Disjoining Pressure and Algebraic Screening of Discrete Charges at Interfaces

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We study the electrostatic properties of discrete charges at an electrolyte−insulator interface. The associated counterion cloud comprises, besides the exponential Debye screening, an algebraic tail with an amplitude that depends on the dielectric constant ϵ_{ins} of the insulator. For very thin electrolyte films, the counterions spread to large distances well beyond the Debye length. At low surface charge density, the disjoining pressure of a thin film is dominated by single-charge effects and depends on ϵ_{ins}.

I. Introduction

The electrostatic forces acting on charges at an electrolyte−insulator interface are of considerable interest in colloid science and biophysics.[1−4] Highly charged DNA and cationic lipids form stable complexes that give rise to a rich phase diagram with a variety of mesoscopic structures.[5,6] Ionized molecules contribute to the disjoining pressure of thin soap films and may significantly enhance the distance of adjacent phospholipid bilayers in lamellar phases.[1,7,8] Charged colloidal particles trapped at a water−oil interface interact through dipolar and capillary forces on the order of 10^{-10} N[9−11] that may result in the formation of a 2D crystal.[12,13]

A charge Q in an electrolyte is dressed by a cloud of counterions and soluted salt ions. In the simplest case of a homogeneous electrolyte, the mean-field counterion distribution $-Q(\kappa^2/4\pi r)e^{-\kappa r}$ decays exponentially on the length scale of the Debye−Hückel screening parameter κ^{-1}. For interfacial charges, a much more complex picture arises due to the confinement of the counterions. Because of the competition of Coulomb interactions and entropy, the effective electrostatic potential of interfacial charges and the soluted counterions constitute an intricate theoretical problem.

Two parallel charged plates separated by an electrolyte film provide a toy model that has been widely studied in the literature, mostly in mean-field approximation with respect to the counterions, i.e., in terms of the Poisson−Boltzmann equation. Its linearized version corresponds to the Debye−Hückel approximation (DHA), where the counterion density is proportional to the screened electrostatic potential inside the film.[2] For uniformly charged plates, the counterions form homogeneous layers that decay exponentially with the vertical distance from the plates. Electrostatic and entropic forces result in a positive disjoining pressure that may be expressed through the counterion density at midplane.[2]

Nonuniform surface charges have been treated in various approximations. Parallel plates with a two-dimensional periodic lattice of charges have been treated by Debye−Hückel approximation (DHA)[14,15] and by a strong coupling theory.[16] At high surface-charge densities, the number of soluted counterions exceeds that of salt ions, and the latter may be neglected. The disjoining pressure of parallel plates has been shown to increase upon charge modulation[17] and to depend on the valency of the counterions.[18] A perturbative treatment beyond mean-field theory showed that long-wavelength modulations enhance the counterion localization near the plates;[19] moreover, fluctuations of the surface charge density significantly reduce the disjoining pressure and may even result in an overall attractive force.[20−22] For high charge densities, these ideas were confirmed by a strong coupling theory that pointed out the role of charge correlations;[23] DNA complexation provides a prominent example.[24−26]

At low number density, however, it turns out essential to retain the discrete nature of the surface charges. Single-charge effects are expected to dominate the electrostatic properties of weakly dissociated ionic molecules in membranes or soap films and charged colloidal particles at an interface. If the lateral distance of the charges exeeds the thickness of the electrolyte film and the Debye length, one has to consider the potential of a single charge that is screened by the associated counterion cloud. The Debye−Hückel theory of a single interfacial charge can be solved in 2D Fourier space.[27,28,31] More recently, the pair potential of two charges has been evaluated for various slab geometries,[32] and the single-charge disjoining pressure of a thin film has been calculated for a zero dielectric constant in the insulating medium, $\epsilon_{ins} = 0$.[33]

In this paper, we consider discrete surface charges confined by two insulating plates with finite dielectric constant. Section II gives a brief review of Debye−Hückel theory. In section III, we derive the counterion distribution as a series in powers of the inverse lateral distance, and we discuss the algebraic tail of the counterion cloud and the case of nonexponential screening. Section IV is devoted to the disjoining pressure and, in particular, to the single-charge contribution and its dependence on ϵ_{ins}. The effective interaction of two surface charges is obtained in section V and evaluated for various limiting cases. Finally we discuss and summarize our results. The appendices contain technical details of the calculations.

II. Discrete Charges at an Interface

A. Debye−Hückel Theory. Our model consists of an electrolyte film confined between two semi-infinite insulators. Each of the interfaces at $z = 0$ and $z = d$ contains $N/2$ discrete

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point charges Q localized at $\{r_\alpha\}$. The charge density of the soluted counterions and salt ions reads

$$n(r) = n_+(r) - n_-(r) \qquad (1)$$

and thus we have the total charge density

$$n_t(r) = Q \sum_\alpha \delta(r - r_\alpha) + n(r) \qquad (2)$$

Electroneutrality of the system imposes $\int n dV = -NQ$. The electrostatic potential $\phi(r)$ is determined by the Poisson equation

$$\text{div}[\epsilon(r)\nabla\phi(r)] + n_t(r) = 0 \qquad (3)$$

The dielectric constant $\epsilon(r)$ is not the same inside and outside the electrolyte film, where it is denoted ϵ_{el} and ϵ_{ins}, respectively.

This paper relies on two basic approximations: first, the bulk charge density is treated in mean-field approximation, resulting in an effective screened interaction of the discrete surface charges at the interfaces. Second, assuming that the electrostatic energy $e\phi$ is smaller than kT at relevant distances, we resort to the DHA. In the first step, the mean-field approximation gives the free energy as a functional of the positive and negative bulk ions densities $n_\pm$

$$F = k_B T \sum_\pm \int d^3r n_\pm(r)(\ln(n_\pm(r)/n_s) - 1) +$$
$$\frac{1}{2} \int\int d^3r d^3r' n_t(r)v(r,r')n_t(r') \quad (4)$$

The first line in eq 4 is the ideal-gas-like entropy of the bulk ions, whereas the second one contains the electrostatic interactions of both surface and bulk charges. n_s is the mean salt ion density in the electrolyte and $v(r,r')$ the electrostatic propagator $v(r,r')$ that obeys the differential equation $\text{div}[\epsilon(r)\nabla v(r,r')] = -\delta(r - r')$. The total electrostatic potential appearing in eq 3 can be written as

$$\phi(r) = \int d^3r' n_t(r')v(r,r')$$

The equilibrium bulk charge densities are obtained by minimizing the free energy, $\delta F/\delta n_\pm = 0$, resulting in

$$n_\pm(r) = n_s e\theta(z)\theta(d - z)e^{\mp e\phi(r)/k_B T} \qquad (5)$$

where the step function θ imposes that the ion density vanishes outside the electrolyte.

