}{k + \exp(-\bar{u})}\frac{\lambda}{h}. \tag{6}$$

Here we have introduced a characteristic length λ defined as

$$\lambda \equiv \frac{k}{1+k}\frac{\sigma_{tot}}{\rho_s} = \frac{\sigma_{max}}{\rho_s}. \tag{7}$$

The length scale λ, incidentally, is a distinguishing feature of the zero-field Donnan limit, being the unscreened pendant of the Debye length

$$\kappa^{-1} = \frac{1}{\sqrt{8\pi\rho_s\ell_B}}, \tag{8}$$

(where ℓ_B is the Bjerrum length), which is the length scale that appears in the exponentially screened repulsions between plates with weak double-layer overlap [1–13]. Whereas κ^{-1} indicates the typical distance over which screening occurs, its pendant λ indicates the inter-plate distance $h \approx \lambda$ at which counter-ions and background salt have a comparable effect on the Donnan potential: for $h \ll \lambda$ counter-ions dominate, while for $h \gg \lambda$ background salt overshadows the contribution of the counter-ions. Alternatively, λ can be expressed in terms of the Gouy–Chapman length $\ell_{GC} = (2\pi\ell_B\sigma_{tot})^{-1}$ of a fully dissociated plate as

$$\lambda = 4\frac{k}{k+1}\ell_{GC}^{-1}\kappa^{-2}. \tag{9}$$

We return to Eq. (6), which on substitution of the Boltzmann distribution, Eq. (1), yields an expression relating potential $\bar{u}$ and inter-plate distance h:

$$\frac{k + \exp(-\bar{u})}{1+k}\sinh\bar{u} = -\frac{\lambda}{h}. \tag{10}$$

This equation is cubic in $\exp(-\bar{u})$. Fig. 1a illustrates that for given inter-plate distance h the absolute value of the zero-field potential in Eq. (10) rises upon increasing the dimensionless dissociation constant k, an increase which corresponds with enhanced surface charge density on the plates, see Eq. (3). If for given k the plates move apart, the Donnan potential decreases and, consequently, the disjoining pressure decays.

To find the leading term in the pressure decay we first expand exponents $\exp(\pm\bar{u})$ in Eq. (10) up to order $\bar{u}^2$, to find the solution

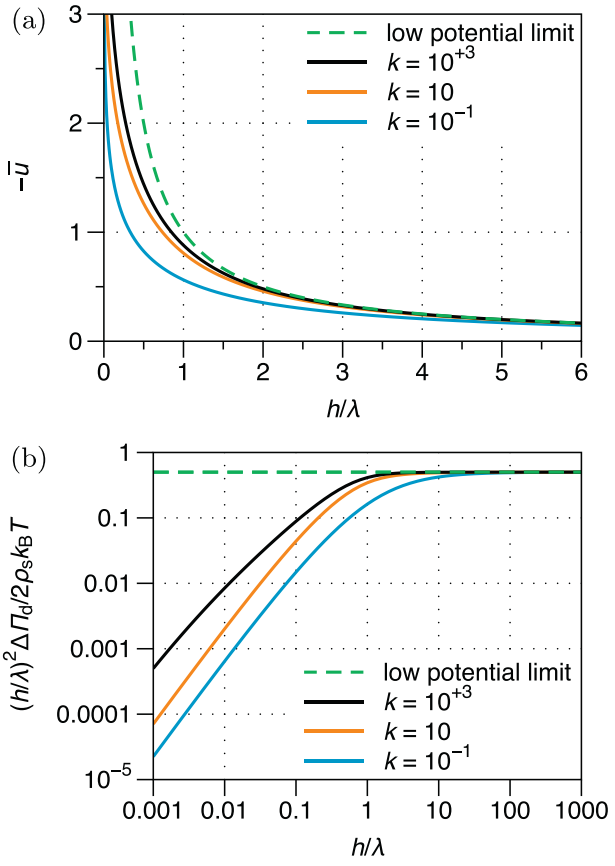

Fig. 1. (a) Zero-field Donnan potential $\bar{u}$ and (b) disjoining pressures $\Delta\Pi_d$ versus the dimensionless inter-plate distance h/λ, with λ defined in Eq. (7). The potential follows from Eq. (10) and the disjoining pressure through subsequent application of Eq. (2). The green dashed lines indicate the low-potential, large separation limits of Eqs. (12) and (15). Increasing the dimensionless dissociation constant k increases the magnitude of $\bar{u}$ for a given inter-plate distance. Both potential and disjoining pressure show universal behavior at large separations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)