

On the Stability of the Common and Newton Black Films

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Received October 17, 2001. In Final Form: January 17, 2002

The effect of electrolyte concentration on the transition from common to Newton black films and the stability of both types of films are explained using a model in which the interaction energy for films with planar interfaces is obtained by adding to the classical DLVO forces the hydration force. The theory takes into account the reassociation of the charges of the interface with the counterions as the electrolyte concentration increases and their replacements by ion pairs. This affects both the double layer repulsion, because the charge on the interface is decreased, and the hydration repulsion, because the ion pair density is increased by increasing the ionic strength. The theory also accounts for the thermal fluctuations of the two interfaces. Each of the two interfaces is considered as formed of small planar surfaces with a Boltzmannian distribution of the interdistances across the liquid film. The area of the small planar surfaces is calculated on the basis of a harmonic approximation of the interaction potential. It is shown that the fluctuations decrease the stability of both kinds of black films.

I. Introduction

It is well-known that free films of water stabilized by surfactants can exist as somewhat thicker primary films, or common black films, and thinner secondary films, or Newton black films. The thickness of the former decreases sharply upon addition of electrolyte, and for this reason its stability was attributed to the balance between the electrostatic double-layer repulsion and the van der Waals attraction. A decrease in its stability leads either to film rupture or to an abrupt thinning to a Newton black film, which consists of two surfactant monolayers separated by a very thin layer of water. The thickness of the Newton black film is almost independent of the concentration of electrolyte; this suggests that another repulsive force than the double layer is involved in its stability. This repulsion is the result of the structuring of water in the vicinity of the surface. Extensive experimental measurements of the separation distance between neutral lipid bilayers in water as a function of applied pressure¹ indicated that the hydration force has an exponential behavior, with a decay length between 1.5 and 3 Å, and a preexponential factor that varies in a rather large range.

The interactions between the surfactant monolayers of the black film consist of a long-range van der Waals attraction, a short range repulsion due to the hydration force, and an electrostatic repulsion with a longer range than the hydration repulsion but shorter than the van der Waals attraction. Their combination can lead, in principle, to an interaction energy possessing three minima: one at a separation distance $d \rightarrow 0$, which implies the rupture of the film, another one at a relatively large distance, which corresponds to the common black film, and finally a third one at an intermediate separation distance, which corresponds to the Newton black film. Only the minimum at $d \rightarrow 0$ is stable; the other two, while metastable, can have relatively long lifetimes.

Experiments on the stability of water/surfactant films at various pressures were performed by Exerowa et al.^{2,3} For a dilute aqueous solution of a nonionic surfactant,³ tetraoxyethylene decyl ether (D(EO)₄, 5×10^{-4} mol/dm³) or eicosaoxyethylene nonylphenol ether (NP(EO)₂₀, 1×10^{-5} mol/dm³), and electrolyte (KCl), thick films (with thicknesses of the order of 100 Å) were observed at low electrolyte concentrations. With an increase of the electrolyte concentration, the film thickness first decreased, which suggests that the repulsion was caused by the double layer. This repulsive force was generated because of the different adsorptions of the two species of ions on the water/surfactant interface. At a critical electrolyte concentration, a black film was formed, and the further addition of electrolyte did not modify its thickness, which became almost independent of the external pressure, until a critical pressure was reached, at which it ruptured. While for NP(EO)₂₀ only one metastable equilibrium thickness was found at each electrolyte concentration, in the case of D(EO)₄ a hysteresis of the film thickness with increasing and decreasing pressure (i.e., two metastable minima) was observed in the range 5×10^{-4} to 3×10^{-3} mol/dm³ KCl. The maximum pressure used in these experiments was relatively low, $\sim 5 \times 10^4$ N/m², and the Newton black films did not rupture in the range of pressures employed.

In the case of ionic surfactants (10^{-3} mol/dm³ sodium lauryl sulfate, NaLS), abrupt transitions from common black films to Newton black films were observed, for NaCl concentrations in the range 0.165–0.31 mol/dm³, by increasing the external pressure.² The Newton black films ruptured at a pressure of about 12×10^4 N/m².

The purpose of this article is to present a model and to calculate on its basis the metastable equilibrium thicknesses of the film as a function of the applied pressure. In section II, the interaction energy of the film was calculated, assuming planar interfaces free of thermal fluctuations. The double layer interaction was calculated by accounting for the charge recombination at the surface with increasing electrolyte concentration. An approximate

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expression derived by Donners et al.⁴ on the basis of the Lifshitz theory was used to calculate the van der Waals interaction energy. For the hydration force, a relation derived recently^{5,6} was used, which accounts for the increase in the hydration force with increasing electrolyte concentration, due to a higher ion-pair (dipole) density produced by the recombination of some charges on the interfaces with counterions. This enhancement of the repulsion at relatively high ionic concentrations might be at the origin of the stability of the Newton black films, as suggested recently;⁷ however, in the present article, the field generated by an ion pair located at the interface is calculated more accurately and the theory is further developed to include the effect of thermal fluctuations.

II. Interaction Energy of Soap Films

Throughout this section, the energy of the film will be calculated by assuming planar, non-undulating, interfaces. Most of the equations of section IIA–E were taken from our previous paper.⁵ We include them without detailed derivation for the completeness of the presentation.

II.A. The Surface Density of Surfactant. The surface density of surfactant is relevant for both the double layer (caused by the surface charge density generated via the dissociation of the surfactant adsorbed at the interface) and the hydration interaction (caused by the ion pair density of the non-dissociated surfactant molecules). The surface density of an anionic surfactant, Γ , will be related to the saturation surface density, Γ_∞ , via the Frumkin adsorption isotherm

$$a_1 C_R = \frac{\frac{\Gamma}{\Gamma_\infty} \exp(-2a_2 \frac{\Gamma}{\Gamma_\infty})}{1 - \frac{\Gamma}{\Gamma_\infty}} \quad (1)$$

where a_1 and a_2 are empirical parameters available from experiment and C_R is the concentration of the surfactant anions in the liquid in the vicinity of the interface. The surfactant in the bulk is considered completely dissociated, and hence the concentration of surfactant in the vicinity of the interface is related to the bulk surfactant concentration through the expression

$$C_R = C_s \exp\left(\frac{e\psi_s}{kT}\right) \quad (2)$$

where C_s is the bulk surfactant concentration, ψ_s is the surface potential, which is negative (hence $C_R < C_s$), e is the protonic charge, k is the Boltzmann constant, and T is the absolute temperature. The parameters a_1 , a_2 , and Γ_∞ are provided by experiment. In what follows the data obtained by Fainerman⁸ at high electrolyte concentrations, namely, $\Gamma_\infty = 5 \times 10^{-6}$ mol/m², $a_1 = 881$ m³/mol, and $a_2 = -1.53$, will be used.

II.B. The Surface Charge. With α denoting the dissociation constant, the surface charge density σ is given by

$$\sigma = -e\alpha\Gamma \quad (3)$$

For simplicity, it will be assumed that the electrolyte is 1:1 and that it has the same type of cation as the surfactant (e.g., NaCl and NaLS). The charge is generated through the following dissociation equilibrium



where R denotes the surfactant anion group and X the cation. At equilibrium, one can write

$$K_D = \frac{C_{R^-}^S C_{X^+}}{C_{R-X}} = \frac{\alpha\Gamma C_{X^+}}{(1-\alpha)\Gamma} = \frac{\alpha}{1-\alpha} C_{X^+} \quad (4)$$

where $C_{R^-}^S$ is the surface density of the dissociated surfactant anions, C_{R-X} is the surface density of nondissociated (ion pair) surfactant molecules, C_{X^+} is the concentration of the cations in the liquid in the vicinity of the surface, and K_D is the equilibrium constant. Assuming that the surfactant in solution and the electrolyte are completely dissociated, one can write

$$C_{X^+} = (C_s + C_e) \exp\left(-\frac{e\psi_s}{kT}\right) \quad (5)$$

where C_e is the bulk electrolyte concentration.

