Lateral interactions of charges in thin liquid films and the Berezinskii-Kosterlitz-Thouless transition

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At certain experimental conditions, foam films drawn from aqueous surfactant solutions can form highly stable Newtonian films. We show that the origin of the film stability can be attributed to specific patterning of surfactant molecules. Due to high dielectric contrast, the charges, together with their electrostatic images, interact as needlelike charged polymers. Below a critical thickness, such quasipolyelectrolytes undergo the Berezinskii-Kosterlitz-Thouless transition from a plasmalike state to a charge neutral one. In the latter, all the charges are bound into dipole pairs. Inherent only in thin films, the effect leads to the surfactant condensation into spots that cannot be observed on a single interface at the same surfactant concentration. We quantify a film resistance to rupture in terms of a pore line tension and show that the corresponding energy barrier needed for pore creation is much greater than the energy of thermal excitations. [S1063-651X(99)04110-0]

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I. INTRODUCTION

Electrostatic forces constitute an important contribution to stability of thin films drawn from electrolyte solutions [1,2]. According to the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory exploiting the idea of overlapped electrochemical double layers, electrostatic repulsion in thin films essentially depends on the thickness of double layers and, consequently, on the ionic strength of the mother solution. Based on the continuum Poisson-Boltzmann model, the DLVO theory ignores the lateral fluctuations of charges in the film. At the same time, the charge concentration might vary in the film plane and charge coupling could be a significant mechanism of film patterning [2,3]. To distinguish a role of lateral correlations between charges from ordinary coupling of double layers, the effect is named the effect of charge discreteness [4]. Since the first works on the effect, there have been numerous attempts to treat correlations by Monte Carlo simulations and other density-functional theories (see, for example, [5] and references therein). In particular, as shown in numeric simulations, the lateral correlation of charges leads to attraction between like-charged plates [6]. The cause of the appearance of conjoining pressure lies in inherent mobility of ions and, as a consequence, in self-organizing configurations of the electrostatic field at each ion. Owing to the latter, thermal excitations result in specific patterning of charges on opposing surfaces, adjusting positive ions against negative ones [6]. Another example in which the effects of long-wavelength correlated charge-density fluctuations are important is the free-standing soap film [3]. In such a film, surfactant molecules spread over the surfaces to form highly concentrated black spots. Notably, the mother solution from which the stable soap film is drawn may be considered as dilute; actually, the surfactant concentration is a little bit greater than the *critical micelle concentration* (CMC) [3]. For example, the CMC of sodium dodecyl sulphate at room temperature is about $c_{\mathrm{CMC}} \sim 8 \ \mathrm{mol/m}^3$, which gives the following estimate for the average distance between molecules $\bar{r} \sim (6 \times 10^{23} c_{\mathrm{CMC}})^{-1/3} \sim 10^{-8}$ m. So, the

average distance between surfactant molecules is at least one order greater than their linear size. In black spots, however, surfactant molecules should be closely packed to form bilayers [7] or stratifying films [8]. Despite the contradictory points of view on mechanisms of film patterning [7–12], and stability [13–15], all research recognizes the fact that the lateral interactions play a significant role here.

In this paper we show that the electrostatic interactions could be responsible for film patterning if the film dielectric constant ϵ is much greater than that of the environment, ϵ_i. In particular, the inequality $\epsilon/\epsilon_i \gg 1$ allows us to consider electrostatic interactions as two-dimensional ones if the average distance between charges is greater than the film thickness. Due to the high dielectric contrast, one may assume that the long-range electrostatic field caused by a test ion does not penetrate through the film surfaces. Considering the film surfaces as mirrors, the ions together with their images can be treated as charged filaments forming two-dimensional Coulomb gas. As the binding energy becomes comparable with the thermal one, the Coulomb gas undergoes the Berezinskii-Kosterlitz-Thouless (BKT) transition [16–18] resulting in ion pairing and, consequently, in surfactant ordering. We estimate the critical conditions for black spot formation and film rupture. The latter is obtained by assessing the energy of pore formation. The seemingly kindred problem of electrostatic edge instability in lipid membranes has been considered recently by Betterton and Brenner [19]. The lipid membrane is modeled as a uniformly charged surface of discontinuity, so that the film thickness plays no role in the hole stability. In the range of salt concentrations suitable for the Debye-Hückel approximation, the electrostatic effects are reduced to a renormalization of the bare edge energy [19]. The present work and the Betterton-Brenner paper do not overlap due to both physically different situations and nonlinearity involved here. In the problem under consideration, (i) the pore radius is comparable with the film thickness, (ii) the border charge is so large that it makes the Debye-Hückel approximation questionable, and (iii) the surface charges and the charges dissolved in the film are mobile. This triplet renders the approach of work [19] inapplicable in