Inserting eq 5 in 3, we obtain the well-known Poisson–Boltzmann equation satisfied by the screened potential ϕ. The DHA consists of linearizing $n_\pm(r)$ in terms of $e\phi/k_B T$. For monovalent ions, this quantity is small at distances larger than the Bjerrum length

$$l_B = \frac{e^2}{4\pi\epsilon_{el}k_B T}$$

As a direct consequence of DHA, the bulk charge density is proportionnal to the screened potential

$$n(r) = -\theta(z)\theta(d - z)\kappa^2\epsilon_{el}\phi(r) \qquad (6)$$

and eqs (1–3) reduce to a linear differential equation with the inverse of the Debye screening length

$$\kappa = (8\pi n_s l_B)^{1/2}$$

The solution of the linearized equation can be written as a superposition

$$\phi(r) = \sum_\alpha \varphi_\alpha(r) \qquad (7)$$

The screened potential $\varphi_\alpha(r)$ arises from the discrete surface charge at r_α and the associated counterion cloud and satisfies

$$\text{div}(\epsilon(r)\nabla\varphi_\alpha(r)) - \kappa^2\epsilon_{el}\theta(z)\theta(d - z)\varphi_\alpha(r) = -Q\delta(r - r_\alpha) \qquad (8)$$

In DHA, all properties derive directly from the screened potential. The detailed calculation for the confined geometry is given in Appendix A.

When inserting the equilibrium bulk charge density eq 5 in eq 4, we obtain the free energy of a given discrete charge distribution $F(\{r_\alpha\})$. Expanding in terms of the potentials φ_α, we obtain the linear Debye–Hückel form

$$F(\{r_\alpha\}) = \frac{Q}{2} \sum_{\alpha,\beta} \varphi_\beta(r_\alpha) \qquad (9)$$

There is no quadratic term; corrections are of third order. Thus the free energy reduces to the electrostatic energy of the surface charges that interact through the screened potential φ_α.

B. Disjoining Pressure: General Expression. Most real systems, such as charged colloidal particles at an interface or charged proteins on a membrane, are two-dimensional fluids, i.e., the discrete charges are mobile at the surface. Then the total free energy

$$\mathscr{F} = -k_B T \ln Z \qquad (10)$$

involves the configurational average with respect to the surface charges

$$Z = \prod_{\alpha=1}^N \int d^3r_\alpha e^{-F(\{r_\alpha\})/k_B T} \qquad (11)$$

It turns out convenient to separate the diagonal, $\varphi_\alpha(r_\alpha)$, or "self-energy" terms, in eq 9 from the remainder, the "interaction energy" of the surface charges

$$\mathscr{F} = \mathscr{F}_{self} + \mathscr{F}_{int} \qquad (12)$$

Noting that $\varphi_\alpha(r_\alpha)$ does not depend on the charge position, one finds in a straightforward manner

$$\mathscr{F}_{self} = \frac{1}{2} \sum_\alpha Q\varphi_\alpha(r_\alpha) = \frac{1}{2} NQ\varphi(0)$$

where $\varphi(r)$ denotes the screened potential of a surface charge located at the origin.

The interaction of a point charge with its electrostatic potential gives rise to an unphysical divergency; accordingly, $Q\varphi_\alpha(r_\alpha)$ in the above expression is infinite. (In principle, $\mathscr{F}$ could be made finite by adding constant counterterms.) Yet since the derivative of $\mathscr{F}_{self}$ with respect to the film thickness d, i.e., the disjoining pressure, is finite in any case, this divergency is irrelevant for our purpose, and we may use the free energy as it stands. The remaining part $\mathscr{F}_{int}$ arises from the interaction of different surface charges $\alpha \neq \beta$ and reads explicitly

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$$\frac{\mathscr{F}_{\text{int}}}{k_{\text{B}}T} = -\ln\left\{\prod_{\alpha,\beta\neq\alpha}\int d^3r_\alpha e^{-\varphi_\beta(r_\alpha)/2k_{\text{B}}T}\right\}$$

Because of its dependence on the film thickness d, the free energy $\mathscr{F}$ contributes to the disjoinig pressure of the aqueous film

$$P = -\frac{1}{S}\frac{\partial\mathscr{F}}{\partial d} \tag{13}$$

which we separate according to eq 12

$$P = P_{\text{self}} + P_{\text{int}} \tag{14}$$

The first one, which is called single-charge pressure in the remainder of the paper, is given by

$$P_{\text{self}} = -\sigma Q \partial_d\varphi(0) \tag{15}$$

where $\sigma = N/2S$ is the mean surface charge density. $P_{\text{self}} \approx N$ is a sum of N independent contributions that express the force resulting from the confinement of the counterion screening cloud of each charge. The second term arises from the screened repulsive interaction of the surface charges and reads

$$P_{\text{int}} = -\sigma Q \sum_{\alpha\neq0}\langle\partial_d\varphi(r_\alpha)\rangle \tag{16}$$

We have taken advantage of the translational symmetry and expressed $\mathscr{F}_{\text{int}}$ by the potential of the charge at the origin, φ. Angular brackets denote the thermal average with statistical weight $e^{-F/k_{\text{B}}T}$

$$\langle...\rangle = \frac{1}{Z}\prod_{\alpha=1}^{N}\int d^3r_\alpha(...)e^{-F(\{r_\alpha\})/k_{\text{B}}T}$$

The single-charge pressure P_{self} constitutes the main results of this section. This term would disappear when using a continuous charge density $\sigma(r)$, i.e., when putting $Q \to 0$ and $N \to \infty$ with $NQ = \text{constant}$. Thus P_{self} is a signature of the discrete nature of the surface charges. Though we postpone the detailed calculation of P_{self} to section IV, we briefly discuss how the two pressure contributions scale with the mean surface charge density $\sigma = N/2S$. Since it involves forces induced by a single charge, the first term is linear, $P_{\text{self}} \approx \sigma$. As to the interaction term, eq 16 clearly indicates a quadratic dependence, $P_{\text{int}} \approx \sigma^2$. Thus the single-charge pressure is expected to be dominant at small densities, i.e., at large lateral distances and weak interactions of surface charges. At the opposite, P_{int} should be dominant when the lateral distance of surface charges is smaller than the interaction range, κ^{-1}. A more quantitative discussion is given in section IV.

The single-charge pressure arises from the confinement-induced modification of the single-charge energy $Q\varphi(0)$. The free ions have to adapt their distribution to the geometrical constraints. The corresponding squeezing of the counterion cloud costs entropic and electrostatic energy that is at the origin of the disjoining pressure acting on the interfaces. In the next section, we discuss how the charge distribution changes upon squeezing.

III. Counterion Distribution

A charge Q in a homogeneous electrolyte with dielectric constant ϵ is screened by an isotropic counterion cloud of radius κ^{-1}

$$n_0(r) = -\frac{Q\kappa^2}{4\pi r}e^{-\kappa r} \tag{17}$$

For a charge at an electrolyte−insulator interface, a more complex picture arises. First, the screening cloud is anisotropic, since confined to one side of the interface. Second, the dielectric constant is in general discontinuous at the interface $\epsilon_{\text{el}} \neq \epsilon_{\text{ins}}$, imposing boundary conditions on the potential. The situation is even more complicated for a thin film, with a second interface at a distance d, the most obvious consequence being the confinement of the counterions from both sides.