II.C. The Double Layer Interaction Energy. The calculation of the double layer interaction is based on the accurate approximation of the solution of the Poisson–Boltzmann equation due to Ohshima and Kondo.⁹ For two parallel plates at a distance z apart, at a surface potential ψ_s , and with a midplane potential ψ_m , they obtained the equation

$$\tanh\left(\frac{e\psi_m}{4kT}\right) = \gamma_0 \frac{1}{\cosh\left(\frac{\kappa z}{2}\right)} - \gamma_0^3 \frac{\left(\frac{\kappa z}{2}\right) \sinh\left(\frac{\kappa z}{2}\right)}{\cosh^4\left(\frac{\kappa z}{2}\right)} + \gamma_0^5 \left\{ \frac{\cosh^2\left(\frac{\kappa z}{2}\right) - 2\left(\frac{\kappa z}{2}\right)^2 - 1}{4 \cosh^5\left(\frac{\kappa z}{2}\right)} - \frac{3\left(\frac{\kappa z}{2}\right) \sinh\left(\frac{\kappa z}{2}\right)}{4 \cosh^6\left(\frac{\kappa z}{2}\right)} \times \right. \\ \left. \left(1 - 4\left(\frac{\kappa z}{2}\right) \tanh\left(\frac{\kappa z}{2}\right)\right) \right\} \quad (6)$$

where $\gamma_0 = \tanh(e\psi_s/4kT)$, $\kappa = (2e^2 C_e / \epsilon \epsilon_0 kT)^{1/2}$ is the Debye length for a 1:1 electrolyte and $\epsilon \epsilon_0$ is the dielectric constant of water. The surface charge density is related to the surface and midplane potentials via

$$\sigma = -\frac{\kappa \epsilon \epsilon_0 kT}{e} \left[2 \left(\cosh\left(\frac{e\psi_s}{kT}\right) - \cosh\left(\frac{e\psi_m}{kT}\right) \right) \right]^{1/2} \quad (7)$$

The double layer force per unit area is given by the Langmuir equation

$$p_{DL}(z) = 2 C_e kT \left(\cosh\left(\frac{e\psi_m(z)}{kT}\right) - 1 \right) \quad (8a)$$

Equations 1–8a can be simultaneously solved to obtain the surfactant density, the degree of dissociation, and the double layer force. The double layer interaction energy

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per unit area, U_{DL} , is obtained by integrating the double layer force per unit area from d to ∞ , where d is the thickness of the water layer

$$U_{DL}(d) = \int_d^{\infty} p_{DL}(z) dz \quad (8b)$$

II.D. The van der Waals Energy. The van der Waals energy per unit area for a triple layer system (hydrocarbon/water/hydrocarbon) in air was calculated on the basis of the Lifshitz theory by Donners et al.⁴ and is well represented by the expression

$$U_{vdW}(d) = \frac{1}{d^2} \left(\frac{b_1 + b_2 d}{1 + b_3 d + b_4 d^2} + b_5 \right) \quad (9)$$

where d is the thickness of the water layer and, for dodecane films with a thickness of 9 Å, the parameters are $b_1 = -3.08 \times 10^{-22}$ J, $b_2 = -6.28 \times 10^{-14}$ J/m, $b_3 = 8.28 \times 10^7$ m⁻¹, $b_4 = 6.13 \times 10^{15}$ m⁻², and $b_5 = -9.00 \times 10^{-23}$ J.

II.E. The Hydration Interaction Energy. The calculation of the hydration interaction is based on a model proposed by Schiby and Ruckenstein,¹⁰ which considers that, in the vicinity of an interface, the water is organized in layers parallel to the interface with the structure of ice. The water molecules from the first water layer are polarized by the nearest dipoles of the headgroups of the surfactant molecules; these dipoles induce an electric field into the adjacent layer, whose induced dipoles generate in turn electric fields in both adjacent layers and so on. When two surfaces approach one another, the polarization layer will increasingly overlap. This decreases the average polarization of the water molecules and hence increases the electrostatic energy, thus generating a repulsion between surfaces. We will only outline the theory here; a detailed presentation was made recently.⁵

The field generated by the surface dipoles, which polarize the first water layer, is given by

$$\bar{E} = \frac{p_{\perp}}{\epsilon'} \frac{1}{2\pi\epsilon_0 \left(\frac{A}{\pi} + \Delta'^2 \right)^{3/2}} \quad (10)$$

where p_{\perp} is the component, normal to the surface, of the dipole moment of an ion pair of the surface, ϵ_0 is the vacuum permittivity, $1/A$ is the ion pair density on the surface, ϵ' is an effective dielectric constant for the interaction between the water molecules of the first water layer and the nearest surface dipole, and Δ' is the distance between the first water layer and the center of the surface dipole. It is important to emphasize that ϵ' is smaller than the dielectric constant of water, ϵ , because of the lower screening of the electric field by the fewer intervening water molecules.

The average polarization of the water molecule is well described by

$$m(z) = m_1 \frac{\sinh\left(\frac{d-2z}{2\lambda}\right)}{\sinh\left(\frac{d}{2\lambda}\right)} \quad (11)$$

where z is the distance normal to the surface, measured from one surface (considered at the external boundary of the first water layer), d is the distance between surfaces,

m_1 is the polarization of the first water layer, and λ is the decay length of the polarization. For a layered structure of water, λ can be calculated using the expression⁵

$$\lambda = \left(\frac{C_1 \Delta^2}{\frac{1}{\gamma} - (C_0 + 2C_1)} \right)^{1/2} \quad (12)$$

where Δ is the distance between the centers of the adjacent layers, γ is the molecular polarizability, and C_k are interaction coefficients that account for the electric field generated by the dipoles of the layer $i + k$ at a site of layer i

$$E_i^{\text{local}} = C_{-1}m_{i-1} + C_0m_i + C_1m_{i+1} \quad (13)$$

For an icelike structure of water, the values of the coefficients are^{5,6}

$$C_0 = -\frac{3.7663}{4\pi\epsilon_0\epsilon''\bar{l}^3} \quad (14a)$$

and

$$C_1 = C_{-1} = \frac{1.8272}{4\pi\epsilon_0\epsilon''\bar{l}^3} \quad (14b)$$

where \bar{l} is the distance between the centers of two adjacent water molecules and ϵ'' is an effective dielectric constant for the interaction between neighboring water molecules; again $\epsilon'' < \epsilon$.

The polarization of the first water layer is produced by the surface dipoles and the water dipoles of the first two layers, hence

$$m_1 = \frac{\gamma \bar{E}}{\left(1 - \gamma \left(C_0 + C_1 \frac{\sinh\left(\frac{d-2\Delta}{2\lambda}\right)}{\sinh\left(\frac{d}{2\lambda}\right)} \right) \right)} \quad (15)$$

and the total energy, per unit area, due to the polarization of water molecules by the surface dipoles, is given by

$$U_H^{\text{total}}(d) = \frac{\gamma \bar{E}^2}{\left(1 - \gamma \left(C_0 + C_1 \frac{\sinh\left(\frac{d-2\Delta}{2\lambda}\right)}{\sinh\left(\frac{d}{2\lambda}\right)} \right) \right)^2} \times \frac{d - \lambda \sinh\left(\frac{d}{\lambda}\right)}{4v \sinh^2\left(\frac{d}{2\lambda}\right)} \quad (16)$$

where v is the volume occupied by a water molecule. The hydration interaction energy per unit area is given by

$$U_H(d) = U_H^{\text{total}}(d) - U_H^{\text{total}}(\infty) \quad (17)$$

II.F. A Simple Model for the Interaction Energy. We will try first to obtain some information about the interaction energy by using some simple approximations.