our case. It seems impossible to find explicit solution to the problem. Nevertheless, asymptotically solving the nonlinear Poisson-Boltzmann equation, we show that the electrostatic forces are responsible for film stabilization against pore formation.

II. CHARGE COUPLING IN THIN FILMS WITH HIGH DIELECTRIC CONTRAST

If a test charge is placed in the liquid at point $(0,0,z_0)$, it creates an electrostatic field, which can be characterized by solving the Poisson equation

$$\Delta_\perp \phi + \frac{\partial^2 \phi}{\partial z^2} = -\frac{4\pi e}{\varepsilon} \delta(\mathbf{r}) \delta(z-z_0), \qquad (1)$$

subject to the boundary conditions at the film surfaces,

$$\phi|_{z=-h/2+0} = \phi|_{z=-h/2-0}; \quad \phi|_{z=h/2-0} = \phi|_{z=h/2+0}, \quad (2)$$

$$\epsilon \frac{\partial \phi}{\partial z}\bigg|_{z=-h/2+0} = \epsilon_- \frac{\partial \phi}{\partial z}\bigg|_{z=-h/2-0};$$

$$\epsilon \frac{\partial \phi}{\partial z}\bigg|_{z=h/2-0} = \epsilon_+ \frac{\partial \phi}{\partial z}\bigg|_{z=h/2+0}, \qquad (3)$$

and at infinity

$$\phi \mapsto 0, \quad r^2 + z^2 \mapsto \infty.$$

Here e is the elementary charge, and the stepwise function ε has three values: $\varepsilon = \epsilon$, if point $(\mathbf{r},z)$ lies within the film, $|z| < h/2$, and $\varepsilon = \epsilon_i$, $i = \pm$, if point $(\mathbf{r},z)$ is considered in the upper $(+)$ or lower $(-)$ semispaces outside the film. As was pointed out by Keldish [20], who analyzed exact solution of the problem, there are two regions distinguished by the asymptotic behavior of the potential. For our objectives, however, his analysis is inapplicable. Therefore, we consider an asymptotic analysis of the problem suitable for any charge distribution, not only for the δ-like one.

Concentrating attention on the long-range field, we integrate Eq. (1) over the film thickness. Then the average potential

$$\varphi = \frac{1}{h} \int_{-h/2}^{h/2} \phi \, dz$$

satisfies the equation

$$\Delta_\perp \varphi + \frac{\epsilon_+}{\epsilon h} \frac{\partial \phi}{\partial z}\bigg|_{z=h/2+0} - \frac{\epsilon_-}{\epsilon h} \frac{\partial \phi}{\partial z}\bigg|_{z=-h/2-0} = -\frac{4\pi e}{h\epsilon} \delta(\mathbf{r}). \qquad (4)$$

Far away from the charge, $r/h \gg 1$, the potential in the film is almost constant. Indeed, if r_0 denotes a length scale in the lateral direction, the first term on the left-hand side of Eq. (1) can be neglected relative to the second due to the estimate $\Delta_\perp \phi / (\partial^2 \phi / \partial z^2) \sim O(h^2/r_0^2)$, $-h/2 < z < h/2$. So, the film potential depends on r only parametrically. Therefore, considering the behavior of the electrostatic field only on large scales, $r/h \gg 1$, the average potential in Eq. (4) can be

replaced by its local value at the film midsurface as $\varphi_\infty = \phi(\mathbf{r},0)$. Accounting for this asymptotic equality, we split the Poisson problem for potentials on two Laplacian equations for upper and lower semispaces, both solutions being coupled at $z=0$ by the continuity condition for potentials and by the following equation for normal derivatives [in Eq. (4) the terms of smaller order are neglected]:

$$\Delta_\perp \phi + \left\{ \frac{\epsilon_+}{\epsilon h} \frac{\partial \phi}{\partial z}\bigg|_{z+0} - \frac{\epsilon_-}{\epsilon h} \frac{\partial \phi}{\partial z}\bigg|_{z=-0} \right\} = -\frac{4\pi e}{h\epsilon} \delta(\mathbf{r}). \qquad (5)$$