We consider a single charge at the origin on the interface at $z = 0$. In DHA, the excess charge density is linear in the screened potential

$$n(\rho,z) = -\epsilon_{\text{el}}\kappa^2\varphi_{\text{el}}(\rho,z) \tag{18}$$

which, in turn, is given in terms of its Fourier transform (eq A5). The inverse Fourier integral cannot be performed exactly but can be written in terms of the series for the electrostatic potential (eq B3). Noting that even terms vanish and inserting in eq 18, we find

$$n(\rho,z) = -\frac{\epsilon_{\text{el}}\kappa^2}{2\pi}\sum_{n=0}^{\infty}\frac{M_{2n+1}}{(2n+1)!}\psi_{2n+1}(z)\rho^{-(3+2n)} \tag{19}$$

A. Semi-Infinite Electrolyte. We start with the case of single interface separating the electrolyte at $z > 0$ from the insulating domain $z < 0$. For zero dielectric constant in the insulator, the linearized Poisson−Boltzmann eq 8 is easily solved. Then the counterion density

$$n(\rho,z) = 2n_0(r)\theta(z) \qquad (\epsilon_{\text{ins}} = 0)$$

depends only on the distance $r = (\rho^2+z^2)^{1/2}$ and thus is isotropic in the upper half space. By comparison with the result for a charge in a homogeneous electrolyte (eq 17), we find that confinement to one half space hardly affects the screening behavior, except for an obvious factor 2.

Now we turn to the case of finite ϵ_{ins}. As long as the dielectric constants satisfy $\epsilon_{\text{ins}} \ll \epsilon_{\text{el}}$, the counterion density at short distances is similar to that of $\epsilon_{\text{ins}} = 0$. At distances well beyond the Debye length, however, a finite ϵ_{ins} results in a qualitatively different screening behavior. Inserting the derivative (eq B7) in the leading term of eq 19 yields the asymptotic form

$$n(\rho,z) = -\frac{\epsilon_{\text{ins}}}{\epsilon_{\text{el}}}\frac{Q}{2\pi\rho^3}e^{-\kappa z} \qquad (\rho \text{ large}) \tag{20}$$

The precise meaning of "large ρ" is discussed below. $n(\rho,z)$ obeys a power law with respect to the lateral distance from the surface charge but decays exponentially in the normal direction. Thus for finite ϵ_{ins}, the counterion density spreads along the interface but hardly penetrates the electrolyte beyond one Debye length.

B. Electrolyte Films. Now we consider how a second interface at $z = d$ modifies the counterion density. Although its asymptotic expression could be written in terms of $\psi_1(z)$ as given in Appendix B, it proves convenient to consider the density integrated along the z axis

$$\sigma(\rho) = \int_0^d n(\rho,z)\,\text{d}z \tag{21}$$

We briefly discuss the limiting case $\epsilon_{ins} = 0$, where $\sigma(\rho)$ can be calculated exactly

$$\sigma(\rho) = -Q \int_0^d dz \int_0^\infty dq q \frac{\cosh(\hat{q}(d-z))}{\hat{q} \sinh(\hat{q}d)} J_0(q\rho)$$

Integrating over z first and using $\int_0^\infty dq q \hat{q}^{-2} J_0(q\rho) = K_0(\kappa\rho)$ yields the result obtained in our previous paper[33]

$$\sigma(\rho) = -\frac{Q\kappa^2}{2\pi} K_0(\kappa\rho) \qquad (\epsilon_{ins} = 0) \qquad (22)$$

where the modified Bessel function of a second kind behaves as $K_0(\kappa\rho) \approx e^{-\kappa\rho}$ at large distances. Thus for a vanishing dielectric constant in the insulating "outside", the counterion density decreases exponentially at large lateral distances ρ, and there is no spreading along the interface. As a consequence, the vertically integrated density $\sigma(\rho)$ is independent of the film thickness d. This result for $\sigma(\rho)$ is identical to that of an infinite charged line in 3D space with charge density Q/d. This analogy may be understood by noting that the boundary conditions for $\epsilon_{ins} = 0$ and $\kappa d \ll 1$ reduce the electrostatic equations to those of a charged line.

Now we turn to the general case $\epsilon_{ins} \neq 0$. By insertion of the Fourier transform (eq A5) in expression 21 for $\sigma(\rho)$ and proceeding as in Appendix B, we obtain the series

$$\sigma(\rho) = \frac{1}{2\pi} \sum_{n=0}^\infty \frac{M_{2n+1}}{(2n+1)!} \tilde{\sigma}^{(2n+1)} \rho^{-(3+2n)}$$

where even terms vanish and the odd coefficients are given in eq B5. $\tilde{\sigma}^{(m)}$ involves m factors d or κ^{-1}. In leading order ($n = 0$), we have

$$\sigma(\rho) = -\frac{\chi Q}{2\pi\kappa\rho^3} \qquad (\rho \gg \rho^*) \qquad (23)$$

where we have introduced the dimensionless parameter

$$\chi = \frac{\epsilon_{ins}}{\epsilon_{el}} \coth \frac{\kappa d}{2} \qquad (24)$$

and the characteristic length

$$\rho^* = \begin{cases} 1/\kappa & (\chi < 1) \\ \chi/\kappa & (\chi > 1) \end{cases} \qquad (25)$$

The long-range tail of $\sigma(\rho)$ implies that part of the screening cloud spreads along the interface to distances well beyond the Debye length; the excess charge density $n(\rho,z)$ decays algebraically with the third power of the inverse laterel distance ρ.

The convergence of the above series for the charge density is poor. To confirm the validity of the first-order approximation (eq 23), we have evaluated the Fourier integral (eq A1) numerically. In Figure 1, we plot $\sigma(\rho)$ for $\epsilon_{ins}/\epsilon_{el} = 1/10$ and different values of the reduced film thickness, κd. For thick films, $\kappa d = 1$ and $\kappa d = 10$, the charge density is close to that of pure exponential screening, eq 22, at moderate distances; an algebraic tail is visible at large distances well beyond the Debye length. For thin films $\kappa d \ll 1$, the charge density at short distances decreases significantly and the counterions are spread to much larger distances, in perfect agreement with the asymptotic analytic expression 23 that is shown as a dotted line.

To quantify the charge contained in the algebraic tail of the distribution, we calculate the bulk charge outside a cylinder of lateral size ρ and centered at the surface charge
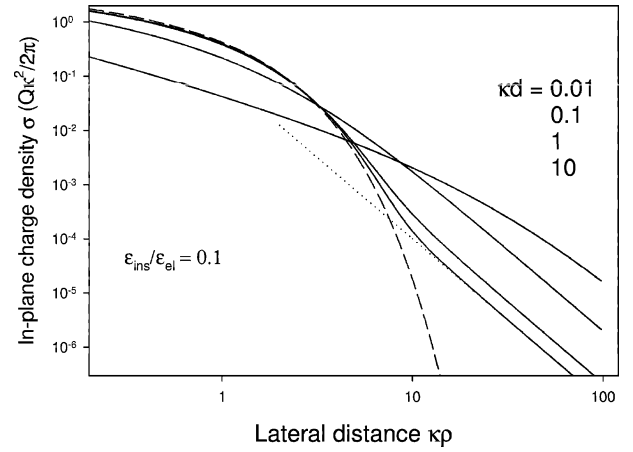
Figure 1. The vertically integrated counterion density $\sigma(\rho)$, as a function of the lateral distance ρ, for several values of the reduced film thickness κd. The dashed line corresponds to $d = \infty$ and $\epsilon_{in} = 0$, as given in eq 22. The dotted line is the asymptotic law (eq 23) for $\kappa d = 10$.

$$Q_>(\rho) = 2\pi \int_\rho^\infty \sigma(\rho')\rho' \, d\rho' \qquad (26)$$

At large distances, eq 23 gives immediately

$$Q_>(\rho) = -\frac{\chi Q}{\kappa\rho} \qquad (\rho \gg \rho^*) \qquad (27)$$

This relation elucidates the physical meaning of the parameter χ and the screening length ρ^*.

