On the rupture of thin films made from aqueous surfactant solutions

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Abstract

This short review describes the work on aqueous foam film stability with the important past contributions of Dotchi Exerowa and Dimo Platikanov, together with advances from other research groups. The review is focused on film rupture, for which few controlled experiments can be found in the literature and as a consequence, our understanding is still limited. The work on rupture of films in foams is described, together with the correlations with the rupture of isolated films. The review addresses mainly the case of aqueous films and foams, but analog studies of emulsions and emulsion films are also briefly discussed.

Keywords

Aqueous liquid films, surfactants, foams, emulsions, disjoining pressure, film rupture

1. Introduction

This article belongs to the special issue honoring the memory of Dotchi Exerowa and Dimo Platikanov, who animated a renowned research group in Sofia, Bulgaria. They both pioneered the research on the behavior of thin liquid films. Their outstanding contributions include the development of sophisticated methods for the study of freely supported films. This allowed them to clarify the phenomena occurring during film thinning and to obtain the first accurate measurements of forces between film surfaces. They also performed careful studies of film rupture, a topic that remains still today far from well understood. Because foams are collections of thin films, they extended the freely supported film studies to foam stability studies. They also showed that the behavior of foam films and emulsions films present close similarities. Their work stimulated many studies, in particular related to film and foam stability.

In this review, the early work on thin liquid films will be briefly described (more details can be found in the very comprehensive book by Exerowa and Krugliakov [1]), followed by a description of the subsequent work of the literature. The discussion will be limited to the case of soluble surfactants, currently used to create aqueous foams, and to small films, of size comparable to those found in foams (less or comparable to 1mm). Many studies in the Sofia's group were devoted to lipid bilayers, which are described in ref 1, but which will not be addressed here.

2. Early work on liquid films

Bubbles and films can hardly be made with pure liquids, they break almost instantaneously. When a surfactant is added in water, for instance soap, bubbles generated from the solution survive longer. The liquid films formed around the soap bubbles thin because of gravity and/or capillary suction into film borders. During thinning, the films exhibit beautiful interference colors in reflected light, an easy to observe and well-known phenomenon. Newton used this feature to investigate the spectral composition of white light[2]. He observed that the films lose colors during the late stage of thinning and appear black, hence the name of "black films" given to the very thin films. At the end of the 19th century, Plateau developed devices for film studies and pointed out the importance of the contact zone with the film holder, called later "Plateau border"[3]. Gibbs introduced the thermodynamic bases of film description, with the important notion of film elasticity[4]. At the beginning of the 20th century, Johnott and Perrin reported the existence of various types of black films and also the existence of stratification in films made from concentrated surfactant solutions[5 6]. This stratification is associated to ordering of surfactant micelles close to the film surfaces and was only explained later, when the existence of micelles was established.

In the 40's and afterwards, more systematic film studies were performed. Mysels and his colleagues studied the thinning of large vertical films on frames and showed the existence of two types of films, mobile and rigid, depending on the surfactant [7]. For instance, mobile films made with sodium dodecyl sulfate (SDS) solutions thin rapidly, their thickness is irregular, with thin regions moving upwards and thick regions downwards. This phenomenon was called "marginal regeneration". Rigid films obtained with mixed solutions of SDS and dodecanol thin more slowly and their thickness remains uniform. The difference in behavior was attributed to the increase in surface viscosity of the surfactant monolayers adsorbed at film surfaces when dodecanol is added.

Derjaguin and Kussakov studied smaller films formed between a bubble immersed in water and a solid surface [8]. They found that if the velocity of approach is sufficiently small, a flat film of constant thickness is formed. If the approach is faster, the film surfaces deform, taking the shape of a "dimple" (the film is thicker in the center than in the borders). Derjaguin and Kussakov attributed the origin of the equilibrium thickness to the balance between the pressure in the film borders (capillary pressure) and the force between film surfaces counted per unit area, called "disjoining pressure" later on. Derjaguin *et al* were the first to measure the disjoining pressure of films formed between two approaching bubbles[9]. This work led Derjaguin to propose later with Landau a theory of stability of colloidal particles, involving the balance between electric double layer repulsive forces and van der Waals attractive forces [10]. Verwey and Overbeek elaborated the same theory independently [11], which is nowadays known as DLVO theory.