Equation (4) reveals two distinguishing asymptotic regimes depending on the priority of the first and second terms on the left-hand side. Introducing a critical length scale, R_0, for which both terms are on the same order of magnitude, and carrying out the dimensional analysis of Eq. (5), one gets $R_0 \sim h\epsilon / \max \epsilon_\pm$. Thus, in the range $r \gg R_0$, the second term dominates the first one, while in the second region, $h \ll r \ll R_0$, the average potential can be found by solving the problem

$$\Delta_\perp \varphi = -\frac{4\pi e}{h\epsilon} \delta(\mathbf{r}). \qquad (6)$$

Notably, the problem for the average potential is decoupled and we arrive at the solution

$$\varphi = -\frac{2e}{h\epsilon} \ln r. \qquad (7)$$

The results of this analysis can be applied to free-standing soap films stabilized by ionic surfactants. As was mentioned in the Introduction, if the surfactant concentration is a little bit greater than CMC, the average distance between molecules could be greater than the film thickness, yet smaller than $h\epsilon$. For example, so-called *Newton* black films stabilized by sodium dodecyl sulphate were identified as corresponding to a typical thickness of a few nanometers. Accounting for the estimate $\bar{r} \sim (6 \times 10^{23} c_{\text{CMC}})^{-1/3} \sim 10^{-8}$ m, we are persuaded that the electrostatic interactions in such aqueous films can be described by the model of the two-dimensional Coulomb gas. For the latter it is known that ions collapse into dipoles as the temperature falls below a certain critical value [16,21,17,18]. In contrast to the situation at ordinary phase transitions in the three-dimensional case, collective effects are unimportant for the appearance of an ordered structure, but two-body interactions play the dominant role. In particular, the temperature of the phase transition can be found by analyzing the partition function for a pair, $\exp(-2e^2 \ln r / h\epsilon k_B T)$. The Boltzmann exponent is integrable over two-dimensional space if and only if the inequality $e^2 / h\epsilon k_B T < 1$ holds. Hence, for surfactants, the film thickness plays the same role as temperature for the two-dimensional Coulomb gas. One expects that at the critical film thickness $h_{\text{cr}} = e^2 / \epsilon k_B T$, surfactant molecules condense into a dense layers. For aqueous films at room temperature, the critical thickness is estimated as $h_{\text{cr}} = e^2 / \epsilon k_B T \sim 10^{-38} / (80 \times 10^{-11} \times 3 \times 10^{-21}) \sim 4 \times 10^{-9}$ m, which is the typical thickness of the Newton black films [3]. The exact equation of state [21]

$$P = 2chk_B\left(T - \frac{e^2}{2\epsilon hk_B}\right), \quad h > h_{cr} \qquad (8)$$

connects the ''spreading pressure'' P and the total volume concentration of chemicals capable of dissociation, c. The ''spreading pressure'' is inherent to lateral hydrodynamics, but it should be distinguished from the ordinary capillary pressure. The latter is the difference between the pressure in the environment and in film liquid. The theory cannot predict the form of this excess pressure. The equation of state (8) is coming from the scaling arguments [21], but the thickness derivative of the excess free energy is a nontrivial quantity implicitly depending on the dimensionless parameter $e^2/\epsilon hk_B T$. Though attractive due to their simplicity, the theories exploiting the Bjerrum model of ion pairing [22] cannot be applied to a description of the near-critical behavior of ions because they ignore specific screening of needle-like dipoles [23]. As the thickness decreases below the critical one, the problem becomes more complicated. Below the critical thickness, short-range correlations between ions dominate in the dense phase, but they are beyond the limitations of the approximation involved. This is why the numeric simulations concerned with the classical Coulomb gas model [24] cannot be used directly for the problem of ion ordering in the films. So the problem of the determination of capillary pressure and other temperature or thickness derivatives of the excess free energy remains unresolved. Nevertheless, the mechanism of surfactant ordering via the BKT transition could underlie the theory of formation of the Newtonian films.

III. A CHARGED PORE

Assuming that a charged pore is present, we consider the problem of thermodynamic stability of a free-standing film. The only interactions that have to be considered are those between the nonscreened pore charges and ions located at a distance greater than h. Other contributions can be included in the pore line tension.

