

## Disjoining Pressure of Discrete Surface Charges on Thin Aqueous Films

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The disjoining pressure of charged parallel interfaces confining an electrolyte solution is to a large extent determined by the screening clouds of the surface charges. We evaluate the pressure in terms of the number density  $\sigma$  of discrete charges and film thickness  $d$  and find, at  $\sigma d^2 \sim 1$ , a crossover from the well-known law  $P \sim \sigma^2$  to a linear behavior  $P \sim \sigma$ . For the latter case, each surface charge results in strongly inhomogeneous pressure profiles at both interfaces.

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Surface charges at an amphiphilic interface are a ubiquitous phenomenon in soft matter and biophysics. They result from ionic surfactants or charged adsorbants and determine to a large extent the physical properties of soap films, foams, and membranes [1–3]. At finite salinity, the surface charges are screened by a cloud of counterions, giving rise to an exponentially decaying electrostatic potential. Because of the large dielectric constant of water,  $\epsilon \sim 80$ , electrostatic energies at a nanometer scale are small as compared to  $k_B T$ , and the linear Debye-Hückel approximation works rather well at room temperature.

The disjoining pressure of ionic surfactant films or parallel charged plates separated by an electrolyte solution is to a large extent determined by the competition of the electrostatic repulsion of screened surface charges and the attractive London forces. The case of a uniform-charge distribution leads to an effective one-dimensional problem that can be solved in the framework of Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1,2]. Though DLVO theory provides a qualitatively correct picture and explains, e.g., the flocculation of certain dispersions, it fails on a quantitative level, as it neglects the discreteness of surface charges, correlations, specific ion effects, and hydration [4]. Considerable effort has been devoted to the corrections due to the finite ion size, which result in the compact Stern layer at the interface [5]. The separation of electrostatic and London forces of DLVO theory has been questioned, and dispersion forces acting on the electrolyte have been shown to be significant at high salinity [6]. On the other hand, there has been evidence from simulations that strongly correlated screening ions may result in attractive electrostatic forces [7]. This has been confirmed recently by an analytic strong-coupling theory for high surface charge density [8].

Nonhomogeneous surface charge distributions may significantly modify the disjoining pressure. At high density, correlations between surface charges and the compact counterion layers may even lead to an attractive force between charged plates [9,10]. Following the recent

observation of the formation of such complexes [11], the interaction of DNA and cationic lipids has been studied theoretically and the essential role of an inhomogeneous surface charge distribution has been pointed out [12,13].

In this Letter, we are interested in the limit of low number density  $\sigma$ , where the discrete nature of the surface charges becomes important and where the continuous treatment of their density does no longer apply. We mention two obvious realizations. (i) For ionic surfactant films, the observed electrostatic pressure is much smaller than expected from the 1D approach. It has been conjectured that only a small fraction of the surfactant molecules are dissociated [14]. Then the lateral distance of the surface charges,  $a$ , may exceed the water core thickness  $d$ . (ii) A similar situation may occur for nonionic surfactant films containing charged molecules; as an example we note phospholipid bilayers and Newton black films with a small amount of melittine, a charged peptide that constitutes a major ingredient of bee's venom [15].

Our model consists of a confined electrolyte solution of thickness  $d$  and  $N/2$  discrete charges  $Q$  on each of the two interfaces at  $z = 0$  and  $z = d$  (cf. Fig. 1). The aqueous core contains monovalent salt ions and surface charge counterions, with the positive and negative charge number densities  $n_{\pm}(\mathbf{r})$ ; neutrality of the whole system requires  $e \int dV(n_+ - n_-) = -NQ$ . As an obvious consequence of discrete surface charges, the electrostatic potential and

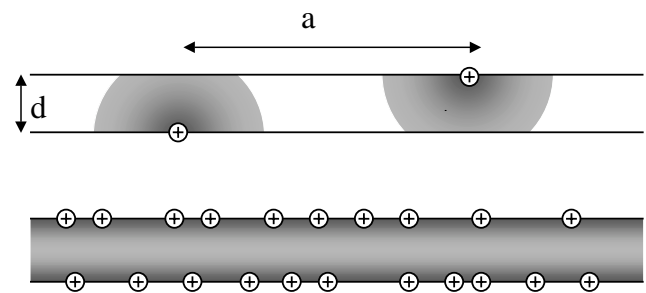


FIG. 1. Schematic view of a charged double layer separated by an aqueous core. The screening clouds for both low and high surface charge density are shown.

the charge density vary in lateral direction, as shown in the upper part of Fig. 1.