In the 50's, Sheludko developed a special cell, holding small liquid films, made of a capillary linked to a reservoir of controlled pressure. In this way, the capillary pressure that sucks the film into the curved Plateau border can be varied and measured[12]. The film thickness is measured by interferometry in reflected light as in Derjaguin experiments. At equilibrium, the disjoining pressure is equal to the capillary pressure (supplemented by eventual contributions of hydrostatic and capillary pressures in the reservoir). A disadvantage of the device is its limitation to small capillary pressure, hence disjoining pressures larger than about 100 Pa cannot be measured. In order to access larger pressures, Mysels proposed to use a porous disc as film holder instead of a capillary. Sheludko and Exerowa used the idea to build a new device, nowadays called "thin film pressure balance" (TFPB), that allows to measure disjoining pressures up to about 10^5 Pa [1]. Miniaturized versions have been proposed later by Velev *et al* [13]and Radke *et al* [14].

TPFBs can be used not only to measure surface forces, but also to study film thinning and rupture. Exerowa and Sheludko introduced the notion of surfactant concentration C_{bl} at which black spots start to form in the film during thinning [1]. When the concentration C is less than C_{bl}, the film breaks a few seconds after formation, while if $C > C_{bl}$, the films can reach an equilibrium thickness and be stable for much longer times. The concentration C_{bl} is typically 10 to 100 times smaller than the critical micellar concentration (*cmc*) of the surfactant and could correspond to the moment when the surfactant monolayers present at the two film surfaces become dense enough to create a repulsive force between these surfaces. The presence of repulsive forces allows the formation of flat films, but does not ensure stability, which is rather related to the rheological properties of the film surfaces as will be discussed in section 5.

In the following the case of small surfactant concentrations will be first discussed, followed by the case of large surfactant concentrations and ending with applications to foam stability.

3. Film rupture at small surfactant concentrations

3.1 Small film formation

Small foam films can be formed between two bubbles or in a TPFB. In the second case, a small drop of liquid is placed in the holder, and the film is formed by suction when the pressure is increased in the liquid reservoir: the experimental configuration is equivalent to two approaching bubbles of radius R equal to that of the holder [15]. The film forms only if the capillary pressure in the bubble is

smaller than the hydrostatic pressure, i.e. when the distance between the bubbles reaches a value h_f such as:

$$h_f = \frac{R}{2}\sqrt{\frac{3\eta V}{\gamma}} = \frac{\sqrt{3}}{2} R\, Ca^{1/2} \quad (1)$$

where V is the velocity of approach, η is the liquid viscosity, γ the surface tension and Ca the capillary number (Ca=ηV/γ) [15].

When there is no or little surfactant ($C < C_{bl}$), the force between surfaces is essentially the attractive van der Waals attraction. If the velocity of approach and/or if the bubbles ' radius are small, h_f is very small, films do not form, and when h becomes comparable to the range of the van der Waals forces, the bubbles coalesce. At larger velocities and/or bubble radius, films may form at $h = h_f$, if h_f is larger than the range of surface forces. In this case, the film surfaces deform shortly after film formation and take the shape of a dimple. Figure 1 illustrates dimple formation in a silicon oil film between two glycerol drops, a situation entirely similar to that of a liquid film between two bubbles from the hydrodynamic point of view. Dimples form at a film thickness h_d (slightly smaller than h_f)[16]:

