

Stability of Soap Films: Hysteresis and Nucleation of Black Films

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We study the stability of soap films of a nonionic surfactant under different applied capillary pressures on the film. Depending on the pressure, either a thick common black film (CBF), or a microscopically thin Newton black film (NBF) is formed as a (metastable) equilibrium state, with a first-order (discontinuous) transition between the two. Studying the dynamics of the CBF-NBF transition, it is found that under certain conditions a hysteresis for the transition is observed: for a given range of pressures, either of the two states may be observed. We quantify the nucleation process that is at the basis of these observations both experimentally and theoretically.

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The stability of foams is important for a large number of applications; examples are detergency, the handling of certain foodstuffs, cosmetics, and fire fighting. When a fresh foam is formed, the soap films between the air bubbles are usually nonequilibrium structures, as they are very thick, on the order of micrometers. The first stage in the destabilization of a foam is generally the drainage of these thick soap films, mainly under the influence of gravity [1].

The thinner films that form in this process need not be out of equilibrium: different (metastable) equilibrium states can exist due to the colloidal interactions between the two surfaces bounding the soap film [1]. The three main interactions are, first, an electrostatic repulsion between the two surfaces that are covered with usually charged surfactant molecules. Second, the net effect of the intermolecular van der Waals interactions is always an effective attraction between the two surfaces, tending to thin the films. Third, a hard-core repulsion between the surfactant molecules, observed for the thinnest films, prevents the surfaces to approach very closely [1].

When, under given experimental conditions, the electrostatic and van der Waals interactions balance each other, long-lived films can form, which are relatively thick, of the order of 10 nm: these are called common black films (CBF). If, subsequently, the external pressure on the film increases, the electrostatic repulsion can be overcome and the CBF destabilizes. Depending on the conditions, it may be that either the film simply breaks, leading to the coalescence of the bubbles on either side of the surface, or a microscopically thin film may form, stabilized by the hard-core repulsion between the surfactants. These films are called Newton black films (NBF) and have a typical thickness of twice the size of the surfactant molecules, roughly 4 nm.

One of the important factors determining foam stability is therefore the probability of the CBF-NBF transition. In this Letter, we will demonstrate that this transition is a first-order surface phase transition through the observa-

tion of a hysteresis; despite the enormous literature on disjoining pressure isotherms, this, to our knowledge, has not been reported before. The hysteresis implies automatically that the transition occurs through a surface nucleation process; we show here that the nucleation process can be understood quantitatively, both experimentally and theoretically.

We study the stability of a single soap film submitted to different external pressures. This allows us to measure the interaction force per unit area the two interfaces exert on each other, the disjoining pressure $\Pi(l)$. Disjoining pressure isotherms were measured with the thin-film balance technique [2,3]. For our experiments, the sample holder consists of a capillary fused to a fritted glass disk; a film is formed in a 2 mm diameter hole in the frit. The sample holder is placed in a gas-tight measuring cell, with the free end of the capillary tube exposed to atmospheric pressure. The external gas pressure within the cell is imposed using a syringe pump; in mechanical equilibrium, the difference between the external and atmospheric pressures equals the disjoining pressure. A thermostat bath (20 °C) circulating around the cell ensured the thermal stability.

The thickness of the films is obtained from interferometry. White light reflected from the film surface is collected by a fiber, and its intensity at $\lambda = 657.5$ nm is measured by a photomultiplier. The thickness of the water core of the film, l , can then be obtained directly from the intensity after calculating the contribution due to the surfactant layers at the air-water interface [2,3]. High purity grade $C_{12}E_6$ (Nikko), where E stands for an ethylene oxide group, was used as a surfactant and ultrapure NaCl from Prolabo. Ultrapure water was used for the sample preparation; all samples had a $pH \approx 7$. The cmc (critical micelle concentration) obtained by surface tension measurements was $7 \times 10^{-5} M$ (mole/l). Although nonionic, surfactant films of this molecule are known to exhibit a slight surface charge, usually attributed to a difference in mobility of H^+ and OH^- ions near the