We start from the free energy that is a functional of the charge densities  $n_{\pm}(\mathbf{r})$ . In mean-field approximation, it comprises two terms,

$$F = k_B T \sum_{\pm} \int dV n_{\pm} \left[ \ln \frac{n_{\pm}}{n_s} - 1 \right] + \frac{e}{2} \int dV n_t \phi, \quad (1)$$

the first one being the mean-field ideal-gas-like entropy, and the second one the electrostatic energy with the potential  $\phi(\mathbf{r})$ . The total number density  $n_t(\mathbf{r})$  is the sum of the bulk electrolyte and the discrete surface charges,

$$n_t(\mathbf{r}) = n_+(\mathbf{r}) - n_-(\mathbf{r}) + \sum_{\alpha} \frac{Q}{e} \delta(\mathbf{r} - \mathbf{r}_{\alpha}), \quad (2)$$

where the former is given by  $n_{\pm}(\mathbf{r}) = n_s e^{\mp e \phi(\mathbf{r})/k_B T}$ . The parameter  $n_s$  is determined by the total salt content.

These equations are closed by the Poisson-Boltzmann equation  $\Delta \phi(\mathbf{r}) + (e/\epsilon)n_t(\mathbf{r}) = 0$ . We resort to the Debye-Hückel approximation (DHA) that consists in linearizing the charge distribution  $n_t(\mathbf{r})$  in terms of the potential  $\phi(\mathbf{r})$ ; it is valid at distances beyond the Bjerrum length  $l_B = e^2/\epsilon k_B T$ , where the electrostatic energy is smaller than  $k_B T$ . The solution of the linearized Poisson-Boltzmann equation reads as  $\phi(\mathbf{r}) = \sum_{\alpha} \varphi_{\alpha}(\mathbf{r})$ , where  $\varphi_{\alpha}(\mathbf{r})$  is the potential of a surface charge at  $\mathbf{r}_{\alpha}$  and, thus, the solution of

$$\Delta \varphi_{\alpha}(\mathbf{r}) - \theta(z)\theta(d-z)\kappa^2 \varphi_{\alpha}(\mathbf{r}) = -\frac{Q}{\epsilon} \delta(\mathbf{r} - \mathbf{r}_{\alpha}). \quad (3)$$

We have introduced the inverse Debye screening length  $\kappa = \sqrt{2n_s e^2/k_B T \epsilon}$ . [The charge density  $n_t(\mathbf{r})$  vanishes outside the film, whereas the potential  $\phi(\mathbf{r})$  does not.]

The Debye-Hückel free energy of the electrolyte solution for fixed surface charge distribution  $\{\mathbf{r}_{\alpha}\}$  is obtained by inserting the equilibrium distribution in (1) and expanding to quadratic order in  $\phi$ ,

$$F(\{\mathbf{r}_{\alpha}\}) = \frac{1}{2} Q \sum_{\alpha, \beta} \varphi_{\beta}(\mathbf{r}_{\alpha}). \quad (4)$$

In real systems, the charges are not fixed but diffuse on the interfaces. Performing the trace over  $\{\mathbf{r}_{\alpha}\}$  leads to the free energy  $\mathcal{F} = -k_B T \ln \text{Tr}\{e^{-F(\{\mathbf{r}_{\alpha}\})/k_B T}\}$  and to the disjoining pressure  $P = -(1/S)\partial \mathcal{F}/\partial d$  that reads explicitly as

$$P = \frac{Q}{2S} \sum_{\alpha, \beta} \langle \partial_d \varphi_{\beta}(\mathbf{r}_{\alpha}) \rangle, \quad (5)$$

where angular brackets  $\langle \dots \rangle$  denote the configurational average with statistical weight  $e^{-F/k_B T}$ .