$$h_d = 0.4\, R\sqrt{\frac{\eta V}{\gamma}} = 0.4\, R\, Ca^{1/2} \quad (2)$$

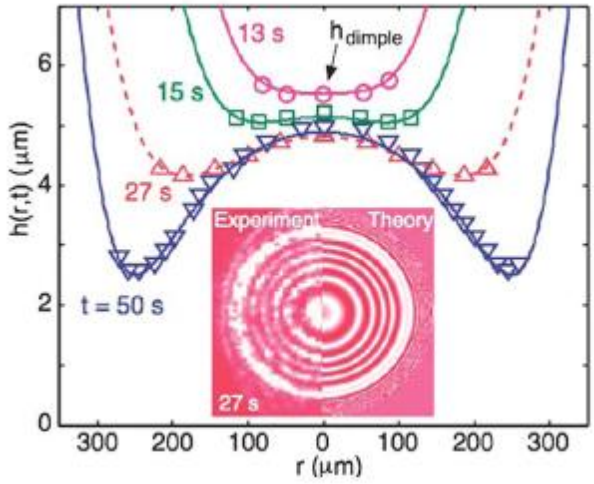


Figure 1. Silicone oil film profile between glycerol drops at various times after the formation of the dimple: experiments (symbols) and theory (lines). Only the upper half of the film is represented. The inset shows interference fringes observed when illuminating the film perpendicularly to its surfaces. Reprinted with permission from [17]

3.2 Film rupture

The lines in Figure 1 are calculated from a model incorporating the hydrodynamic pressure and the capillary pressure, and are in perfect agreement with the experiments. The repulsion between surfaces is due to the hydrodynamic pressure, and it is only at very small distances that the van der Waals disjoining pressure becomes important and induces film rupture. The calculated rupture times are in excellent agreement with the experiments [17].

Other models have been proposed to explain film rupture in systems with attractive forces. Sheludko

considered that thermal fluctuations induce thickness fluctuations and that some of them spontaneously grow[12]. The model was refined later by Vrij, evidencing its analogy with spinodal decomposition in thin films on solid substrates [18]. The model however assumes that the average film thickness remains constant, while this condition requires the presence of repulsive forces. Furthermore, the full hydrodynamic model of section 3.1 is able to describe film rupture without including thermal fluctuations. Fluctuations could however play a role in certain cases, for instance in systems with ultralow interfacial tensions, where surface fluctuations associated to coalescence events have been visualized with an optical microscope. [19]

3.3 Surface mobility

In most models, the surfaces are assumed to be deformable but immobile, meaning that the surface velocity is zero. This condition is far from obvious, especially in systems without adsorbed surfactant. The problem has been discussed by Horn *et al* who showed that very small surface tension gradients $\Delta\gamma$ can immobilize a bubble surface [16]:

$$\Delta\gamma \gtrapprox \frac{\eta R V}{h} \qquad (3)$$

In the experiments analyzed in different studies [16 17], the surface velocity is indeed zero if $\Delta\gamma$ remains below about 0.1 mN/m. Such a small value could easily arise from residual contamination.

At high velocity of approach, small surface tension gradients are no longer able to immobilize the surfaces, and film thinning is very rapid (inertia controlled). This situation has been encountered with water films and also with purified oils films, for which surface tension gradients are smaller (the surface tension of oils is significantly smaller than the surface tension of water, hence very few substances are able to change their surface tension)[16].

The case of water at small velocities of approach is peculiar, with films forming when $h >> R\, Ca^{1/2}$. This is because the surface of water is charged, and there is an electrostatic repulsion between film surfaces that opposes the capillary pressure. The disjoining pressure can then be much larger than the hydrodynamic pressure explaining why h_f is much larger than predicted by equation 1. The films formed in this way are able to reach equilibrium and are stable for hours, even days [16]. When salt is added, the electrostatic repulsion is screened and the films rupture rapidly as in the intermediate velocity regime.