First we discuss the case $\chi < 1$. At a radius equal to the Debye length, we have $Q_>(\kappa^{-1}) \simeq -Q\chi$. Thus χ gives the fraction of the counterion charge located in the algebraic tail, well beyond the Debye length, whereas the remaining part $1 - \chi$ is contained within the exponential screening cloud. Now we turn to $\chi > 1$. The relation $Q_>(\rho^*) = -Q$ in eq 27 implies that the typical radius of the counterion cloud is given by $\rho^* = \chi/\kappa$, thus justifying the definition of the screening length ρ^*.

In summary, for $\chi \ll 1$, the screening cloud is confined within a distance of the order of the Debye length, though there is a small algebraic tail of weight χ. In the opposite case $\chi > 1$, which requires thin films ($\kappa d < 1$) and a large ratio of dielectric constants, the counterions spread well beyond the Debye length, with the characteristic distance

$$\rho^* = \frac{\epsilon_{ins}}{\epsilon_{el}} \frac{2}{\kappa^2 d}$$

These analytic results are confirmed by Figure 2, where we plot numerical results for the integrated charge $Q_>(\rho)$ at different values of the screening parameter χ.

IV. Disjoining Pressure

We start with the case of low surface charge density. Because of their large lateral distance, the surface charges do not interact with each other and can be taken as isolated. Then the disjoining pressure arises from the electrostatic properties of a single charge and the squeezing of the associated screening cloud. The pressure is obviously linear in the surface charge density; yet the dependencies on film thickness, salinity, and on the dielectric constants require a detailed analysis.

By insertion of the screened potential (eq A5) in the single-charge pressure (eq 15) and taking the derivative with respect to z, we obtain the general form

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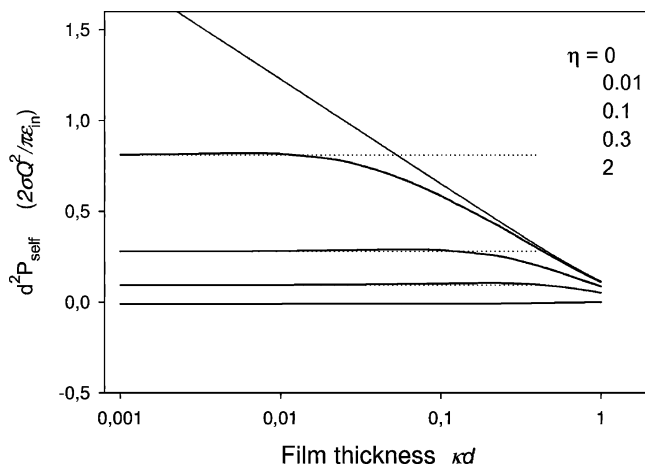
Figure 2. The integrated counterion density $Q_>(\rho)$ located beyond a distance ρ, for several values of the screening parameter χ and $\epsilon_{ins}/\epsilon_{el} = 1/10$. Note that $\chi = 0$ implies $\epsilon_{ins} = 0$.

$$P_{self} = \frac{2\sigma Q^2}{\pi\epsilon_{el}d^2} I(\kappa d, \eta) \qquad (28)$$

where we have defined the integral

$$I(\kappa d, \eta) = d^2 \int_0^\infty dq\, q \frac{\hat{q}^2\Delta_+\Delta_-}{[\Delta_+^2 e^{\hat{q}d} - \Delta_-^2 e^{-\hat{q}d}]^2} \qquad (29)$$

with the shorthand notation

$$\Delta_\pm = \hat{q} \pm \eta q \qquad \hat{q} = (q^2 + \kappa^2)^{1/2} \qquad (30)$$

and the ratio of the dielectric constants of the outside medium and the aqueous core

$$\eta = \frac{\epsilon_{ins}}{\epsilon_{el}} \qquad (31)$$

A. Single-Charge Pressure. Most real systems involve an aqueous core with the dielectric constant of water, $\epsilon_{el} \approx 80\epsilon_0$, and an outside material (air, oil, ...) with a much lower dielectric contstant, satisfying $\epsilon_{ins} \ll \epsilon_{el}$. In a previous work,[33] we have studied the technically simple case $\eta = 0$, where the integral (eq 29) reduces to $\int_0^\infty dq\, q\, \sinh^{-2}(\hat{q}d)$, resulting in the pressure

$$P_{self} = \frac{\sigma Q^2}{2\pi\epsilon_{el}d^2} [\kappa d \coth(\kappa d) - \ln(2\sinh(\kappa d))] \qquad (32)$$

The expression in brackets simplifies to $1 - \ln(2\kappa d)$ for thin films or $\kappa d \ll 1$ and to $\kappa d e^{-2\kappa d}$ for thick films or $\kappa d \gg 1$.

It turns out, however, that small but finite values of the ratio η may significantly modify the screening behavior and thus the pressure. Here we extend our previous work to finite η. In Figure 3 we plot the numerical results for $d^2 P_{self}$ as a function of the reduced thickness κd for several values of η. In films thinner than the Debye length, the pressure strongly depends on the ratio of dielectric constants. Increasing η reduces the pressure; for $\eta > 1$, the force may even become attractive for very small values of κd.

Analytical asymptotic expressions can be obtained for films with a thickness much larger or much smaller than the Debye screening length. In the following we report on these calculations in two limiting cases.
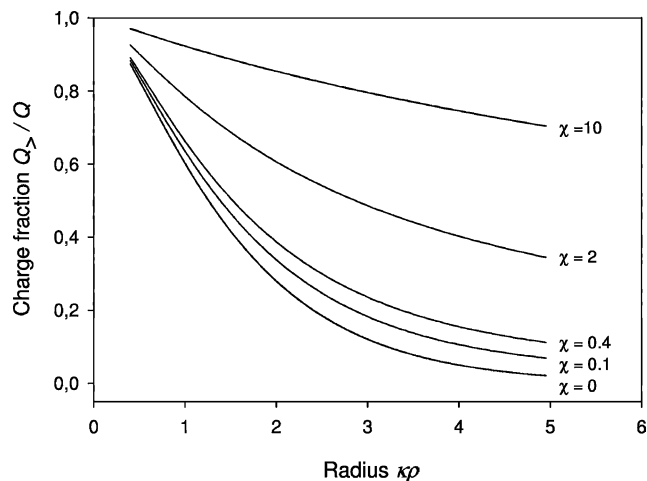
Figure 3. Single-charge pressure P_{self} as a function of the reduced film thickness κd. The curve for $\eta = 0$ is given by eq 32, those for finite η are evaluated numerically. The dotted lines are the analytic approximation (eq 36) for $\kappa d < \eta$.