The following approximate expressions will be used for the interaction energies per unit area:

$$U_H = A_1 \exp\left(-\frac{d}{\lambda_1}\right) \quad (18a)$$

$$U_{DL} = \frac{64C_e kT}{\kappa} \tanh^2\left(\frac{e\psi_s}{4kT}\right) \exp(-\kappa d) = A_2 \exp\left(-\frac{d}{\lambda_2}\right) \quad (18b)$$

$$U_{vdW} = -\frac{A_H}{12\pi d^2} \quad (18c)$$

which are rough approximations of the interaction energies provided by the equations presented above (eqs 17, 8b, and 9, respectively).

Neglecting the double layer interaction (neutral interfaces), one obtains for the disjoining pressure (the negative of the derivative of the interaction energy) the expression

$$\Pi(d) = \frac{A_1}{\lambda_1} \exp\left(-\frac{d}{\lambda_1}\right) - \frac{A_H}{6\pi d^3} \quad (19)$$

Newton black films, which are the only ones that can exist in the absence of double layer interactions, can be obtained only if the disjoining pressure has a positive value (otherwise, the film will collapse). The extrema of the disjoining pressure are obtained through the derivation of eq 19 with respect to d

$$\frac{d^4}{\lambda_1^4} \exp\left(-\frac{d}{\lambda_1}\right) = \xi^4 \exp(-\xi) = F_1(\xi) = \frac{A_H}{2\pi A_1 \lambda_1^2} \quad (20)$$

where $\xi = d/\lambda_1$. The function $F_1(\xi)$ in eq 20 has a maximum at $\xi = 4$ (see Figure 1a); therefore, eq 20 has solutions only if the Hamaker constant $A_H < 2\pi A_1 \lambda_1^2 F_1(4) = 29.46 A_1 \lambda_1^2$. In such cases, eq 20 has two solutions. The smaller one corresponds to a maximum disjoining pressure and the other one to a local minimum. A useful lower bound is obtained when the maximum value of the disjoining pressure vanishes, $\Pi(d) = 0$. Using eqs 19 and 20, one obtains for the latter case

$$d^* = 3\lambda_1 \quad (21a)$$

$$A_1^* = \frac{A_H}{162\pi \lambda_1^2 \exp(-3)} \quad (21b)$$

A stable film can be obtained only if the hydration repulsion is stronger than the above critical value, hence if $A_1 > A_1^*$, and the maximum disjoining pressure occurs at a distance $d < d^* = 3\lambda_1$.

When all three interactions are taken into account, the extrema of the disjoining pressure are given by

$$\xi^4 (\exp(-\xi) + r_1^2 r_2 \exp(-r_1 \xi)) = F_2(\xi) = \frac{A_H}{2\pi A_1 \lambda_1^2} \quad (22)$$

where $r_1 = \lambda_1/\lambda_2$ and $r_2 = A_2/A_1$. The left-hand term of eq 22 is a positive function of ξ , which vanishes at $\xi = 0$ and $\xi \rightarrow \infty$. This function is represented in Figure 1 for various values of the ratios r_1 and r_2 . If the right-hand term is sufficiently large to exceed the maximum value of $F_2(\xi)$ (strong attraction), eq 22 has no solution and the film collapses. For $r_2 = 0$ (Figure 1a), $F_2(\xi) \equiv F_1(\xi)$ and there are two solutions if $A_H < 29.46 A_1 \lambda_1^2$. For $r_2 = 0.05$ and

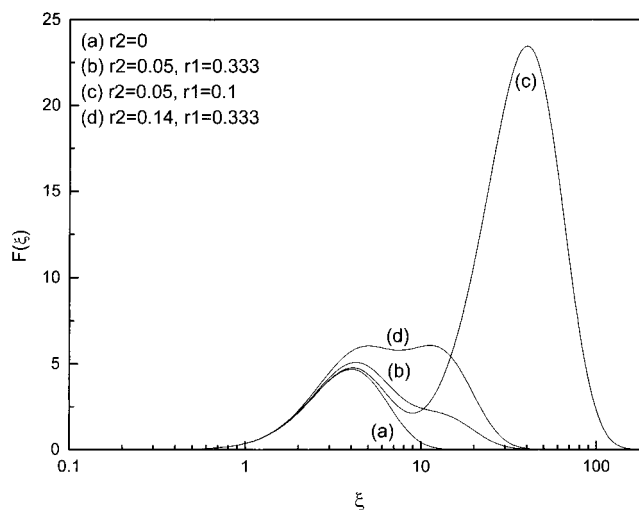


Figure 1. $F_2(\xi) = \xi^4 (\exp(-\xi) + r_1^2 r_2 \exp(-r_1 \xi))$ (eq 22) for (a) $r_2 = 0$, (b) $r_1 = 0.333$ and $r_2 = 0.05$, (c) $r_1 = 0.1$ and $r_2 = 0.05$, and (d) $r_1 = 0.333$ and $r_2 = 0.14$.

$r_1 = 0.333$ (Figure 1b), eq 22 still has only two solutions; hence there is only one maximum of the disjoining pressure. At metastable equilibrium, the disjoining pressure equals the external pressure. Starting with a thick film and increasing the external pressure, the thickness decreases continuously, until the film ruptures. However, if the ratio r_1 is sufficiently small ($r_1 = 0.1$ and $r_2 = 0.05$, Figure 1c), there is a range of Hamaker constants ($13.5 A_1 \lambda_1^2 < A_H < 29.9 A_1 \lambda_1^2$), in which eq 22 has four solutions. In these cases there are two maxima in the disjoining pressure, located at distances d_1 and d_2 . Let us first consider that the maximum at d_1 is higher (see Figure 2a). Starting with a thick film and increasing the external pressure, the thickness of the film decreases continuously up to the distance d_2 , when the external pressure reaches the value Π_2 . A further increase of the pressure produces a jump from the distance d_2 to the distance d_1 , which corresponds to a stable Newton black film. On the other hand, if the maximum at d_2 is the higher one (Figure 2b), then the increase of the pressure above Π_2 produces the rupture of the film. However, the existence of a domain with four solutions for eq 22 does not necessarily imply that both Newton and common black films can be stable. While two maxima of the disjoining pressure exist for $r_1 = 0.333$ and $r_2 = 0.14$ (Figure 1d), the value of the second one is negative (Figure 2c) and hence only the Newton black film is stable.