One can wonder why equilibrium water films are not observed in the intermediate velocity regime. At these velocities, the films form dimples. A second instability can then occur, leading to film asymmetric shapes. This second instability is analog to the marginal regeneration observed in large vertical films and occurs when the surface viscosities are small [20]. This is certainly the case of the water surface, which has non-measurable surface viscosity. Asymmetric films thin much more rapidly than symmetric films. It is therefore possible that during fast thinning, the contaminants at the surface of the water films are displaced and some surface regions being bare, film rupture may initiate in these regions.

4. Equilibrium films

When surfactant is present, the disjoining pressure Π_d of liquid films contains contributions not only

from attractive van der Waals forces, but also from repulsive electrostatic forces if the surfactant is ionic, the sum of the two being the so-called "DLVO forces". In addition, short range forces due to hydration, steric, hydrophobic and other contributions can also be present with both ionic and non-ionic surfactants and are much less well known [21] [22].

It should be stressed that even the DLVO forces are difficult to handle. The correct expressions of electrostatic and van der Waals forces are far from simple. The electrostatic repulsion between two charged surfaces in an electrolyte solution decays exponentially with film thickness as $\exp(-\kappa h)$, κ^{-1} being the Debye length. The prefactor depends on surface boundary conditions, which are generally taken to be either constant charge or constant potential. However, boundary conditions may change during film thinning and charge regulation models should be used, introducing numerical complexity. When the electrolyte concentration is above 0.05 M, ion specific effects show up and the classical treatments become inadequate. The description of interactions in biological systems becomes for instance difficult, the ion concentration in these systems being about 0.1 M.

The van der Waals contribution to the disjoining pressure $\Pi_{d\,vdw}$ is usually written as $H/(6\pi h^3)$, H being the Hamaker constant. This simple expression is however only valid for small h, because at large h, the contribution of retardation becomes important. In the case of water films in air, the Hamaker constant is large and retardation can be neglected when h < 10 nm. For water films in oil (or oil films in water), the Hamaker constant is small and varies appreciably with film thickness, even for h < 10 nm. At smaller film thickness, $\Pi_{d\,vdw}$ is also no longer proportional to $1/h^3$, because it is the sum of functions of $H_1/(h-2l)^3$, $H_2/(h-l)^3$ and H_3/h^3 , where H_1, H_2 and H_3 are different Hamaker constants and l is the thickness of the surfactant layer [23]. With a typical value of l ~ 0.2 nm, one can estimate that h should be at least larger than 2 nm to be able to approximate $\Pi_{d\,vdw}$ by $H_{eff}/(6\pi h^3)$, H_{eff} being then an "effective" Hamaker constant. The range of thicknesses where the effective Hamaker constant is truly constant is therefore small: 2 nm < h < 10 nm for water films in air, while H_{eff} it is never constant for water films in oil (or oil films in water). When an electrolyte is present, part of the van der Waals force (the contribution of the permanent dipoles of water) is screened, the screening length being $\kappa^{-1}/2$, and the complete force no longer varies as $1/h^3$.

At small film thickness, non- DLVO forces are observed, called "hydration" forces in the case of water, which originate from surface induced ordering of dipoles or hydrogen bonds. The corresponding density profiles at each film surface overlap at small h leading to oscillatory forces. However, when the surfaces are rough at a molecular level, e.g. the polar heads of surfactant molecules, the oscillations are smoothed out. The force decays exponentially with a range of the order of a molecular diameter (0.3 nm) and generally dominates van der Waals interactions for h < 3 nm. The resolution of TFPB instruments is not sufficient to measure the decay length and the contribution of the hydration force to the disjoining pressure does not change appreciably with h for surfactants with small polar heads. For nonionic surfactants with a polar head made of oxyethylene groups, the heads are somewhat compressible and the disjoining pressure slightly varies with film thickness when the number of oxyethylene groups is larger than 6 [24].