Diagonal and off-diagonal parts of the double sum in (5) give rise to very different contributions to the pressure. In physical terms, the diagonal ones ( $\alpha = \beta$ ) describe the interaction of each of the  $N$  surface charges with its

proper screening cloud, whereas the off-diagonal parts ( $\alpha \neq \beta$ ) account for the screened interaction of discrete charges at  $\mathbf{r}_{\alpha}$  and  $\mathbf{r}_{\beta}$ . Accordingly, the pressure may be separated into two parts,  $P = P_1 + P_2$ , where

$$P_1 = \sigma Q \partial_d \varphi(0), \quad P_2 = \sigma Q \sum_{\alpha}^{\prime} \langle \partial_d \varphi(\mathbf{r}_{\alpha}) \rangle, \quad (6)$$

and the prime indicates that the term evaluated at the origin ( $\mathbf{r}_{\alpha} = 0$ ) is missing in the sum. Both terms are expressed through the screened potential of a charge at the origin  $\varphi(\mathbf{r})$ , and the number density of surface charges on each interface,  $\sigma = N/2S$ . The isolated-charge contribution is linear in the number density,  $P_1 \sim \sigma$ , and the remaining one quadratic,  $P_2 \sim \sigma^2$ . The present Letter is mainly concerned with  $P_1$ .

Equations (5) and (6) relate the disjoining pressure to the potential of a single charge at the origin,  $\varphi(\mathbf{r}) = \varphi(\rho, z)$ . We solve the linearized Poisson-Boltzmann equation by taking advantage of the cylindrical symmetry and using the 2D Fourier transform  $\tilde{\varphi}(\mathbf{q}, z)$  [16],

$$\varphi(\rho, z) = \int \frac{d^2 q}{(2\pi)^2} \tilde{\varphi}(\mathbf{q}, z) e^{i\mathbf{q}\cdot\rho}. \quad (7)$$

Equation (3) thus reduces to the ordinary differential equation

$$\partial_z^2 \tilde{\varphi} - q^2 \tilde{\varphi} - \kappa^2 \theta(z)\theta(d-z) \tilde{\varphi} = -\frac{Q}{\epsilon} \delta(z). \quad (8)$$

In Fourier space, this equation can be solved for the usual boundary conditions of electrostatics that impose continuity at the interfaces on both the potential  $\tilde{\varphi}$  and the derivative  $\epsilon \partial_z \tilde{\varphi}|_{\text{inside}} = \epsilon_0 \partial_z \tilde{\varphi}|_{\text{outside}}$  [17]. As the dielectric constant outside the film is much smaller than inside ( $\epsilon \sim 80$  for water), we consider the limit  $\epsilon/\epsilon_0 = 0$ ; then the second boundary condition reduces to  $\partial_z \tilde{\varphi} = 0$  and the solution inside simplifies significantly,

$$\tilde{\varphi}(\mathbf{q}, z) = \frac{Q}{\epsilon} \frac{\cosh[\sqrt{q^2 + \kappa^2}(z-d)]}{\sqrt{q^2 + \kappa^2} \sinh(\sqrt{q^2 + \kappa^2}d)}. \quad (9)$$

For a film thickness much larger than the Debye screening length,  $\kappa d \gg 1$ , inverse Fourier transformation gives  $\varphi(\mathbf{r}) \simeq (Q/2\pi\epsilon r) e^{-\kappa r}$ , i.e., the potential in a semi-infinite electrolyte solution. The counterion distribution is just twice that for the entire space. In the opposite case of thin films or weak screening,  $\kappa d \ll 1$ , the potential cannot be evaluated analytically, except for very large distances  $\rho \gg d$ , where it is independent of  $z$  and reads as  $\varphi(\mathbf{r}) \simeq (Q/2\pi\epsilon d) K_0(\kappa\rho)$ , with the modified Bessel function of the second kind and zeroth order  $K_0$ .