B. Single-Charge Pressure of Thick Films with $\epsilon_{ins} > 0$. For thick films, with $\kappa d \gg 1$, one has $e^{\hat{q}d} \gg 1$ in (29); accordingly, the integral can be approximated as

$$I(\kappa d, \eta) = d^2 \int_0^\infty dq\, q \frac{\hat{q}^2\Delta_-}{\Delta_+^3} e^{-2\hat{q}d} \qquad (33)$$

In Appendix C, we apply a general method for the series expansion of a Laplace transform and obtain in eq 59 the asymptotic form of $I(\kappa d, \eta)$ for large κd, resulting in

$$P_{self} = \frac{\sigma Q^2 \kappa}{\pi\epsilon_{el}d} e^{-2\kappa d}\left[1 - \frac{4(2)^{1/2}\eta}{(\kappa d)^{1/2}} + \mathcal{O}\left(\frac{1}{\kappa d}\right)\right] \qquad (34)$$

The leading term is independent of $\eta = \epsilon_{ins}/\epsilon_{el}$ and provides a good approximation as long as $\eta \ll (\kappa d)^{1/2}$. The opposite case $\eta \gg (\kappa d)^{1/2} \gg 1$ turns out to be of little relevance, since for real systems with an aqueous core, the ratio $\eta = \epsilon_{ins}/\epsilon_{el}$ hardly exceeds unity. As a consequence, eq 34 provides in general a proper description for thick films, and we may conclude that their disjoining pressure does not depend on the dielectric constant of the outside medium.

C. Single-Charge Pressure of Thin Films with $\epsilon_{ins} > 0$. For thin films, the numerical results of Figure 3 indicate that the pressure significantly depends on the parameter η. Evaluation of the integral (eq 29) is, however, not an easy matter in the limit $\kappa d < 1$. In Appendix D, we derive the dominant behavior in terms of an asymptotic expansion. We find that the integral $I(\kappa d, \eta)$ indeed varies with the ratio $\eta/\kappa d$. Note that for thin aqueous films, both η and κd are small. Thus their ratio may take any positive value. (For thin films, the screening parameter (eq 24) simplifies to $\chi = 2\eta/\kappa d$.)

We start with the case $\eta \ll \kappa d$, that is realized, e.g., by a very small dielectric constant outside and a moderate value of κd. With the integral (eq 67), the pressure reads

$$P_{self} = \frac{\sigma Q^2}{2\pi\epsilon_{el}d^2} [1 - \ln(2\kappa d)] \qquad (\eta \ll \kappa d \ll 1) \quad (35)$$

Not surprisingly, this corresponds to eq 32, evaluated in the limit of small κd.

Now consider the opposite case of a large screening parameter, $1 \ll \chi$ or $\kappa d \ll \eta$, that is realized by very thin films, large

Debye length, and not too small ϵ_{ins}. (There is no constraint on the parameter η that may be smaller or larger than unity.) With eq 66, the expansion of the integral to first order in κd leads to

$$P_{self} = \frac{\sigma Q^2}{2\pi\epsilon_{el}d^2}\frac{\ln[(\eta+1)^2/4\eta]}{1-\eta^2} \qquad (\kappa d \ll \eta) \qquad (36)$$

Note that, in leading order, the pressure is independent of κ and thus independent of temperature and salinity. The force is entirely due to the interaction of the surface charge with the dielectric medium. In other words, it is reduced to the bare electrostrictive force created by the discrete charges on the interfaces of a dielectric pancake $\epsilon_{ins}/\epsilon_{el}/\epsilon_{ins}$. Because of the second factor in eq 36, this force vanishes at $\eta = 1$, i.e., $\epsilon_{ins} = \epsilon_{el}$; it is repulsive if $\eta < 1$ ($\epsilon_{ins} < \epsilon_{el}$) and attractive if $\eta > 1$ ($\epsilon_{ins} > \epsilon_{el}$). This may be understood by noting that the electrostatic field prefers passing through the medium with the lower dielectric constant.

We complete the discussion by considering the case $\eta = 1$ in more detail. Because of the uniform dielectric constant, $\epsilon_{ins} = \epsilon_{el}$, there is no electrostrictive force and eq 36 vanishes. There is, however, a small entropic contribution that arises from the confinement of the screening cloud and that shows a logarithmic behavior

$$P_{self} = -\frac{\sigma Q^2 \kappa^2}{4\pi\epsilon_{el}}\ln(2\kappa d) \qquad (\kappa d \ll \eta = 1) \qquad (37)$$

This pressure is a factor $(\kappa d)^2$ smaller than the electrostrictive force derived above for thin films and $\eta \neq 0$ and thus had been neglected in eq 36.

Summarizing our results for thin films, we find that for sufficiently different dielectric constants, i.e., η much smaller or much larger than unity, the electrostrictive force exceeds the entropic pressure; the latter is relevant at $\eta \approx 1$ only. It turns out that the single-charge pressure P_{self} depends on the screening paramter $\chi = 2\eta/\kappa d$, i.e., on the shape of the screening cloud. If $\chi \gg 1$, the pressure is dominated by the bare electrostrictive force eq 36 induced by the surface charge. The counterion density spreads well beyond the Debye length, far from the surface charge, and the disjoining pressure is independent of the electrolyte. In the opposite case of $\chi \ll 1$, the counterion cloud is located within one Debye length, and the disjoining pressure (eq 35) is due to its confinement.

In most real systems, such as soap films, lamellar phases of microemulsions, or colloids, the outside medium (air, oil, ...) has a low dielectric constant of the order of the vacuum permittivity, $\epsilon_{ins} \approx \epsilon_0$. The large value for the aqueous core, $\epsilon_{el} \approx 80\epsilon_0$, thus implies $\eta \ll 1$. With typical values for the Debye length, $10 < \kappa^{-1} < 100$ nm, even a film thickness of a few nanometers leads to screening parameter smaller than unity, $\chi < 1$, and to the pressure (eq 32) or, equivalently, eq 35. With very low salinity, i.e., small κ^{-1}, and somewhat larger ϵ_{ins}, one may, however, reach a situation where the screening parameter χ is larger than unity. In such a system, the single-charge pressure would be dominated by the bare electrostrictive force (eq 36).