Placing the origin of the coordinate at the pore center, we rewrite the equation for the average potential as

$$\frac{d^2\varphi}{dR^2} + \frac{1}{R}\frac{d\varphi}{dR} = -\frac{4\pi\rho}{\epsilon}. \qquad (9)$$

The volume charge density ρ is the sum of positive and negative charge densities. The charge density will be assumed to obey the Boltzmann distribution,

$$\rho_{\pm} = \pm ec_0 \exp(\mp e\varphi/k_B T), \qquad (10)$$

$$\rho = \rho_+ + \rho_- = -2ec_0 \sinh(e\varphi/k_B T) \qquad (11)$$

with a constant c_0 determined by the condition of chemical equilibrium at infinity, where $\varphi = 0$.

Introducing dimensionless variables and functions as

$$u = \frac{e\varphi(r)}{k_B T}, \quad r = \frac{R}{a}, \quad q = \frac{2\pi Ne^2}{h\epsilon k_B T},$$

$$k^{-1} = (8\pi e^2 c_0/\epsilon k_B T)^{-1/2},$$

the problem (9)–(11) can be reformulated as

$$\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} = (ka)^2 \sinh u(r) \qquad (12)$$

and the boundary conditions for Eq. (12) are

$$\left.\frac{du}{dr}\right|_{r=1} = -2q, \quad u(\infty) = 0, \qquad (13)$$

where a is the pore radius and N denotes the number of nonscreened charges at the pore wall. As was mentioned, Newtonian films exist near the critical conditions for the Berezinskii-Kosterlitz-Thouless transition. At the near-critical conditions, parameter q is greater than unity, while parameter $ka \sim a(1.5\times10^{25}h_{cr}c_{CMC})^{1/2}$ is small. For example, for sodium dodecyl sulphate we have $ka \sim a/h_{cr} < 1$.

So we arrive at the so-called Manning condensation phenomenon well known in polyelectrolytes [25]. Due to the specific conditions $q > 1$ and $ka < 1$, the magnitude of the dimensionless potential near the pore is much greater than unity so that counterions pile up the pore to form an effective screen for pore charge. This leads to a renormalized pore charge. The phenomenon has received a great deal of attention in recent decades [26–30] but we are unaware of its application to the problem of pore stability. Since the exact solution of the nonlinear Poisson-Boltzmann equation is very complicated [31], our attention is concentrated on asymptotic laws of ion distribution in the region close to the pore (the Manning region) and in the distant region (the Debye-Hückel region). This asymptotic laws allow one to clarify the peculiarities of the BKT transition in the inhomogeneous case.

A. The Manning region of counterion condensation

Accounting for both inequalities $q > 1$ and $ka \ll 1$, Eq. (12) can be approximately written in the vicinity of the pore as

$$\frac{d^2u_i}{dr^2} + \frac{1}{r}\frac{du_i}{dr} = \frac{(ka)^2}{2}\exp u_i(r). \qquad (14)$$

This is the problem for calculating the principal term $u_i(r)$ of the *inner approximation* [32] of the solution. Substituting the ansatz [33]

$$p = u + 2\ln r, \quad P = \ln r$$

into Eq. (14) and then multiplying the result by dp/dP, one gets

$$\frac{d}{dP}\left[\frac{dp}{dP}\right]^2 = (ka)^2\frac{de^p}{dP}.$$

This equation has two solutions [33],

$$C^{-1/2}\ln\frac{[C+(ka)^2e^p]^{1/2}-C^{1/2}}{[C+(ka)^2e^p]^{1/2}+C^{1/2}} = \ln\frac{r}{R_M} \quad \text{if} \quad C > 0 \qquad (15)$$

and

$$\frac{2}{\sqrt{-C}} \arctan \frac{[C+(ka)^2 e^p]^{1/2}}{\sqrt{-C}} = \ln \frac{r}{R_M} \qquad \text{if } C<0. \tag{16}$$