It is interesting to note that the vertically integrated density,  $\int_0^d (n_+ - n_-) dz = -(Q\kappa^2/2\pi e) K_0(\kappa\rho)$ , is independent of the film thickness  $d$ . This means that reducing the film thickness leads to densification of the screening cloud rather than to spreading.

We calculate the two contributions to the disjoining pressure (6) in terms of the potential (9). We start with  $P_1$  that arises from the interaction of a single-charge  $Q$  with its screening cloud. When inserting the Fourier transform  $\tilde{\varphi}(\mathbf{q}, z)$  in  $P_1 = \sigma Q \partial_d \varphi(0)$ , taking the derivative, and performing the integral, we obtain

$$P_1 = \frac{\sigma Q^2}{2\pi\epsilon d^2} [k d \coth \kappa d - \ln(2 \sinh \kappa d)]. \quad (10)$$

For thick films or high salinity, the pressure decreases exponentially,

$$P_1 = \frac{\sigma Q^2 \kappa e^{-2\kappa d}}{\pi\epsilon d} \quad (\kappa d \gg 1).$$

(Note the factor 2 in the exponent.) In the opposite case of thin films or large screening length, we find a power law behavior with a logarithmic correction,

$$P_1 = -\frac{\sigma Q^2 \ln(\kappa d)}{2\pi\epsilon d^2} \quad (\kappa d \ll 1).$$

Now we turn to the second part of the disjoining pressure,  $P_2$ , that involves interaction of different screened charges. Because of the relatively weak electrostatic energies, we may approximate the distribution function of the average by a constant density  $\sigma$  on both interfaces. Then the weighted sum over  $\alpha$  in (5) reduces to the integral  $\sigma \int d^2\rho$ . Inserting the electrostatic potential (7) and (9), we thus recover the well-known expression for the disjoining pressure of uniformly charged parallel plates [1],

$$P_2 = \frac{\sigma^2 Q^2}{2\epsilon} \frac{1}{\sinh^2(\kappa d/2)}. \quad (11)$$

Within Debye-Hückel approximation, Eq. (11) becomes exact in the limit of a uniform-charge density; on the other hand, it provides a good approximation for the dilute case, since the ‘‘correlation hole’’ in the two-particle correlation function is weak for  $Q\varphi < k_B T$ .

According to (10) and (11), the main effect of the discrete charges on the pressure  $P = P_1 + P_2$  consists in the additional term  $P_1$ . Note that  $P_1$  vanishes in the limit of a uniform-charge density,  $Q \rightarrow 0$  with  $Q\sigma = \text{const}$ . As is obvious from  $P_1 \sim \sigma$  and  $P_2 \sim \sigma^2$ , the new term is most significant when the number density of surface charges  $\sigma$  is small. For thick films or strong screening the ratio of the two pressure contributions reads as

$$\frac{P_2}{P_1} = \frac{\sigma d}{\kappa} e^{\kappa d} \quad (\kappa d \gg 1). \quad (12)$$

For very large  $\kappa d$  this ratio is larger than unity, and  $P_1$  is of little relevance; yet for moderate values of  $\kappa d$  and low number density ( $\sigma d^2 \ll 1$ ), the additional term  $P_1$  may exceed the uniform-charge pressure  $P_2$ . In the case of thin films or weak screening we have

$$\frac{P_2}{P_1} = \frac{\sigma}{\kappa^2} \frac{1}{\ln(1/\kappa d)} \quad (\kappa d \ll 1). \quad (13)$$