II.G. Model Calculations. In what follows it will be shown that the general behavior discussed above is consistent with realistic calculations. An important parameter, which is however unknown, is the equilibrium constant of the association–dissociation equilibrium, K_D . The dissociation constant of the ion pair NaSO_4^- was estimated to be $K_D = 10^{-0.7} \text{ mol/dm}^3 = 0.1995 \text{ mol/dm}^3$.¹¹ Because of the repulsion among the headgroups on the interface, the dissociation constant is expected to be lower in the present case. In what follows, we will use $K_D = 0.050 \text{ mol/dm}^3$. For this value, the pressures at which the transitions from the common to the Newton black films occur are in agreement with the experiments of Exerowa et al.²

As noted in the previous section, to obtain a transition from the common to a Newton black film, the decay lengths of the hydration and double layer repulsions must be

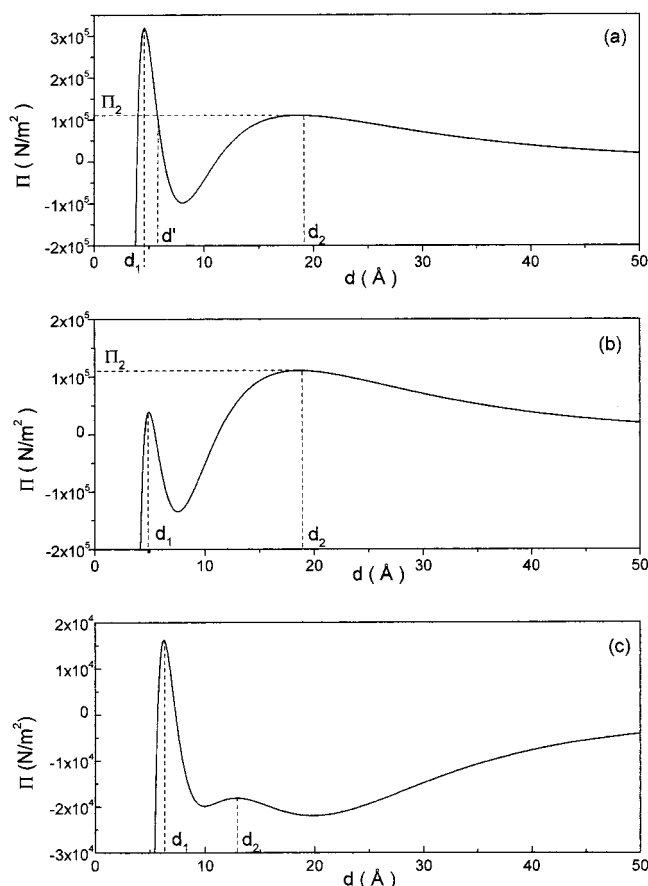


Figure 2. Disjoining pressure $\Pi(d)$ vs d : (a) $A_H = 10^{-20}$ J, $A_1 = 0.017$ J/m², $\lambda_1 = 1.5$ Å, $A_2 = 0.001$ J/m², $\lambda_2 = 15.0$ Å; (b) the same values for the parameters as in (a), except $A_1 = 0.016$ J/m²; (c) $A_H = 10^{-20}$ J, $A_1 = 0.0121$ J/m², $\lambda_1 = 1.5$ Å, $A_2 = 6.05 \times 10^{-4}$ J/m², $\lambda_2 = 4.5$ Å (these values correspond to the domain of four solutions of eq 22 of curve d of Figure 1; hence $r_1 = 0.333$, $r_2 = 0.05$, $F_2(\xi) = 5.85$).

sufficiently different. A transition from the common to the Newton black film was observed experimentally² to start when the electrolyte concentration exceeded 0.165 mol/dm³, and transitions were observed to take place up to the highest concentration (0.31 mol/dm³) used in experiment. For these two concentrations, the Debye lengths are $\lambda_2 = (\kappa)^{-1} = 7.5$ and 5.5 Å, respectively. To obtain a separation between the pressure peaks, the decay length for the hydration repulsion should be much smaller. For a molecular polarizability $\gamma = 8.6 \times 10^{-40}$ C² m²/J, calculated using the Debye–Lorentz model, the upper bound for the hydration decay length, λ_1 , calculated assuming $\epsilon'' = 1$, is 2.96 Å.⁵ Lower values can be obtained when the effective dielectric constant ϵ'' for the interaction between molecules is larger than 1. The decay length is also decreased by the structural disorder of the water layers.⁶ While recent experiments indicated that for lipid bilayers λ_1 is close to 2 Å,¹² there are no such experimental results for soap films. In what follows, we will use $\epsilon'' = 9$, which introduced in eqs 14 and using eq 12 provides $\lambda_1 = 1.0$ Å.

In Figure 3, the disjoining pressure, calculated as described above, is plotted for $C_s = 10^{-3}$ mol/dm³ and $p_1/\epsilon' = 3.45$ D. For $C_e = 0.15$ mol/dm³ (Figure 3a), the first maximum of the disjoining pressure is somewhat

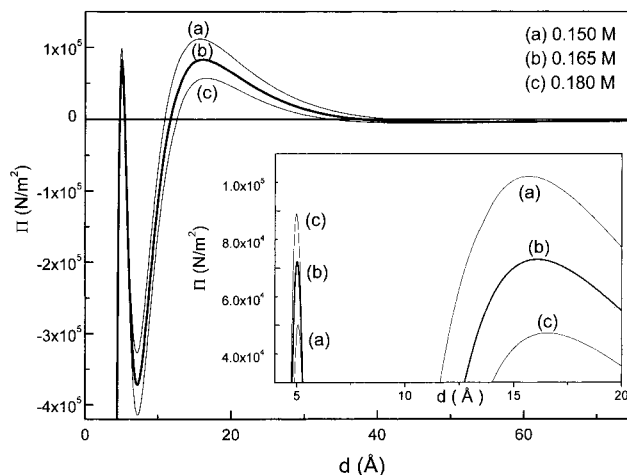


Figure 3. Disjoining pressure $\Pi(d)$ vs d for $\Gamma_\infty = 5 \times 10^{-6}$ mol/m², $a_1 = 881$ m³/mol, $a_2 = -1.53$, $b_1 = -3.08 \times 10^{-22}$ J, $b_2 = -6.28 \times 10^{-14}$ J/m, $b_3 = 8.28 \times 10^7$ m⁻¹, $b_4 = 6.13 \times 10^{15}$ m⁻², $b_5 = -9.00 \times 10^{-23}$ J, $K_D = 0.050$ mol/dm³, $C_s = 1 \times 10^{-3}$ mol/dm³, $\lambda_1 = 1.0$ Å, $p_1/\epsilon' = 3.45$ D: (a) $C_e = 0.150$ mol/dm³; (b) $C_e = 0.165$ mol/dm³; (c) $C_e = 0.180$ mol/dm³. In the inset, the peaks of the disjoining pressure are presented at a smaller scale.

lower than the second maximum, which corresponds to the common black film. Therefore, the increase of the external pressure produces in this case the rupture of the common black film. The increase of the electrolyte concentration has two effects. First, it decreases the double layer repulsion leading to a lower height of the second peak, and secondly, the recombination of surface charges on the interfaces with counterions provides an increase in the hydration repulsion (via the increase of the ion pair density) and hence an increase of the height of the first peak. In Figure 3b ($C_e = 0.165$ mol/dm³), there is a very narrow range of pressures in which the Newton black film is the only stable one (the value $p_1/\epsilon' = 3.45$ D was selected to provide about the same height for the two peaks of the disjoining pressure at $C_e = 0.165$ mol/dm³). A further increase of the electrolyte concentration ($C_e = 0.18$ mol/dm³, Figure 3c) lowers the transition pressure from the common to the Newton black film (because of the screening of the double layer) and also slightly increases the rupture pressure of the Newton black film (because of the increase in the hydration repulsion with increasing ionic strength). At high electrolyte concentrations, the Newton black films might be the only stable ones.

The calculations presented in this section show that the behavior of the black films can be understood in terms of the interaction energy between planar films. However, they cannot explain why, for the same electrolyte concentration, the transition from the common to the Newton black film occurs at various pressures (for example, for $C_e = 10^{-3}$ mol/dm³, $p = (2.5 \div 9.8) \times 10^4$ N/m²).² In addition, the thickness at the transition apparently does not depend on the electrolyte concentration (while the Debye length λ_2 does) and is larger than the upper bound $3\lambda_2$ (which is obtained, when only the double layer and van der Waals interactions are present, using the approach employed to derive eq 21). In the next section, it will be shown that by accounting for the thermal fluctuations of the interfaces one can provide answers to these questions.