Here

$$C = 4(1-q) - (ka)^2 \exp u(1). \tag{17}$$

R_M is an arbitrary integration constant, and in Eq. (16) we mean the principal branch of arctan. The solution applicability has to be checked by making use of definition (17). Even though the value of $u(1)$ is unknown in advance, due to the inequality $q>1$ one can select the necessary solution right now, i.e., Eq. (16). Making use of the denotation $z = \sqrt{-C}/2$, we rewrite Eq. (16) in the form [34–36]

$$u_i(r) = -\ln\left[\left(\frac{ka}{2z}\right)^2 r^2 \cos^2\left(z \ln \frac{r}{R_M}\right)\right]. \tag{18}$$

Then the boundary condition at the pore wall takes the form

$$1 - z \tan\left(z \ln \frac{1}{R_M}\right) = q. \tag{19}$$

Accounting for the explicit equations for potential and pore charge, one can determine the number of counterions in the Manning region as

$$\rho_M = \frac{(ka)^2}{4} \int_1^r r \, dr \exp u = z \tan(z \ln r/R_M) + q - 1. \tag{20}$$

In particular, one reveals that $q-1$ charges are confined in the layer of radius R_M and screen the pore charge. So, the critical radius R_M can be treated as the border of the counterion cloud in the Manning region. In the two-phase model [25,26], these counterions are attributed to the surface adsorbed ones.

The inner solution (18) is in contradiction with the second boundary condition in Eqs. (13), so that we have to find an outer expansion of the solution, which could obey the boundary condition at infinity.

B. The Debye-Hückel region of charge screening

Following the method of matched asymptotic expansions [32], we rescale the variable as

$$\xi = kar$$

and consider the outer region $\xi>1$ in which the potential diminishes, $u(\xi) \ll 1$. In other words, one assumes that at distances much greater than the Debye radius, k^{-1}, the electrostatic coupling energy of mobile ions is smaller than their thermal energy. Thus the outer solution obeys the Debye-Hückel equation,

$$\frac{d^2 u_e}{d\xi^2} + \frac{1}{\xi} \frac{du_e}{d\xi} = u_e(\xi). \tag{21}$$

The solution of Eq. (21) is well known,

$$u_e = q_0 K_0(\xi) = q_0 K_0(kar), \tag{22}$$

where $K_0(x)$ is the modified Bessel function and q_0 is still the undetermined apparent pore charge. The modified Bessel function behaves like a logarithm for a small argument, which suggests that the first approximation in the inner expansion has the form

$$u_e \approx -q_0 \ln \frac{kar}{2} - q_0 C_E + o(1), \tag{23}$$

with Euler's constant $C_E = 0.577\,215...$. On the other hand, in the vicinity of $r = R_M$, Eq. (18) can be written as

$$u_i \approx -2 \ln \frac{kar}{2} + 2 \ln z + o(1). \tag{24}$$

It is apparent that both asymptotic solutions overlap in the vicinity of point $r = R_M$, whereupon

$$q_0 = 2 \qquad \text{and } z = e^{-C_E}. \tag{25}$$

Substituting z into the boundary condition at the pore wall, one gets the expression for R_M in the form

$$R_m = \exp(-e^{C_E} \arctan e^{C_E}[1-q]). \tag{26}$$

For strongly charged pores, $q \to \infty$, the radius of the Manning region tends to its asymptote $R_M \to R_\infty = \exp(\pi e^{C_E}/2) \sim 16.407$. In dimensional variables, the Manning region is estimated as $\sim 16a$, so that the two-dimensional theory is applicable if the pore radius is about the film thickness. Since the Debye radius near the BKT transition is about the film thickness, $k^{-1} \sim h_{cr}$, we are persuaded that the second term on the left-hand side of Eq. (5) is still unimportant.

C. The free energy of a pore

Traditionally, discussing the mechanism of film stability or membrane fusion, one determines the barrier energy of a hole [37–41]. In customary models, the energy consists of two parts: the first is the surface energy lost due to pore formation in the film,

$$\Delta F_s = -\pi a^2 \gamma, \tag{27}$$

and the second energy is attributed to the surface energy of the pore border (or to the edge energy for bilayers),