The discrete nature of the charges is relevant at densities below  $\sigma \approx \kappa^2$ , i.e., when the lateral distance  $a = \sigma^{-1/2}$  is comparable to or larger than the screening length  $1/\kappa$ . One can show that DHA breaks down at a density  $\sigma_{\text{DH}}$  that is larger than  $\kappa^2$  [17]. Thus the pressure shows three regimes as a function of density: discrete-charge behavior  $P_1$  at small  $\sigma$ , the well-known 1D pressure  $P_2$  at intermediate density, and beyond DHA for  $\sigma > \sigma_{\text{DH}}$ . The single-charge expression is valid for  $d \leq \kappa^{-1} < a$ . Such a situation is realized, e.g., in neutral phospholipid black films with a small amount of the charged peptide melittine ( $Q = 6e$ ) [15]. More generally, it should apply to various weakly dissociated ionic amphiphilic layers, where the lateral distance  $a$  may easily exceed hundreds of angstroms.

Up to now we have considered a rigid interface. Solute or self-supporting amphiphilic layers, however, are flexible and will respond locally to the pressure due to a discrete charge. Here we study the case of an isolated surface charge in the lower interface and evaluate the resulting force per unit area  $\pi_{l,u}(\rho)$  on the upper and lower interfaces, with profiles  $\delta h_l(\rho)$  and  $d + \delta h_u(\rho)$ . The local pressure is the functional derivative of the free energy with respect to the profiles and can be defined through the linear term of the expansion

$$\mathcal{F}[\delta h_i(\rho)] = \mathcal{F}[0] - \int_{S'} d^2\rho \pi_i(\rho) \delta h_i(\rho), \quad (14)$$

with  $i = l, u$ . This free energy, and thus  $\pi_{l,u}(\rho)$ , is calculated from the screened potential  $\psi(\mathbf{r})$  of a surface charge at the origin, where  $\psi(\mathbf{r})$  is the solution of  $\Delta\psi - \kappa^2\psi = -\epsilon^{-1}Q\delta(\mathbf{r})$ , with the deformed interface profile defining the surface  $S'$ . (For  $\epsilon_0/\epsilon = 0$  the normal gradient of  $\psi$  vanishes on  $S'$ .) We introduce the propagator  $G(\mathbf{r}, \mathbf{r}')$  for the solution of this equation at planar interfaces,  $\delta h_i \equiv 0$ . Using Green's theorem, one can show that  $\psi$  is the solution of the integral equation

$$\psi(\mathbf{r}) = G(\mathbf{r}, 0) - \frac{\epsilon}{Q} \int_{S'} ds' \psi(\mathbf{r}') \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial n'}, \quad (15)$$

where  $\partial/\partial n'$  is the normal component of the gradient on  $S'$  that can be decomposed in  $\partial_z$  and  $\partial_\rho$  [18]. Equation (14) is evaluated perturbatively by expanding the right-hand side in terms of  $\delta h_i(\rho')$ . (Details of this calculation are given elsewhere [17].)

With the relations for a single surface charge,  $\varphi(\mathbf{r}) = G(\mathbf{r}, 0)$  and  $\mathcal{F} = Q\psi(0)$ , we finally obtain the local pressure on the interface opposite to the single-charge  $Q$ :

$$\pi_u = \frac{\epsilon}{2} \{ \kappa^2 \varphi(\rho, d)^2 + [\partial_\rho \varphi(\rho, d)]^2 \}. \quad (16)$$

The unperturbed potential  $\varphi(\rho, z) = \varphi(\mathbf{r})$  is calculated numerically from its Fourier transform (9). In Fig. 2 we