III. The Role of Thermal Fluctuations of the Interfaces

The first quantitative theory, which accounted for the repulsion between phospholipid bilayers due to a steric

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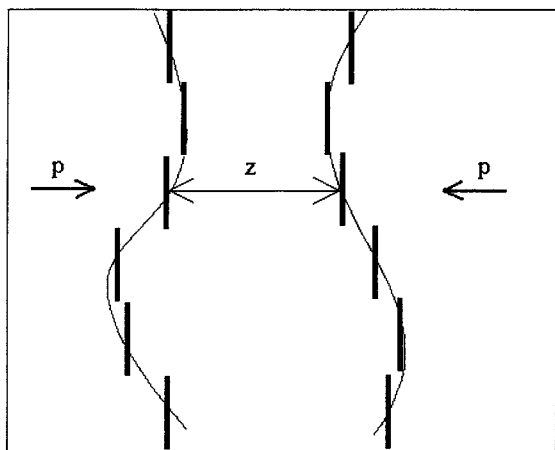


Figure 4. The fluctuating interfaces are approximated by independent small, planar surfaces of area S separated by the distance z .

(rigid wall) confinement of their undulation by the neighboring bilayers, was developed by Helfrich.¹³ Since then a number of attempts were made to extend the Helfrich theory to arbitrary interaction potentials.^{14–16} The last two approaches involved the observation that the partition function of an undulating bilayer in an external potential can be calculated exactly for a harmonic potential. However, in the present case, we are interested in the equilibrium position as a function of the applied pressure in a metastable state and the interaction potential (which possesses two local minima) cannot be approximated by a harmonic one. A new approach is therefore suggested below.

III.A. The Thermal Fluctuations of the Interfaces for Arbitrary Interactions. After the Helfrich initial theory,¹³ Helfrich and Servuss¹⁷ suggested an alternate derivation of the entropic repulsion due to the confinement of a membrane between rigid walls, by considering the lipid bilayer composed of many independent “pieces”, whose area is related to the root mean square fluctuations of the positions of the undulating bilayer. As shown below, this representation can be extended to interfaces interacting via arbitrary potentials.

In what follows, the two fluctuating interfaces will be replaced by many small, independent surfaces of area S , separated by a distance z (see Figure 4). The (metastable) distribution of the distances between the surfaces, in an ensemble subjected to a constant pressure, will be assumed Boltzmannian. It will be also assumed that the fluctuating interfaces have constant total areas and an elastic bending modulus K_C . Let us first consider that the interfaces interact per unit area through a harmonic potential

$$U(z) = \frac{1}{2} B(z - z_0)^2 \quad (23)$$

where B is the spring constant, z is the distance between two small surfaces, and z_0 is the average thickness of the

film. The Boltzmannian distribution of the thicknesses has the form

$$\rho(z) \propto \exp\left(-\frac{SU(z)}{kT}\right) \propto \exp\left(-\frac{SB(z - z_0)^2}{2kT}\right) \quad (24)$$

However, as demonstrated by Helfrich,¹³ the distribution of thicknesses in a harmonic potential is given by

$$\rho(z) = \frac{1}{(2\pi)^{1/2}\sigma} \exp\left(-\frac{(z - z_0)^2}{2\sigma^2}\right) \quad (25)$$

where the root mean square fluctuation of the thickness, σ , obtained from the partition function has the form^{13,18}

$$\sigma^2 = \frac{kT}{8(K_C B)^{1/2}} \quad (26)$$

Comparing eqs 24 and 25, and taking into account eq 26, one obtains

$$S = \frac{kT}{B\sigma^2} = 8\left(\frac{K_C}{B}\right)^{1/2} \quad (27)$$

For a constant applied pressure p , the distribution of distances between the small surfaces can be calculated using the enthalpy instead of the energy

$$\rho(z) \propto \exp\left(-\frac{S\left(\frac{1}{2}B(z - z_0)^2 + pz\right)}{kT}\right) = \exp\left(-\frac{S\left(\frac{1}{2}B(z - z_0')^2 + C\right)}{kT}\right) \quad (28)$$

where z_0 is the average thickness at $p = 0$, $z_0' = z_0 - (p/B)$ is the average thickness at pressure p , and $C = z_0 p - (p^2/2B)$. The constant C is independent of z and hence does not affect the distribution $\rho(z)$, being eliminated through normalization. As expected, the new equilibrium distance is the thickness where the elastic force equilibrates the external pressure, $B(z_0 - z_0') = p$. Let us first note that in this case, there is no repulsion due to the entropic confinement, because the spring constant does not depend on the applied pressure, and therefore the intersurfaces distance distribution, $\rho(z)$, and the mean square fluctuation, $\sigma^2 = \langle (z - z_0')^2 \rangle$, are independent of the applied pressure and, hence, on the average distance. Because the free energy due to the entropic confinement is given by $(kT)^2/(128K_C\sigma^2)$,^{13,18} the undulation force is zero in this case.

The above derivation will be extended to a well-behaved interaction potential, $U(z)$, for which $U(0) \rightarrow \infty$, $U(\infty) \rightarrow 0$ and has a minimum at a distance z_0 . In the vicinity of the minimum of the enthalpy (per unit area) $H(z) = U(z) + pz$, the potential will be approximated by a harmonic one, with the effective spring constant $B' = \partial^2 H(z)/\partial z^2|_{z=z_0'}$, where z_0' is the solution of $\partial H(z)/\partial z = 0$. It will be assumed that the areas of the small independent surfaces into which the interfaces are decomposed are still given by eq 27, but

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with a new spring constant B . In this case, the distribution of distances is given by

$$\rho(z) = \frac{1}{N} \exp \left(-8 \left(\frac{K_C}{\left| \frac{\partial^2 H(z)}{\partial z^2} \right|_{z=z_0'}} \right)^{1/2} \frac{H(z)}{kT} \right) \quad (29)$$

where N is obtained through normalization: $N = \int_0^\infty \rho(z) dz$.

The average thickness, $\langle z \rangle$, is obtained from

$$\langle z \rangle = \int_0^\infty z \rho(z) dz \quad (30)$$

while the mean square fluctuation is given by

$$\sigma^2 = \int_0^\infty (z - \langle z \rangle)^2 \rho(z) dz \quad (31)$$

For nonvanishing values of p , both integrals (30) and (31) converge.

Using eqs 29–31, one can calculate the average thickness and the root mean square fluctuation of the inter-surfaces separation as a function of the applied pressure, once the interaction potential is known. For illustration purposes, let us first apply the method to the simple interaction potential

$$U(z) = A_1 \exp \left(-\frac{z}{\lambda_1} \right) - \frac{A_H}{12\pi z^2} \quad (32)$$

with $A_1 = 0.07 \text{ J/m}^2$, $\lambda_1 = 1.0 \text{ \AA}$, and $A_H = 10^{-20} \text{ J}$, which are some typical values of the parameters. The potential is not well-behaved (in the sense described above) because $U(0) \rightarrow -\infty$. The stable equilibrium position corresponds in this case to the trivial case $z = 0$ (the film ruptures). However, we are interested in the behavior of the film at the metastable equilibrium (the secondary minimum of the enthalpy, at z_0' , see Figure 5). At metastable equilibrium, the film can have a thickness between z_1' , corresponding to the maximum of the enthalpy, and $z = \infty$.

Figure 5 presents the enthalpy and the distribution $\rho(z)$ for various values of K_C and (a) $p = 1.0 \times 10^4 \text{ N/m}^2$ and (b) $p = 1.0 \times 10^6 \text{ N/m}^2$. The asymmetry of the distributions depends on the pressure applied and is a consequence of the anharmonicity of the interaction potential. The lifetime of the film (until it ruptures) depends on the value of $\rho(z)$ at $z = z_1'$. Curves 1–3 provide the ratios $\rho(z)/\rho(z_0')$, for various values of K_C . They are negligible at $z = z_1'$; hence the metastable state at the secondary minimum has a long lifetime.