$$\Delta F_l = +2\pi a \gamma_l. \tag{28}$$

Here γ is the film tension and γ_l is the line tension. If, as a crude estimate, we set $\gamma_l \sim \sigma h$ and $\gamma = 2\sigma$, where σ is the ordinary surface tension, the barrier $\Delta F^* = \pi \gamma_l^2/\gamma$ and the critical pore radius $a_{cr} = \gamma_l/\gamma$ can be assessed as $\Delta F^* \sim \pi \sigma h^2/2$ and $a_{cr} \sim h$. For ultrathin foam films these values serve as upper estimates, because the line tension could be much smaller than σh [39,40]. The theory including only surface energies may fail in the case of charged pores. Indeed, formulas for the barriers do not take into account the contributions from long-range forces, because the line tension is mostly dictated by short-range forces with a length scale approximately equal to the intermolecular distance. On
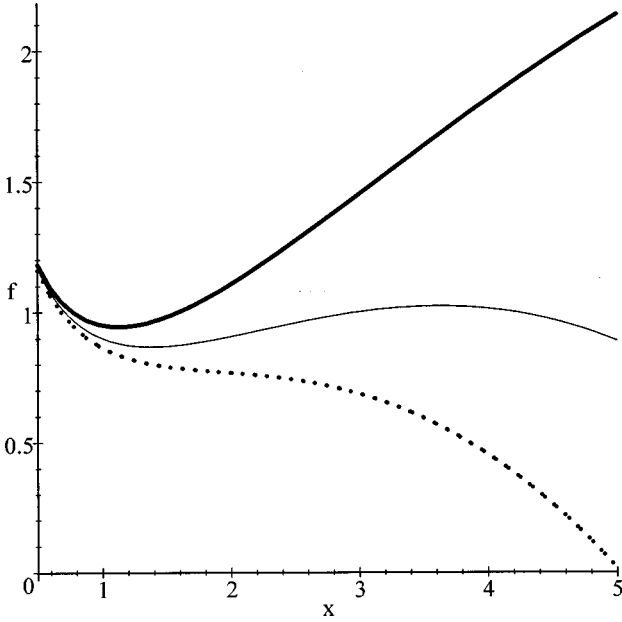
FIG. 1. Energy as a function of pore radius for three film tensions: dashed line, $\alpha=0.135$; thin solid line, $\alpha=0.1$; thick solid line, $\alpha=0.05$.

the other hand, if the pore is charged, the long-range electrostatic forces stabilize it against shrinkage. Substituting the asymptotic formula for the surface potential,

$$u_i(1) = -2\ln(ka) + \ln\{4[e^{-2C_E} + (q-1)^2]\}, \quad (29)$$

into the electrostatic component of the free energy,

$$\Delta F_e = Nk_BT \int_0^N u_i(1)dN, \quad (30)$$

we obtain the radius-dependent part as

$$\Delta F_e = -2Nk_BT\ln(ka). \quad (31)$$

Introducing dimensionless variables as

$$\alpha = Nk_BT\gamma/2\pi\gamma_l^2 \quad \text{and} \quad x = \pi a\gamma_l/Nk_BT,$$

the total free energy is rewritten in the form

$$f = (\Delta F_s + \Delta F_l + \Delta F_e)/2Nk_BT + \ln(kNk_BT/\pi\gamma_l)$$
$$= -x^2\alpha + x - \ln x. \quad (32)$$

In Fig. 1 we plot two distinguishing regimes of film stretching. If the film tension is small enough, it is apparent that the energy grows as the pore radius diminishes, and the greater the pore radius, the smaller the energy. Between these asymptotes, there is a metastable region with a barrier. The barrier disappears as the film tension approaches the critical value. Thereafter, no local minima occur and the only one is at infinity. In principle, at different tensions the pores may have the same energy, f_{cr}, i.e., the energy attributed to different wells is the same. So, the scenario of film rupture is as follows. Once nucleated, the pore grows under the film stretching until the tension on the pore reaches a critical value corresponding to the energy f_{cr}. Just after the critical

tension has been reached, the pore suddenly opens to the larger radius. Further stretching decreases the energy, thus favoring the film rupture. The critical conditions can be found by analyzing the force balance for both pores corresponding to the critical energy f_{cr},

$$\frac{-x+1}{x^2} = \frac{-y+1}{y^2}, \quad (33)$$

and by equating their energies,

$$-x^2\alpha + x - \ln x = -y^2\alpha + y - \ln y, \quad (34)$$

where y is the dimensionless radius of the larger pore. The system of transcendental equations can be solved by classical methods [42], and has the following parametric solution:

$$x = \frac{-1+e^{2s}}{-1+e^s}, \quad (35)$$

$$y = \frac{-1+e^{2s}}{-1+e^s}e^{-s}, \quad (36)$$

$$\alpha = (e^s-1)\frac{e^s-e^{-s}+1-e^{2s}-s+se^s}{(e^{2-s}-1)(e^{2s}-1)^2}, \quad (37)$$

where parameter s ranges from minus infinity to zero. Therefore, the smaller radius changes from 1 to 2, while the larger one grows from 2 to infinity. The dimensionless tension can vary within the gap $0 \le \alpha \le \exp(-2) \approx 0.135\,34$. If the tension is greater than $\exp(-2)$, the film, most likely, rips. Substituting a maximal value for α, one gets $N_{cr} = 2\pi\gamma_l^2\exp(-2)/k_BT\gamma$. So, the critical radius is estimated as $a_{cr} = 4\gamma_l\exp(-2)/\gamma$. If we set $\gamma_l \approx \sigma h$ and $\gamma \approx 2\sigma$, the upper bound for the allowed radius is assessed as $a_{cr} \approx 2h\exp(-2) \approx 0.27h$.

IV. CONCLUSIONS

Considering the mechanism of surfactant ordering in lamellae, we focused on the specific case of a large dielectric contrast, for example aqueous films in an air environment fall into this class. If the surfactant solution is dilute, i.e., if the average distance between the ions is much greater than the film thickness, yet is smaller than $h\epsilon/\max\epsilon_\pm$, the charges interact in lateral directions via the logarithmic potential. In other words, placed in the film, the charges induce the images, which in the principal approximation with respect to small parameter $1/\epsilon$ can be treated as charged needles. Similar to the two-dimensional Coulomb gas, the opposite charges form dipole pairs as the temperature decreases. In this phenomenon, known as the Berezinskii-Kosterlitz-Thouless transition, two-body interactions are dominant. Remarkably, the film thickness plays the same role here as the temperature in the Coulomb gas, so that the critical condition for the onset of surfactant ordering can be found analytically as $h_{cr} = e^2/\epsilon k_BT$. For aqueous films at room temperature this thickness is about the thickness of Newtonian film. For the latter, the surfactants are densely packed to form a bilayer, although typically Newtonian films are drawn from dilute solutions with surfactant concentration a little bit greater than the CMC. The fact that the thickness

of Newtonian films is practically unaffected by the electrolyte concentration [40] favors the mechanism of the Berezinskii-Kosterlitz-Thouless transition. Within the same limitations, the BKT theory explains the film stability. We showed that near the BKT transition the Debye radius is about the film thickness, so that the charge of a pore is significantly screened by counterions. Due to mathematical analogy, the problem of charge reduction of a pore can be considered similar to the Manning condensation in polyelectrolytes, whereupon, at distances much greater than the Debye length, the counterions are amassed at the pore to reduce the bare line density of charges, $2\pi aNe$, to the apparent density $ah\epsilon k_B T/e$. This saturation effect manifests itself in the charge independence of the critical pore radius $a_{cr} \approx 2h\exp(-2)$, provided that the edge energy is estimated as $\gamma_l \approx \sigma h$. The corresponding barrier energy is much greater than the thermal one, $\Delta F_{bar} \sim 2\pi\sigma h_{cr}^2 \sim 10^3 k_B T$. Therefore, the origin of the astonishing stability of the Newton black films lies in specific long-range surfactant interactions preventing films from pore creation.

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[1] J. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).

[2] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Consultants Bureau, New York, 1987).

[3] D. Exerowa and P. Kruglyakov, *Foam and Foam Films* (Elsevier, Amsterdam, 1998).

[4] R. T. Mathias, G. J. Baldo, K. Manivannan, and S. McLaughlin, in *Electrified Interfaces in Physics, Chemistry and Biology*, edited by R. Guidelli (Kluwer Academic, Dordrecht, The Netherlands, 1992), p. 473.

[5] R. Kjellander, T. Åkesson, B. Jönsson, and S. Marcelja, J. Chem. Phys. **97**, 1424 (1992).

[6] I. Rouzina and V. A. Bloomfield, J. Phys. Chem. **100**, 9977 (1996).

[7] O. Belorgey and J. J. Benattar, Phys. Rev. Lett. **66**, 313 (1991); S. E. Friberg, Langmuir **8**, 1889 (1992).

[8] V. Bergeron and C. J. Radke, Langmuir **8**, 3020 (1992).