surface [3]. Therefore, there should also be an electrostatic contribution to the disjoining pressure. Such weak surface charges ensure that the electrostatic repulsion can be reasonably described by the linearized form of the Poisson-Boltzmann equation [1]. This leads to $\Pi_{\text{electrostatic}}(l) = Ce^{-\kappa l}$, with C a constant depending on the surface charge, and κ^{-1} the Debye screening length set by the electrolyte concentration, $\kappa^{-1} = 0.304/\sqrt{[\text{NaCl}]}$ nm for our system [1]. The total mechanical equilibrium condition for the system can then be written as [4,5]

$$\Pi(l) = Ce^{-\kappa l} - \frac{A}{l^3} + \frac{B}{l^9} = P_{\text{ext}} - P_{\text{atmosphere}} \equiv \Delta P, \quad (1)$$

where the second term on the right hand side accounts for the van der Waals interactions; A is the Hamaker constant [5]. The third term accounts for the steric repulsion between the surfactant molecules; the $1/l^9$ form originates from the assumption that the intermolecular interactions are given by a Lennard Jones potential. In the following, we will consider a fixed concentration of $1.36 \times 10^{-4} M$, twice the cmc. It is well known that micellar structure can also contribute to the disjoining pressure; however, for these low concentrations this contribution is negligible [2]. In order to be able to compare with Eq. (1) we therefore fix the surfactant concentration and vary the salinity.

Figure 1 depicts the measured disjoining pressure isotherms. For low salinities both CBF and NBF branches can be observed, whereas only the NBF branch of the isotherm can be measured for $[\text{NaCl}] \geq 3 \times 10^{-3} M$. This implies that the addition of salt screens the electrostatic interactions to such an extent that the long-lived thick films of the CBF state can no longer be observed: only the NBF is observed. For lower salt, the electrostatic interactions are sufficient to stabilize CBF's. From Eq. (1) one then anticipates the occurrence of a first-order (discontinuous) transition between a CBF and a NBF. Probably the easiest way to see this is to realize that $\Pi(l) = -dV(l)/dl$, with $V(l)$ the interaction energy between the two surfaces. Graphically, this means that the intersec-

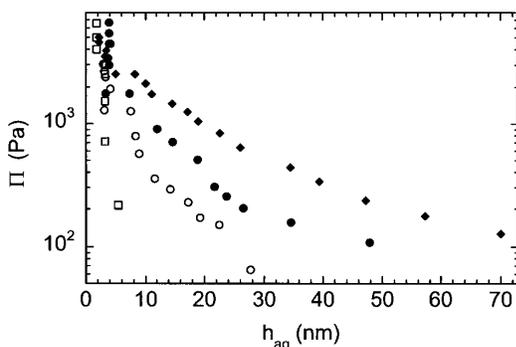


FIG. 1. Disjoining pressure $\Pi(l)$, for $1.36 \times 10^{-4} M$ $C_{12}E_6$; diamonds: $2 \times 10^{-4} M$ NaCl; filled circles: $4.5 \times 10^{-4} M$ NaCl; open circles: $10^{-3} M$ NaCl; and squares: $3 \times 10^{-3} M$ NaCl.

tions of $\Pi(l)$ with ΔP correspond to extrema of the energy; for not too high ΔP , three intersections occur; these correspond to the CBF and NBF as minima with an intermediate maximum: hence the transition between the two states is of first order.

The unambiguous demonstration of the first-order nature of the transition follows from the observation of a hysteresis: for a range of pressures, either of the two states can be found. This directly shows that the two energy minima are separated by a maximum, and that a nucleation process is necessary to transit from one state to another. Figures 2(a)–2(c) depict the results for the disjoining pressure for different salinities, on increasing and decreasing the external pressure. Figure 2(a) shows a “standard” disjoining pressure curve in the sense that the CBF-NBF transition occurs at a certain external pressure; the inverse transition occurs when ΔP is subsequently reduced, and happens at the same pressure. A more surprising result is shown in Fig. 2(b): if the pressure is reduced after the formation of the thin from the thick film, it can be reduced below the CBF-NBF transition pressure, without the formation of a thick film happening. Increasing the salinity even further, this effect becomes even more pronounced. Figure 2(c) shows a CBF-NBF transition brought about upon applying a certain pressure, and subsequently waiting. If from the NBF state ΔP is subsequently decreased somewhat, no transition back to the CBF is observed on the largest time scale the film was followed: several hours. In order to observe the inverse transition, the pressure has to be lowered substantially [Fig. 2(c)]. All these features are very characteristic of the occurrence of a first-order transition, in which the new state has to form by a nucleation process.