In Figure 6, the pressure (a) and the root mean square fluctuation (b) are plotted as functions of the average thickness of the film, for $K_C = 10 \times 10^{-19} \text{ J}$ and for (1) the anharmonic (eq 32) and (2) the harmonic (eq 23) interaction potentials. The spring constant for the second case was obtained from the harmonic approximation of eq 32 around its minimum, at $p = 0$.

We already noted that, for a harmonic interaction, $\sigma_h = \text{constant}$ and $\langle z \rangle = z_0' = z_0 - (p/B)$ varies linearly with the applied pressure. However, for an anharmonic interaction, σ_a is a function of the applied pressure (or, equivalently, of the average thickness of the film $\langle z \rangle$, which differs from z_0' because of the asymmetry of the distribution). The functional dependence of the pressure on the average thickness differs in the anharmonic and harmonic cases. The pressure is higher in the former case, because of the

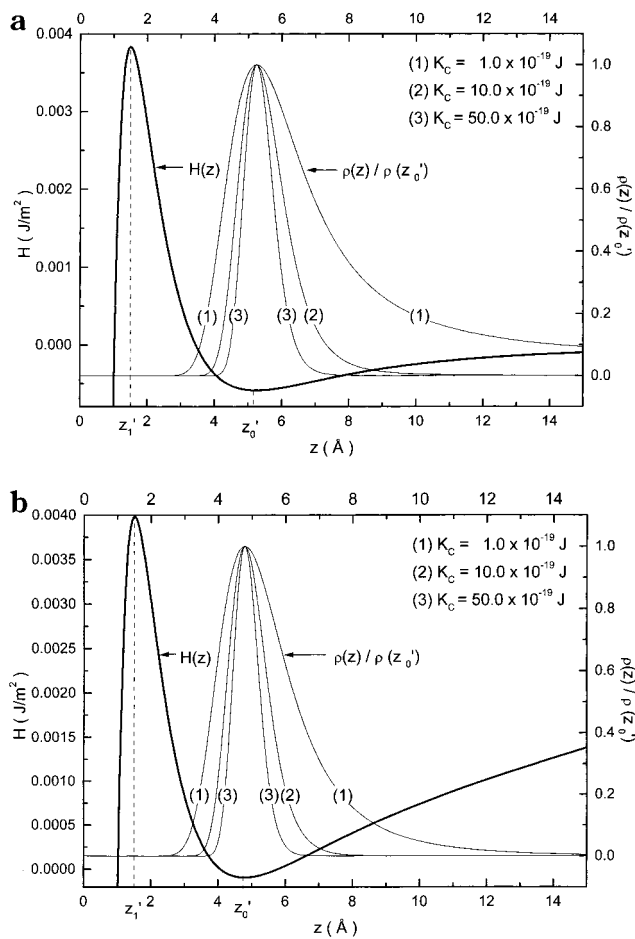


Figure 5. The enthalpy H (thick line) and the ratio $\rho(z)/\rho(z_0')$ vs the distance z for an anharmonic interaction potential (eq 32) with $A_H = 10^{-20} \text{ J}$, $A_1 = 0.07 \text{ J/m}^2$, $\lambda_1 = 1.0 \text{ \AA}$: (1) $K_C = 1.0 \times 10^{-19} \text{ J}$; (2) $K_C = 10.0 \times 10^{-19} \text{ J}$; (3) $K_C = 50.0 \times 10^{-19} \text{ J}$. The applied pressures were (a) $p = 1.0 \times 10^4 \text{ N/m}^2$; (b) $p = 1.0 \times 10^6 \text{ N/m}^2$.

“undulation repulsion”, which increases with decreasing bending modulus. The undulation repulsion, however, depends on the interaction potential and vanishes for a harmonic interaction.

The lifetime of the film depends on $\rho(z_1')$; hence it decreases for interfaces with low bending moduli (less rigid interfaces are likely to fluctuate with a larger amplitude and thus can reach easier the maximum of the enthalpy). Therefore, while the undulation repulsion increases the average thickness of the film at a given external pressure (Figure 6a), it decreases its stability (Figure 5).

III.B. The Role of Thermal Fluctuations on the Transition from Common Black Films to Newton Black Films. The method described in the previous section will be now applied to thin films with fluctuating interfaces, with the interaction energy calculated as in section II.G. For low values of the external pressure, the enthalpy has two metastable minima at z_N and z_C , and a stable one at $z \rightarrow 0$ (the former two correspond to the Newton and to the common black films, respectively, and the latter implies the rupture of the film), separated by two maxima located at z_1 and z_2 (see Figure 7a). At metastable equilibrium the distances between the surfaces are distributed between z_1 and z_2 for the Newton black film and between z_2 and $z \rightarrow \infty$ for the common black film. The stability of the metastable states depends on the chance for a small area S of the interface to reach the

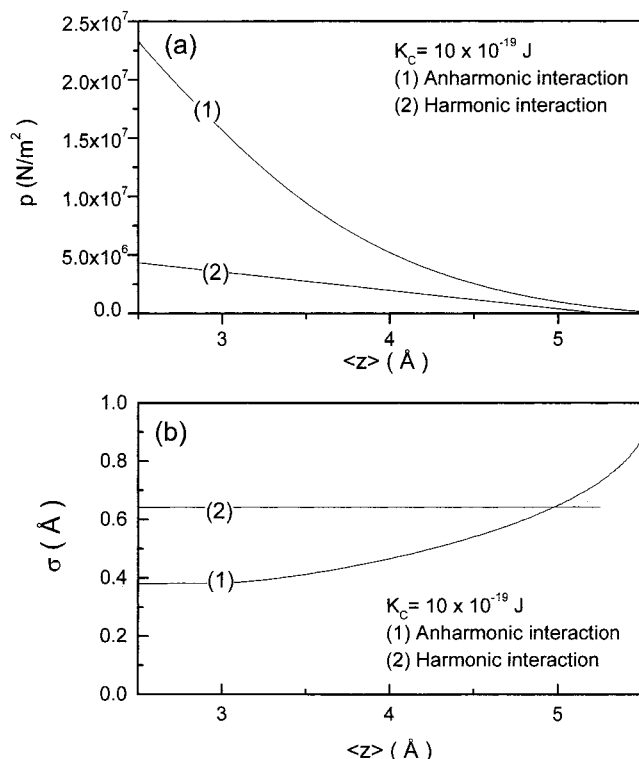


Figure 6. (a) The applied pressure p and (b) the root mean square fluctuation σ vs average thickness $\langle z \rangle$ for (1) anharmonic interaction potential (eq 32) and (2) its harmonic approximation (at $p = 0$).

limits of the domain (the heights of the adjacent peaks). The lifetime of a state in the potential well is proportional to the factor $\exp(S\Delta H/kT)$; hence the lifetime until the common black film transforms into a Newton black film, $t_{C \rightarrow N}$ is proportional to

$$t_{C \rightarrow N} \propto \exp\left(\frac{S_C(H(z_2) - H(z_C))}{kT}\right) \propto \frac{\rho_C(z_C)}{\rho_C(z_2)} \quad (33a)$$

while the lifetimes of a Newton black film until it ruptures, $t_{N \rightarrow R}$, or until its transition to a common black film, $t_{N \rightarrow C}$, are given by

$$t_{N \rightarrow R} \propto \exp\left(\frac{S_N(H(z_1) - H(z_N))}{kT}\right) \propto \frac{\rho_N(z_N)}{\rho_N(z_1)} \quad (33b)$$

and

$$t_{N \rightarrow C} \propto \exp\left(\frac{S_N(H(z_2) - H(z_N))}{kT}\right) \propto \frac{\rho_N(z_N)}{\rho_N(z_2)} \quad (33c)$$

respectively.