[9] J. W. Keuskamp and J. Lyklema, *Adsorption at Interfaces; ACS Symposium Series 8*, edited by K. L. Mittal (American Chemical Society, Washington, D.C., 1975), p. 191.

[10] A. D. Nikolov, P. A. Kralchevsky, I. B. Ivanov, and D. T. Wasan, J. Colloid Interface Sci. **133**, 13 (1989).

[11] O. Krichevsky and J. Stavans, Phys. Rev. Lett. **74**, 2752 (1995).

[12] B. Cabane and R. Duplessix, J. Phys. (Paris) **48**, 651 (1987); S. Lionti-Addad and J. M. Meglio, Langmuir **8**, 324 (1992); R. Bruinsma, J. M. Meglio, D. Quere, and S. Cohen-Addad, *ibid.* **8**, 3161 (1992).

[13] B. W. Ninham, Chem. Scr. **25**, 3 (1985).

[14] J. W. Israelachvili and H. Wennerstrom, Langmuir **6**, 873 (1990).

[15] V. A. Parsegian and R. P. Rand, Langmuir **7**, 1299 (1991).

[16] V. L. Berezinskii, Zh. Eksp. Teor. Fiz. **59**, 907 (1970) [Sov. Phys. JETP **32**, 493 (1970)]; **61**, 1144 (1971) [**34**, 610 (1972)].

[17] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).

[18] J. M. Kosterlitz, J. Phys. C **7**, 1046 (1974).

[19] M. D. Betterton and M. P. Brenner, Phys. Rev. Lett. **82**, 1598 (1999).

[20] L. V. Keldysh, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 716 (1979) [JETP Lett. **29**, 658 (1979)].

[21] E. H. Hauge and P. C. Hemmer, Phys. Norv. **5**, 209 (1971).

[22] J. P. Hansen and P. Viot, J. Stat. Phys. **38**, 823 (1985).

[23] K. Kornev, Phys. Rev. E **49**, 575 (1994).

[24] J. M. Caillol and D. Levesque, Phys. Rev. B **33**, 499 (1986).

[25] G. S. Manning, Annu. Rev. Phys. Chem. **23**, 117 (1972).

[26] F. Oosawa, *Polyelectrolytes* (Marcel Dekker, New York, 1971).

[27] M. Fixman, J. Chem. Phys. **70**, 4995 (1979).

[28] C. F. Anderson and M. T. Record, Annu. Rev. Phys. Chem. **33**, 191 (1982).

[29] M. D. Frank-Kamenetskii, V. V. Anshelevich, and A. V. Lukashin, Usp. Fiz. Nauk **30**, 595 (1987) [Sov. Phys. Usp. **151**, 317 (1987)].

[30] J. L. Barrat and J. L. Joanny, Adv. Chem. Phys. **94**, 1 (1996).

[31] C. A. Tracy and H. Widom, Physica A **244**, 402 (1997).

[32] A. H. Nayfeh, *Introduction to Perturbation Techniques* (Wiley, New York, 1981).

[33] A. D. Polyanin and V. F. Zaitsev, *Handbook of Exact Solutions for Ordinary Differential Equations* (CRC, Boca Raton, 1995).

[34] R. M. Fuoss, A. Katchalsky, and S. Lifson, Proc. Natl. Acad. Sci. USA **37**, 579 (1951).

[35] T. Alfrey, P. W. Berg, and H. Morawetz, J. Polym. Sci. **7**, 543 (1951).

[36] B. Zimm and M. LeBret, J. Biomol. Struct. Dyn. **1**, 461 (1983).

[37] B. V. Derjaguin and Yu. V. Gutop, Kolloid-Z. **24**, 431 (1962).

[38] A. Scheludko, Adv. Colloid Interface Sci. **1**, 391 (1967).

[39] Yu. A. Chizmadzhev and V. F. Pastushenko, in *Thin Liquid Films: Fundamentals and Applications*, edited by I. B. Ivanov (Marcel Dekker, New York, 1988), p. 1059.

[40] D. Exerowa, D. Kashchiev, and D. Platikanov, Adv. Colloid Interface Sci. **40**, 201 (1992).

[41] J. D. Moroz and P. Nelson, Biophys. J. **72**, 2211 (1997).

[42] J. Lekner, Am. J. Phys. **50**, 161 (1982).