D. Interaction Contribution. At higher densities, the interaction of charges on opposite interfaces contributes significantly to the disjoining pressure. Accounting for charge correlations would render the thermal average (eq 16) quite a difficult undertaking.[14] In DHA, however, it is consistent to neglect correlations and to replace the surface charge number density on both interfaces with the mean value $\sigma = N/2S$. Then
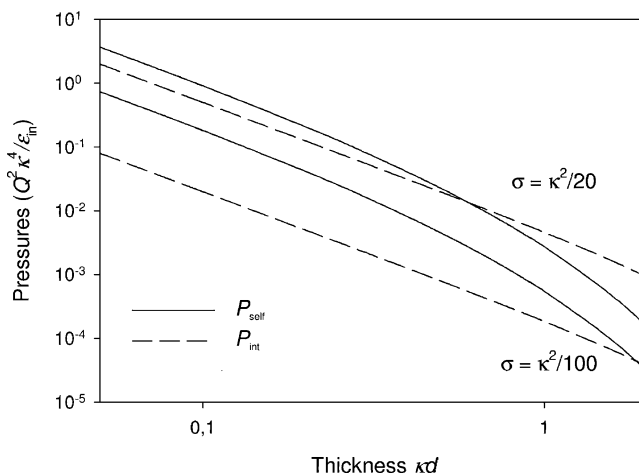
Figure 4. Comparison of the two contributions to the disjoining pressure as a function of the reduced film thickness κd for two values surface charge density σ. The single-charge pressure P_{self} dominates for thin films.

the linearized Poisson−Boltzmann equation reduces to a simple 1D differential equation, resulting in the well-known disjoining pressure of parallel charged plates

$$P_{int} = \frac{\sigma^2 Q^2}{2\epsilon_{el}}\frac{1}{\sinh^2(\kappa d/2)} \qquad (38)$$

(Lowest-order corrections due to charge correlations involve the small parameter l_B/d; they are negative, thus slightly softening the pressure as compared with the uniformly charged case.)

It is important to note that the pressure of uniformly charged plates does not depend on the dielectric constant of the outside medium. Thus P_{int} does not vary with the parameter $\eta = \epsilon_{ins}/\epsilon_{el}$, contrary to the single-charge contribution P_{self}. Thus we do not discuss P_{int} further but generalize our previous study of the relative magnitude of single-charge and interaction terms[33] to the case of finite η.

For thick films, we may put $\sinh^2(\kappa d/2) \approx e^{\kappa d}$ and find the pressure ratio

$$\frac{P_{int}}{P_{self}} \approx \frac{\sigma d}{\kappa}e^{\kappa d} \qquad (\kappa d \gg 1) \qquad (39)$$

This quantity is large because of the factor $e^{\kappa d}$, and the single-charge term P_{self} will hardly be significant for thick films. In the opposite limit of thin films, we have to compare eqs 35 and 36 with $P_{int} = (2\sigma^2 Q^2/\epsilon_{el})/(\kappa d)^2$. When neglecting logarithmic factors, we find for any value of χ the ratio

$$\frac{P_{int}}{P_{self}} \approx \sigma\kappa^{-2} \quad (\kappa d \ll 1) \qquad (40)$$

The single-charge term P_{self} exceeds P_{int} at low charge density $\sigma \ll \kappa$, i.e., if the typical lateral distance of surface charges, $a = \sigma^{-1/2}$, is larger than the Debye length, $a > \kappa^{-1}$. The crossover is illustrated in Figure 4 for two values of the surface charge σ.

Thus the discrete nature of the surface charges is relevant for the disjoining pressure, if the Debye length is smaller than the film thickness and larger than the lateral charge distance, $d < \kappa^{-1} < a$. The first inequality ($d < \kappa^{-1}$) is easily satisfied by Newton black films and lamellar phases of microemulsions at moderate salinity, whereas the second one ($\kappa^{-1} < a$) requires

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a rather low surface charge density σ. This latter condition is met by weakly dissociated surfactants or by films made of mixtures of ionic and neutral molecules.

V. Discussion

A. DHA. In a bulk solution, the criterion of validity of DHA, $n_s\kappa^{-3} \gg 1$, expresses that the screening cloud should contain a large number of salt ions. In thin films ($\kappa d \ll 1$), it is replaced by the condition $n_s\kappa^{-2}d \gg 1$, which implies the inequalities $\kappa^{-1} \gg d \gg l_B$. At room temperature, the Bjerrum length of water takes the value $l_B = 7$ Å. Typical screening lengths are in the range $10 < \kappa^{-1} < 1000$ Å; electrolyte films are hardly thinner than several nanometers and thus satisfy the above condition.

For the case of many charges on a surface, there is a second criterion involving the mean charge density σ. DHA applies if the concentration of soluted ions in the screening layer is smaller than salinity; this condition can be written as $\sigma < \kappa^2 d/l_B$ for thin films and $\sigma < \kappa/l_B$ for thick ones.

B. Nonexponential Screening. All results of this paper are derived from the 2D Fourier transform of the screened potential in DHA, eq 46, and the power series for the potential in real space, eq 48. The leading term of this series has been derived previously for classical plasmas[28−30] and, in the domain of soft matter, for particular cases of confined electrolytes.[10,11,31,36] In the present work, we have studied in detail the shape of the screening cloud, in terms of the parameter χ, that is associated to a novel caracteristic length ρ^*.

For a finite dielectric constant ϵ_{ins} of the insulating medium, part of the counterions spread along the interface. As a consequence, the screening cloud comprises an algebraic tail that varies with the lateral distance as ρ^{-3}. For a semi-infinite electrolyte or a thick film, the weight χ of the algebraic tail is given by the ratio $\epsilon_{ins}/\epsilon_{el}$ and is thus much smaller than unity. For very thin films, however, the weight χ may attain unity; then the Debye length κ^{-1} loses its physical meaning and the characteristic length of the counterion cloud, ρ^*, significantly exceeds κ^{-1}. One convinces oneself easily that the criterion for the validity of DHA, $n_s\kappa^{-2}d \gg 1$, is still satisfied in this range.

C. Disjoining Pressure. For thin films at low densities, the discreteness of the surface charges is relevant, and the disjoining pressure deviates significantly from that of homogeneously charged plates. The confinement of the counterion clouds give rise to a single-charge contribution that is linear in the average surface charge density σ and depends on the dielectric constant of the insulating medium. At low density, the single-charge pressure is dominant, whereas at higher densities, one finds that of homogeneously charged plates, proportional to σ^2. For thin films with $\kappa d \leq 1$, the crossover occurs at a density $\sigma \approx \kappa^2$

$$P = \begin{cases} P_{self} \approx \sigma & \text{if } \sigma \ll \kappa^2 \\ P_{int} \approx \sigma^2 & \text{if } \kappa^2 \ll \sigma \ll \kappa^2 d/l_B \end{cases} \quad (41)$$

The upper limit $\kappa^2 d/l_B$ characterizes the breakdown of the DHA. Thus the crossover at $\sigma \approx \kappa^2$ described by eq 41 occurs well in the range of validity of DHA.

The single-charge contribution P_{self} results in an *enhancement* of the disjoining pressure as compared to the case of uniformly charged plates. It is interesting to compare this result to ref 19 where it is shown that a long-wavelength modulation of a uniform charge density *reduces* the disjoining pressure. First note that the reduction of ref 19 arises from higher-order corrections in terms of the charge density, whereas the present work deals with the modulation on a linear level (DHA). Second, ref 19 applies to *weak* modulations of a continuous surface

charge density, whereas the discrete charges considered here rather correspond to a small mean density that shows rapidly varying large-amplitude modulations. One may conclude that discrete charges show a behavior qualitatively different from that of a weakly modulated continuous charge density.