Both minima of the enthalpy, while metastable, might have a relatively long lifetime, and a system prepared in one state (common black film or Newton black film) might remain in that state during the time of the experiment, if the potential barriers are sufficiently high. However, because of the thermal fluctuations, it is possible to have, for the same experimental conditions, a transition in a range of pressures, and this explains one of the experimental results of Exerowa et al.²

When both the Newton and the common black films have lifetimes exceeding the duration of the experiment in a domain of applied pressures, the common black film

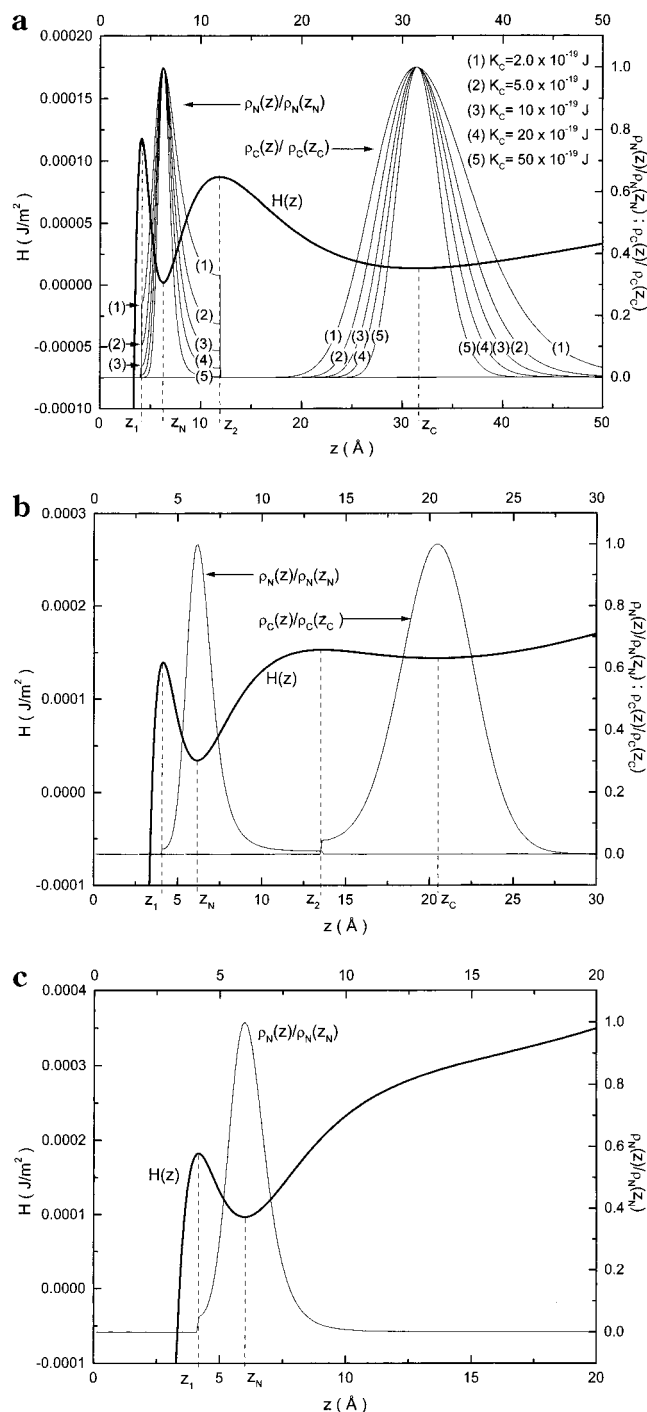


Figure 7. The enthalpy H (thick line) and the ratios $\rho_N(z)/\rho_N(z_N)$ and $\rho_C(z)/\rho_C(z_C)$ vs the distance z for the parameters $\Gamma_\infty = 5 \times 10^{-6}$ mol/m², $a_1 = 881$ m³/mol, $a_2 = -1.53$, $b_1 = -3.08 \times 10^{-22}$ J, $b_2 = -6.28 \times 10^{-14}$ J/m, $b_3 = 8.28 \times 10^7$ m⁻¹, $b_4 = 6.13 \times 10^{15}$ m⁻², $b_5 = -9.00 \times 10^{-23}$ J, $K_D = 0.050$ mol/dm³, $C_s = 1 \times 10^{-3}$ mol/dm³, $\lambda_1 = 1.0$ Å, $p_L/\epsilon' = 3.7$ D, $C_e = 0.165$ mol/dm³: (a) $p = 1.0 \times 10^4$ N/m², $K_C = (2.0, 5.0, 10.0, 20.0, 50.0) \times 10^{-19}$ J; (b) $p = 6.2 \times 10^4$ N/m², $K_C = 20.0 \times 10^{-19}$ J; (c) $p = 1.6 \times 10^5$ N/m², $K_C = 20.0 \times 10^{-19}$ J.

transforms into a Newton one at the upper bound of the domain, while the Newton black film can have a transition to the common one at the lower bound of the pressure domain. This results in a hysteresis in thickness with increasing and decreasing pressure.

The bending modulus K_C of the interfaces of the soap films is unknown; however, one expects to be comparable to those of the lipid bilayers in water, which are of the

order of 10^{-19} J.¹² In Figure 7a, the distributions of the thicknesses of the Newton and common black films, $\rho_N(z)/\rho_N(z_N)$ and $\rho_C(z)/\rho_C(z_C)$, respectively, are calculated for $C_e = 0.165$ mol/dm³, $p_l/\epsilon' = 3.7$ D, $p = 1.0 \times 10^4$ N/m², and various values of K_C (2, 5, 10, 20, and 50×10^{-19} J), the other parameters being as in section II.G. While the first metastable minimum (corresponding to a Newton black film) is somewhat deeper, the second one (corresponding to a common black film) is more stable to fluctuations, because $\rho_C(z_2)/\rho_C(z_C)$ is negligible, while $\rho_N(z_2)/\rho_N(z_N)$ is much larger. This is a result of the stronger spatial confinement of the undulation modes in the first minimum, which leads to a higher effective spring constant.

In what follows, it will be considered that the lifetime of a metastable state exceeds the duration of experiment if the potential barrier for a small surface of area S , $S\Delta H$, exceeds $3kT$. For the first minimum in Figure 7a, the potential barrier is higher than $3kT$ for $K_C > 20 \times 10^{-19}$ J; hence the Newton black films, once formed, remain stable in cases 4 and 5 during the experiment. In contrast, if the interfaces are more flexible (low K_C , cases 1, 2, and 3), the probability for an individual small surface to reach the height which separates two minima is much higher. In this case, the metastable equilibrium of the Newton black film has a shorter lifetime; while the film can either rupture or have a transition to a common black film, the second process has a higher chance. On the other hand, the common black films are more stable, because, while the minimum of the enthalpy is higher, the interfaces have more room to fluctuate.

The increase of the applied pressure decreases the stability of the common black film and the probability for a transition from a Newton to a common black film but also increases the probability of the rupture of the Newton black films. Figure 7b plots the enthalpy and the ratios $\rho_N(z)/\rho_N(z_N)$ and $\rho_C(z)/\rho_C(z_C)$, for $p = 6.2 \times 10^4$ N/m² ($K_C = 20 \times 10^{-19}$ J). The common black film becomes unstable (and a transition to a Newton black film occurs), while the Newton black film has a longer lifetime. At even a higher pressure (Figure 7c, $p = 1.6 \times 10^5$ N/m², $K_C = 20 \times 10^{-19}$ J) the Newton black film ruptures.