These observations were made for pressures that were not too high. If, starting from zero applied pressure, the pressure was increased rapidly to a high value, a NBF forms directly. This suggests that we have reached the spinodal of the first-order transition, after which the formation of the NBF state happens directly by a surface spinodal decomposition process, rather than by nucleation. This can easily be understood by comparing the measured disjoining pressure curves with the model disjoining pressure of Eq. (1): if ΔP is increased beyond the value of the maximum of $\Pi(l)$, the CBF is no longer a (metastable) equilibrium solution of Eq. (1). This in turn implies that the maximum of the disjoining pressure isotherm corresponds to the spinodal.

Figures 2(a)–2(c) also show the comparison with Eq. (1). It is easy to demonstrate by calculating $d^2V(l)/dl^2$ that the decreasing part (with decreasing pressure) corresponds to films that are unstable, whereas the two distinct increasing parts correspond to the CBF and NBF. The fits give $A = 9.9 \times 10^{-21}$ J, which is of the order of the Hamaker constant for the air/water/air system [5]. For the electrostatic term, we find $\kappa^{-1} = 0.29 \pm 0.02/\sqrt{[\text{NaCl}]}$ nm, in agreement with theory; the surface

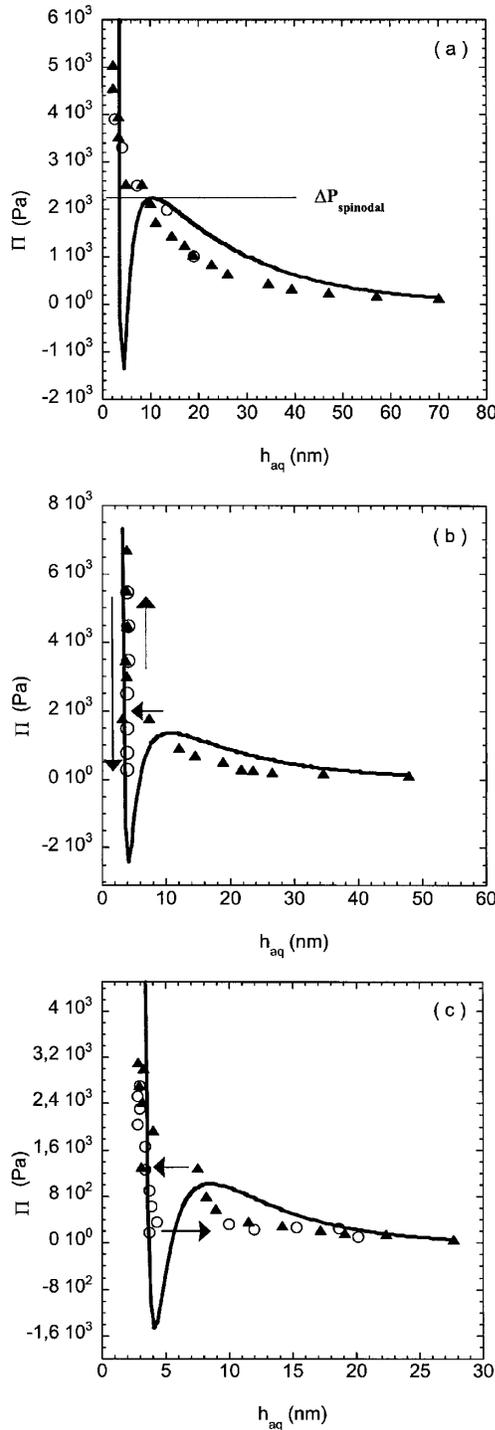


FIG. 2. $\Pi(l)$, for $1.36 \times 10^{-4} M$ $C_{12}E_6$ obtained: triangles upon increasing and circles upon decreasing the pressure. Drawn lines are fits using Eq. (1): (a) $2 \times 10^{-4} M$ NaCl, (b) $4.5 \times 10^{-4} M$ NaCl, and (c) $10^{-3} M$ NaCl.

charge density $\sigma = 0.9 \pm 0.2 \text{ mCm}^{-1}$, a value similar to that obtained in previous experiments [6].