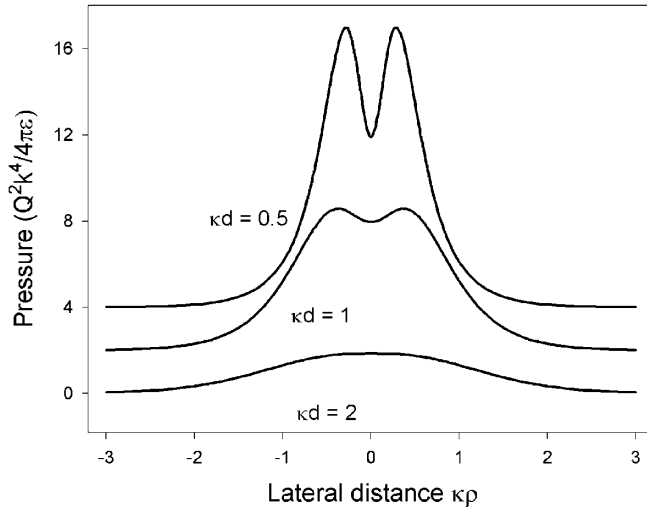


FIG. 2. The pressure profile at the upper interface  $\pi_u(\rho)$  produced by a charge on the lower one, for several values of the reduced thickness  $\kappa d$ .

plot  $\pi_u$  as a function of the reduced lateral distance  $\kappa\rho$  for several values of  $\kappa d$ . Surprisingly, the maximum of  $\pi_u(\rho)$  is not necessarily at the origin. Whereas the potential  $\varphi(\rho, d)$  is largest at  $\rho = 0$ , its derivative  $\partial_\rho \varphi$  vanishes at the origin and takes its maximum value at finite distance. This latter contribution becomes more important as  $\kappa d$  decreases. Figure 2 indicates that the typical size of the pressure distribution  $\pi_u(\rho)$  is given by the film thickness  $d$  and not by the Debye screening length  $1/\kappa$ . The Debye-Hückel approximation breaks down at distances shorter than the Bjerrum length  $\ell_B \sim 8 \text{ \AA}$ . Since for low salinity,  $n_s \sim 10 \text{ mM}$ , this occurs at  $\kappa\rho \sim 0.05$ , our main results are well in the range of validity.

Quite a different behavior is found for the pressure at the lower interface,

$$\pi_l = \frac{\epsilon}{2} \{ \kappa^2 \varphi(\rho, 0)^2 + [\partial_\rho \varphi(\rho, 0)]^2 - Q \partial_z \varphi(\rho, 0) \delta(\rho) \}. \quad (17)$$

The two positive terms arise from the counterion cloud, whereas an opposite contribution occurs at the position of the charge  $Q$ . Both positive and negative terms in  $\pi_l(\rho)$  diverge; yet these singularities cancel each other. The pressure profile  $\pi_l$  is significant within one screening length  $1/\kappa$  of the origin and hardly depends on the film thickness  $d$ . Integrating  $\pi_l$  and  $\pi_u$  and multiplying with the number of surface charges  $N$ , we recover, of course,  $P_1$  as given in (10).

From these profiles we conclude that charged interfaces with  $\sigma d^2 \leq 1$  experience a highly inhomogeneous pressure. Since amphiphilic layers are flexible objects, the pressure, i.e., the force acting on an area of the size of the persistence length, may induce long-range interactions between discrete charges and local deformations [17]. According to recent ellipsometry measurements, a neutral black film ( $d \sim 2 \text{ nm}$ ) thickens upon adding a

small amount of the charged peptide melittine [15]. At low charge density, our results would suggest formation of blobs of the size of the screening cloud of a single melittine [17]. As a consequence, increasing the number of surface charges would lead to an inhomogeneous thickening of the core.

In summary, we have studied the disjoining pressure of discrete charges on an aqueous film. Besides the well-known contribution  $P_2 \sim \sigma^2$ , we find an additional term linear in the surface charge density  $P_1 \sim \sigma$ . According to (13), the new term is dominant for thin films at low salinity and few surface charges,  $d < \kappa^{-1} < a$ , with the lateral distance  $a \sim \sigma^{-1/2}$ . In this case, the usual expression of the continuously charged plates model ceases to be valid, since it is based on a uniform surface charge with a pressure quadratic in  $\sigma$ . At low surface charge density, the disjoining pressure is not uniform but concentrated in an area  $\sim d^2$  about each charge. For weak screening,  $\kappa d < 1$ , the local pressure takes its maximum at a finite lateral distance from the charge, as shown in Fig. 2. Equilibrating this pressure with London forces and elasticity is likely to induce local deformations on the interfaces.

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