Assuming that a film is stable when the potential barrier for the individual surfaces in which the interface were decomposed is higher than a critical value (selected $3kT$ in the present paper), one can identify the regions of stability of the films. When the ratio of the distributions at the adjacent maximum and minimum of the enthalpy, $\rho(z_{\max})/\rho(z_{\min})$, exceeds $\exp(-3) = 0.05$, a transition to the next minimum is likely. In Figure 8a $\exp(-S\Delta H/kT)$ is plotted for $C_e = 0.165$ mol/dm³ and $K_C = 20 \times 10^{-19}$ J against the applied pressure for Newton black films at the first ($\rho_N(z_1)/\rho_N(z_N)$, curve 1) and second maximum ($\rho_N(z_2)/\rho_N(z_N)$, curve 2) and for the common black film, at the second maximum ($\rho_C(z_2)/\rho_C(z_C)$, curve 3). Below $p = 6.0 \times 10^4$ N/m², both the Newton and the common black films have a long lifetime. When the external pressure exceeds 6.0×10^4 N/m² (marked C - N in Figure 8a) the common black film is likely to have a transition to a Newton black film, and the latter has a long lifetime. However, when the pressure exceeds 1.5×10^5 N/m² (marked N - R in Figure 8a), the Newton black film is likely to rupture. Therefore, both kinds of films have a long lifetime below 6.0×10^4 N/m², only the Newton black films exist for pressures in the range 6.0×10^4 to 1.5×10^5 N/m² and no black films exist at higher pressures.

It is clear that the stability of the films depends on the interaction between surfaces; in addition, the domains of stability of the black films are strongly dependent on their rigidity. The calculations presented in Figure 8b differ

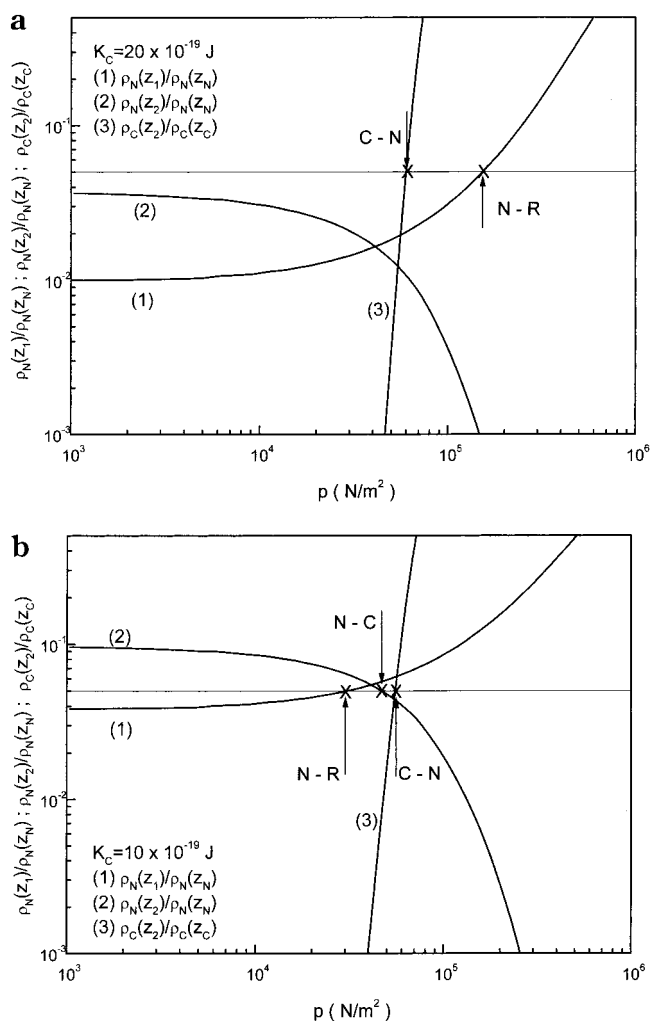


Figure 8. The ratios $\rho_N(z_1)/\rho_N(z_N)$, $\rho_N(z_2)/\rho_N(z_N)$, and $\rho_C(z_2)/\rho_C(z_N)$ as functions of the applied pressure for the same parameters as before ($\Gamma_\infty = 5 \times 10^{-6}$ mol/m², $a_1 = 881$ m³/mol, $a_2 = -1.53$, $b_1 = -3.08 \times 10^{-22}$ J, $b_2 = -6.28 \times 10^{-14}$ J/m, $b_3 = 8.28 \times 10^7$ m⁻¹, $b_4 = 6.13 \times 10^{15}$ m⁻², $b_5 = -9.00 \times 10^{-23}$ J, $K_D = 0.050$ mol/dm³, $C_s = 1 \times 10^{-3}$ mol/dm³, $\lambda_1 = 1.0$ Å, $p_l/\epsilon' = 3.7$ D, $C_e = 0.165$ mol/dm³): (a) $K_C = 20.0 \times 10^{-19}$ J; (b) $K_C = 10.0 \times 10^{-19}$ J.

from those of Figure 8a, only through a new value of the bending modulus, $K_C = 10 \times 10^{-19}$ J. However, the Newton black films are in this case unstable at any pressure; they are likely to have a transition to a common black film up to $p = 3.0 \times 10^4$ N/m², and either to rupture or to transform into common black films for pressures between 3.0×10^4 and 4.7×10^4 N/m². For higher pressures the Newton black films rupture immediately. The common black films are stable for pressures up to 5.5×10^4 N/m², after which they rupture. Therefore, in this case, the black films can exist only as common black films, at low applied pressures, but rupture at higher pressures.

The fluctuations increase the equilibrium thicknesses of the films (see Figures 5, 6a, and 7a), an effect which is particularly important for the common black films (see Figure 7a). This effect was found in the experiments of Exerowa et al.,² who noted that the DLVO theory (for planar surfaces) predicts a too small repulsion and suggested that the hydration force (which has a shorter range) cannot account for the discrepancy.

IV. Conclusions

In the first part of the paper, the interaction energy of thin soap films was calculated, assuming planar, parallel

interfaces ($K_C \rightarrow \infty$). The interaction energy (and hence the disjoining pressure) could explain qualitatively the behavior of the black films and the existence of a transition from the common black films to the Newton black films. At low electrolyte concentrations, the disjoining pressure peak due to the double layer force (corresponding to the common black film) is high and might exceed the first peak, caused by the hydration repulsion (corresponding to the Newton black film). Hence, the increase of the pressure leads to the rupture of the common black film. The increase of electrolyte concentration has two opposite consequences: the double layer repulsion decreases and, hence, the height of the second peak decreases, while the charge recombination increases the ion-pair density on the surface and, hence, increases the hydration force, raising the height of the first peak.

However, the theory involving planar interfaces does not account completely for the transition from the common to the Newton black films and for the rupture of the

common black films, which can occur in a range of pressures for the same remaining conditions. In the second part it is shown that the fluctuations of the thicknesses of the films lead to transitions which occur with different probabilities at an applied pressure.

The stability of the undulating films depends not only on the difference between the corresponding local minimum of the enthalpy and the adjacent maximum but also on the shape of the enthalpy in the vicinity of the minimum. The thermal fluctuations affect especially the stability of the Newton black films, because their spatial confinement is stronger. The confinement of the fluctuating interface can drive the Newton black films either to the common black film or to rupture. The present analysis indicates that the fluctuations of the interfaces, while decreasing the stability of the film, lead to larger thicknesses, in agreement with experiment.

LA011569W