The important observation is that the CBF-NBF transition does not take place instantaneously. Applying a constant pressure to a CBF film, we find that the NBF forms after a certain delay time. We start counting the

delay time after the system has stabilized mechanically; in the experiments this corresponds to a constant signal from the photomultiplier, i.e., a stable film thickness. The delay is measured as soon as this metastable state goes unstable; the hydrodynamics of film thinning/thickening consequently does not intervene in the nucleation time. For a given pressure, the distribution of delay times is a Poisson distribution (Fig. 3). This demonstrates the random nature of the transition process, and allows one to define a mean nucleation time t_b . By changing the pressure, the mean nucleation time t_b can be found as a function of the pressure (Fig. 4).

If an energy barrier for nucleating a patch of NBF within the CBF exists, and the nucleation is thermally activated, t_b should be inversely proportional to the nucleation probability $p \sim \exp(-E_{\text{act}}/k_B T)$, where E_{act} is the activation energy for the nucleation process, k_B Boltzmann's constant, and T the temperature [7]. The nucleation of a patch of thin film within the thick film cannot be observed directly for our system, as the thickness difference is too small to give a sufficient contrast. Additional observations with the charged surfactant $C_{14}TAB$, for which this contrast is sufficient, demonstrates that the nucleation takes place at random positions in the flat portion of the film; we believe that the same thing happens in the $C_{12}E_6$.

This nucleation problem is rather unique, since the barrier E_{act} can be calculated directly because the interactions are known. To go from the thick to the thin film, a hole larger than a critical size needs to open in the thick film and to grow. Because of the up/down and rotational symmetry, a single scalar function $l(r)$ is sufficient to describe this critical thickness fluctuation, where r is the

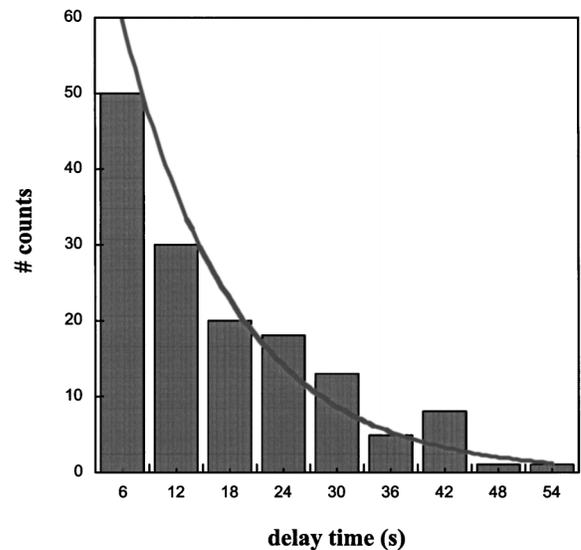


FIG. 3. Probability distribution of CBF-NBF transitions as a function of the delay time, for $1.36 \times 10^{-4} M$ $C_{12}E_6$ and $2 \times 10^{-4} M$ NaCl, applying a constant pressure $\Pi = 900 \text{ Pa}$. The full line gives the exponential behavior corresponding to a Poisson distribution.

radial coordinate with its origin at the center of the hole at the random site where the nucleation occurs. The film is assumed to be initially flat, with thickness of the CBF. The function $l(r)$ follows from extremizing:

$$E = 2\pi \int r dr \left[\frac{\gamma}{2} \left(\frac{dl(r)}{dr} \right)^2 + V(l(r)) + \Delta P l(r) \right] \quad (2)$$

with γ the surface tension; $V(l)$ can be obtained directly by integrating $\Pi(l)$: $V(l) = -\int_{\infty}^l \Pi(l') dl'$. Using the Debye length κ^{-1} to rescale the thickness, $r_0 = \kappa^{-2} \sqrt{\gamma/A}$ to rescale the radius, and $E_0 = \gamma \kappa^{-2}$ to rescale energy, stationarity of Eq. (2) yields

$$l'' + l'/r + \alpha e^{-l} - l^{-3} + \beta l^{-9} - \Delta P = 0, \quad (3)$$

where l , r , and P are dimensionless. Calculation of $l(r)$ from (3) and subsequent insertion into (2) yields the activation energy as the energy extremum.