Finally we discuss the relevance of the single-charge pressure for real systems. Putting $\sigma = a^{-2}$ relates the density of surface charges to their mean nearest-neighbor distance a. For weakly dissociated surfactants or nonionic membranes with adsorbed charged molecules, the lateral distance a attains values between 10 and 100 nm and thus exceeds the Debye length at moderate or strong salinity.[37] Then the disjoining pressure is dominated by the single-charge contribution P_{self}. As a most striking consequence, this pressure is not homogeneous but located at the surface charges. Depending on bending rigidity and surface tension, this may result a significant deformation of the interface.

VI. Summary

In this paper, we have studied the electrostatics of discrete charges at an interface. Here we briefly summarize our main results:

(i) It is known that the screening cloud of a surface charge contains an algebraic tail that is localized close to the interface;[28] its weight varies with the dielectric constant ϵ_{ins} of the insulating medium. As a novel result, we find that the screening parameter χ may exceed unity for very thin films, resulting in a spreading of the counterions to large distances, well beyond the Debye length. At large lateral distance ρ, the counterion density varies as ρ^{-3}.

(ii) At low surface charge density, the disjoining pressure of thin films is due to single-charge effects. Depending on the ratio $\epsilon_{ins}/\epsilon_{el}$, it is given by the electrostrictive force or by the entropic pressure of the confined counterion clouds.

Appendix A: The Screened Potential

The electrostatic potential, created by a discrete surface charge and its counterions, is a solution of eq 8. By use of the cylindrical symmetry of the system, we take the 2D Fourier transform of the potential in the interface plane

$$\varphi(\rho,z) = \int \frac{d^2q}{(2\pi)^2} \tilde{\varphi}(\mathbf{q},z)e^{i\mathbf{q}\rho} = \frac{1}{2\pi} \int dq\, q\, \tilde{\varphi}(q,z)J_0(q\rho) \quad (A1)$$

with the zero-order Bessel function of the first kind J_0. Then $\tilde{\varphi}$ is solution of an ordinary differential equation

$$\partial_z[\epsilon(z)\partial_z\tilde{\varphi}] - \epsilon_{el}[q^2 + \kappa^2\theta(z)\theta(d-z)]\tilde{\varphi} = -Q\delta(z) \quad (A2)$$

The potential inside the aqueous core, $\tilde{\varphi}_{el}$, is a superposition of $e^{\pm(q^2+\kappa^2z)^{1/2}}$. Those in the insulating regions involve $e^{\pm qz}$ and are denoted $\tilde{\varphi}_<$ and $\tilde{\varphi}_>$ for $z < 0$ and $z > d$, respectively. The coefficients are determined by the usual boundary conditions of electrostatics. Continuity of the potential at the interfaces requires

$$\tilde{\varphi}_<(q,0) = \tilde{\varphi}_{el}(q,0)$$

$$\tilde{\varphi}_{el}(q,d) = \tilde{\varphi}_>(q,d) \quad (A3)$$

The difference between the normal component of the displacement vector $\epsilon(\mathbf{r})\nabla\varphi(\mathbf{r})$ through an interface is equal to the surface charge, resulting in

$$\epsilon_{el}\partial_z\tilde{\varphi}_{el}|_{z=0} = \epsilon_{ins}\partial_z\tilde{\varphi}_<|_{z=0} - Q$$

$$\epsilon_{el}\partial_z\tilde{\varphi}_{el}|_{z=d} = \epsilon_{ins}\partial_z\tilde{\varphi}_>|_{z=d} \tag{A4}$$

Solving these equations and using eq 30, we find the Fourier transform of the potential in the insulating domains

$$\tilde{\varphi}_<(q,z) = \frac{Q}{\epsilon_{el}} \frac{\Delta_+ e^{\hat{q}d} + \Delta_- e^{-\hat{q}d}}{\Delta_+^2 e^{\hat{q}d} - \Delta_-^2 e^{-\hat{q}d}} e^{qz}$$

$$\tilde{\varphi}_>(q,z) = \frac{Q}{\epsilon_{el}} \frac{2\hat{q}}{\Delta_+^2 e^{\hat{q}d} - \Delta_-^2 e^{-\hat{q}d}} e^{q(d-z)}$$

and in the aqueous core

$$\tilde{\varphi}_{el}(q,z) = \frac{Q}{\epsilon_{el}} \frac{\Delta_+ e^{\hat{q}(d-z)} + \Delta_- e^{-\hat{q}(d-z)}}{\Delta_+^2 e^{\hat{q}d} - \Delta_-^2 e^{-\hat{q}d}} \tag{A5}$$

We close this appendix with the corresponding result for an semi-infinite electrolyte. Replacing the above boundary condition at d with $\tilde{\varphi}_{el}(q,d) = 0$ for $d \to \infty$, we find the potential in the electrolyte half-space

$$\tilde{\varphi}_{el}(q,z) = \frac{Q}{\epsilon_{el}} \frac{e^{-\hat{q}z}}{\Delta_+} \quad (d \to \infty) \tag{A6}$$

Appendix B: In-Plane Counterion Density

The screened potential $\varphi(\rho,z)$ and derived quantities, such as the charge density $\sigma(\rho)$, are given in terms of the 2D Fourier transform of the potential inside the film, $\tilde{\varphi}_{el}(q, z)$; cf. eqs 21 and 42. Here we show how the resulting integrals can be evaluated as an asymptotic series.

For a sufficiently well-behaved function $\tilde{\varphi}_{el}(q,z)$, the integral (eq 42) is determined by small wave vectors, $q \leq 1/\rho$. Thus we expand $\tilde{\varphi}_{el}(q,z)$ in powers of q

$$\tilde{\varphi}_{el}(q,z) = \sum_{n=0}^{\infty} \frac{1}{n!} \psi_n(z) q^n \tag{B1}$$

with the derivatives

$$\psi_n(z) = \frac{d^n \tilde{\varphi}_{el}(q,z)}{dq^n}\Big|_{q=0} \tag{B2}$$

Inserting this series in eq 42, substituting $x = q\rho$, and integrating over x, we find

$$\varphi_{el}(\rho,z) = \frac{1}{2\pi} \sum_{n=0}^{\infty} \frac{M_n}{n!} \psi_n(z) \frac{1}{\rho^{2+n}} \tag{B3}$$

where we have defined the integrals

$$M_n = \int_0^\infty dx\, x^{n+1} J_0(x) \tag{B4}$$

Those with n even vanish, $M_{2m} = 0$, whereas the odd ones read[38]

$$M_{2m-1} = (-1)^m [(2m - 1)!!]^2$$

we note explicitly $M_1 = -1$, $M_3 = 3^2$, $M_5 = -3^2 5^2$, $M_7 = 3^2 5^2 7^2$, etc. For large n, the factor $M_n/n!$ in eq 50 is of the order unity. Besides prefactors d and $1/\kappa$, the coefficients ψ_n vary only weakly with n, and the series does not satisfy the criterion of absolute convergence.