However, one can do even better, and obtain an analytical expression for the activation energy, supposing one is close to the spinodal of the transition. The spinodal of the transition is the external pressure for which the CBF destabilizes instantaneously [see Fig. 2(a)] $\Delta P = \max[\Pi(l)]$, i.e., the external pressure for which the free energy minimum corresponding to the CBF ceases to exist.

Following [7], the activation energy can be calculated by expanding the interaction potential around the spinodal point. In the vicinity of the spinodal, the critical fluctuation needed to pass the barrier is small, and, consequently, the thickness remains very close to the CBF; this implies that the hard-core repulsion can be neglected. The dimensionless potential $V(l) = -l^{-2}/2 + \alpha e^{-l} + \Delta P l$ may then be expanded around the spinodal point l_s , ΔP_s . To third order in $\varphi = 1 - l_s$: $V(l) - V(l_s) = (\Delta P - \Delta P_s)\varphi + \chi\varphi^3$, with $\chi = (-\alpha e^{-l_s}/6) + (2/l_s^5)$. Then, in exactly the same way as in previous calculations [7], the activation energy follows as

$$E_{\text{act}} = \frac{(\Delta P - \Delta P_s)}{\chi} \int s ds \left[\frac{1}{2} \left(\frac{\partial u}{\partial s} \right)^2 - (u - u_0) + (u^3 - u_0^3) \right], \quad (4)$$

where the function u extremizes the integral and $u_0 = 1/\sqrt{3}$; as observed previously [7], the integral converges and is consequently a numerical proportionality constant. The energy barrier close to the spinodal limit is therefore directly proportional to $\Delta P - \Delta P_s$.

This can be compared directly to the experiment. The probability of nucleation follows as $p \propto e^{-E_{\text{act}}/k_B T}$, and the lifetime of the metastable CBF is simply proportional to $1/p$. Figure 4 shows the measured average lifetime as a function of the applied external pressure on a semilog scale. The data are in good agreement with the theoretical prediction from Eq. (4) that they should fall onto a

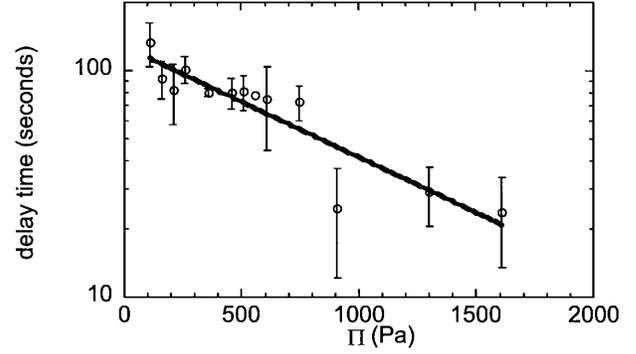


FIG. 4. Mean delay time t_b for the common black film–Newton black film transitions as a function of the applied pressure, for $1.36 \times 10^{-4} M$ $C_{12}E_6$ and $2 \times 10^{-4} M$ NaCl.

straight line. Therefore, this simple theory allows us to account for the experimental results.

In summary, we have studied a unique nucleation problem in the sense that the interactions involved in the nucleation barrier can be measured directly. This allows us to relate the lifetime of the metastable states directly to the colloidal interactions, and accounts for the stability (or instability) of soap films, a problem of considerable practical importance. In the experiment, we created the simplest model situation possible, in order to be able to compare with the theory in a meaningful way. Now that this is done, other contributions, for instance from the micelles, may be included both in theory and experiment.

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