The leading term of the above series involves the first derivative

$$\psi_1(z) = -\frac{Q}{\epsilon_{el}} \frac{\eta}{\kappa^2} \frac{2\cosh\kappa(d-z)\coth\kappa d - \sinh\kappa(d-z)}{\sinh\kappa d}$$

The bulk charge density $\sigma(\rho)$ requires the integral of the derivatives with respect to z

$$\tilde{\sigma}^{(n)} = -\epsilon_{el}\kappa^2 \int_0^d dz\,\psi_n(z) \tag{B5}$$

the leading term reads

$$\tilde{\sigma}^{(1)} = -\frac{Q\eta}{\kappa}\coth\frac{\kappa d}{2} \tag{B6}$$

Finally we give the coefficient for the potential in a semi-infinite electrolyte. Evaluating the derivative of eq 47 at $q = 0$, we have

$$\psi_1(z) = -\frac{Q}{\epsilon_{el}} \frac{\eta}{\kappa^2} e^{-\kappa z} \quad (d \to \infty) \tag{B7}$$

Appendix C: Single-Charge Pressure of Thick Films

Here we derive an asymptotic expression for the disjoining pressure in the case $\kappa d \gg 1$. In mathematical terms, we expand the approximate form (eq 33) of the integral $I(\kappa d, \eta)$ in powers of a new variable $t^{1/2}$ that is defined through $(t + 1)\kappa = (q^2 + \kappa^2)^{1/2}$. We rewrite the integral (eq 33) as a Laplace transform

$$I(\kappa d,\eta) = (\kappa d)^2 e^{-2\kappa d} \int_0^\infty dt\, f(t) e^{-2t\kappa d} \tag{C1}$$

of the function

$$f(t) = (t + 1)^3 \frac{t + 1 - \eta(t^2 + 2t)^{1/2}}{(t + 1 + \eta(t^2 + 2t)^{1/2})^3} \tag{C2}$$

$f(t)$ being a rational function, the integral is dominated by contributions from $t \leq (\kappa d)^{-1}$. Because of $\kappa d \gg 1$, we may expand $f(t)$ in powers of $t^{1/2}$

$$f(t) = 1 - 4\eta(2)^{1/2}t^{1/2} + (1 + 18\eta^2)t + \mathcal{O}(t^{3/2}) \tag{C3}$$

and truncate the resulting series for the integral at finite order.

An asymptotic expression arises from the following theorem: If a given function $f(t)$ can be expanded in a power series, $f(t) = \sum_{m=1}^{\infty} a_m t^{m/r-1}$, then its Laplace transform reads

$$\int_0^\infty dt\, f(t)\, e^{-zt} = \sum_{m=1}^{\infty} a_m \Gamma\left(\frac{m}{r}\right) z^{-m/r} \tag{C4}$$

where Γ is the Gamma function and the integer r accounts for the possibility to have a series of noninteger powers. The leading term of the series gives the asymptotic limit of the Laplace transform for large z. In the present case, we have $r = 2$ and $a_1 = 0$, $a_2 = 1$, $a_3 = -4\eta(2)^{1/2}$, ..., leading to

$$I(\kappa d,\eta) = (\kappa d)^2 e^{-2\kappa d}\left[\frac{1}{2} - \frac{2(2)^{1/2}\eta}{(\kappa d)^{1/2}} + \mathcal{O}\left(\frac{1}{\kappa d}\right)\right] \tag{C5}$$

This expression gives the disjoining pressure (eq 34) of thick films.

Appendix D: Single-Charge Pressure of Thin Films

We rewrite the integral (eq 29) with the new variable $y = (q^2 + \kappa^2)^{1/2}d$

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$$I(\kappa d, \eta) = \int_{\kappa d}^{\infty} dy \, \frac{y^3 \delta_+ \delta_-}{[\delta_+^2 e^y - \delta_-^2 e^{-y}]^2} \tag{D1}$$

where we have defined $\delta_\pm = y \pm \eta (y^2 - (\kappa d)^2)^{1/2}$. To obtain an approximate expression in terms of the small parameter $\kappa d \ll 1$, we split the range of integration at $y = \alpha \kappa d$, with a given factor α satisfying $(\kappa d)^{-1} \gg \alpha \gg 1$, and define two dimensionless integrals $K_<$ and $K_>$

$$I(\kappa d, \eta) = K_< + K_> \tag{D2}$$

We start with the second one, $K_>$, where y runs from $\alpha \kappa d$ to infinity. Because of $y \gg \kappa d$, we may put $\delta_\pm = y(1 \pm \eta)$

$$K_> = \int_{\alpha \kappa d}^{\infty} \frac{y(1 - \eta^2) dy}{[(\eta + 1)^2 e^y - (\eta - 1)^2 e^{-y}]^2} \tag{D3}$$

resulting in

$$\frac{-\ln[e^{2\alpha \kappa d} - \psi^2] + 2\alpha \kappa d (1 - \psi e^{-2\alpha \kappa d})^{-1}}{4(\eta^2 - 1)} \tag{D4}$$

with $\psi = (1 - \eta)/(1 + \eta)$. Noting $\alpha \kappa d \ll 1$, we expand the exponentials, truncate at linear order, $e^{\pm 2\alpha \kappa d} = 1 \pm 2\alpha \kappa d$, and thus have

$$K_> = \frac{1}{4(\eta^2 - 1)} \ln \frac{(\eta + 1)^2}{4\eta + 2\alpha \kappa d (\eta + 1)} + \frac{1}{4(\eta^2 - 1)} \frac{2\alpha \kappa d (\eta + 1)^2}{4\eta + 2\alpha \kappa d (\eta^2 + 1)} \tag{D5}$$

Now we turn to the second integral $K_<$. Since the upper bound satisfies $\alpha \kappa d \ll 1$, we may replace $e^{\pm y}$ in the denominator by $1 \pm y$, leading to

$$K_< = \int_{\alpha \kappa d}^{\infty} dy \, \frac{y^3 \delta_+ \delta_-}{[\delta_+^2 (1 + y) - \delta_-^2 (1 - y)]^2} \tag{D6}$$

We consider the cases $\kappa d \ll \eta$ and $\eta \ll \kappa d$ separately. For $\kappa d \ll \eta$, we may choose α such that $\alpha \kappa d \ll \eta$. Putting $\delta_\pm = y(1 \pm \eta)$, we find that the dominant contribution to the integral, $K_< \approx \alpha \kappa d / \eta$, is negligible as compared to $K_>$. Using $\alpha \kappa d \ll \eta$ in $K_>$, we finally have

$$I = \frac{1}{4(\eta^2 - 1)} \ln \frac{(\eta + 1)^2}{4\eta} \qquad (\kappa d \ll \eta) \tag{D7}$$

which is independent of κd and leads to the disjoining pressure of thin films, eq 36.

In the opposite case, $\eta \ll \kappa d \ll 1$, we may put $\delta_\pm = y$ in $K_<$ and obtain upon integration

$$K_< = \frac{1}{4} \ln \alpha$$

whereas eq D5 reduces to

$$K_> \simeq (1 - \ln(2\kappa d) - \ln \alpha)/4$$

Thus the terms depending on α cancel each other, and the integral

$$I = \frac{1 - \ln(2\kappa d)}{4} \qquad (\eta \ll \kappa d) \tag{D8}$$

results in the pressure (eq 37). These approximate results have been checked numerically.

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