The dependence of the disjoining pressure with film thickness is schematically represented in Figure 2. If a small pressure ΔP is applied to the film (gravity, hydrostatic pressure, Laplace pressure), its thickness decreases down to h_1, determined by the DLVO contribution, and typically around 10 nm; the corresponding equilibrium film is usually called "common black film" (CBF). If the applied pressure ΔP is larger than the electrostatic barrier $\Pi_d(h_{max})$, a very small film thickness h_2 is reached:

the corresponding film is called “Newton black film” (NBF). These films contain little water and are essentially surfactant bilayers. They are more densely packed than the monolayers at the surface of the common black films, and have a smaller permeability to gas (or oil in the case of emulsion films) despite their much smaller thickness[25]. Films stabilized by nonionic surfactants are also NBF, excepted below the *cmc*. This has been explained by assuming that there are still OH^- ions at the film surfaces that create extremely long range electrostatic repulsion in view of their small concentration. Above the *cmc*, the surfactant displaces these ions and NBFs are obtained [26]. Recent numerical simulations show however that the surface charge of water is positive and that the charges found experimentally are likely due to contamination (a concentration of negatively charged contaminant as low as 30 nM can create a surface potential of -80 mV) [27].

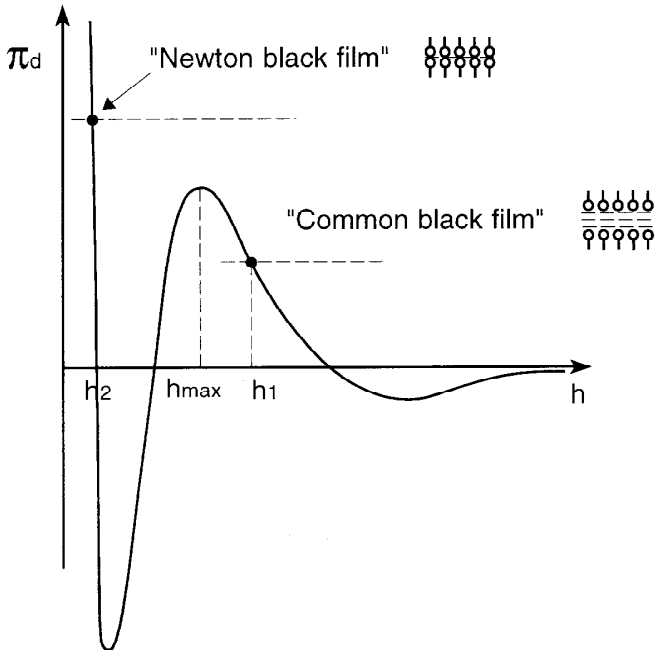


Figure 2. Schematic representation of the variation of the disjoining pressure Π_d with film thickness *h*. The horizontal dashed lines correspond to different applied pressures ΔP and the vertical ones show the final equilibrium thicknesses of the film.

At equilibrium, it is not possible to measure negative disjoining pressures with a TPFB, because the applied pressure cannot be negative. To overcome this difficulty, the measurement of the velocity of thinning can be used. This velocity, in the case of films with immobile surfaces has been calculated by Reynolds and writes:

$$V_{\mathrm{Re}} = -\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{2h^3}{3\eta R^2}\Delta P \qquad (4)$$

where ΔP the difference in pressure between film centre and border; ΔP is the sum of the capillary pressure γ/r, r being the radius of curvature of the film border, of the hydrostatic pressure and of the disjoining pressure. In this way, the negative minimum of the DLVO contribution to Π_d ($h \gg h_2$, right of figure 2) has been evidenced by Exerowa and coworkers [1].

In these experiments as well as in many others performed afterwards with ionic surfactants, the

measured pressures generally exhibit an asymptotic exponential decay with a characteristic length in good agreement with the Debye length. However, the agreement is less good for the expected amplitudes of the van der Waals and electrostatic contributions [1]. The origin of the discrepancy lies either in errors in the determination of film thickness (obtained by an interference method, so the estimation of the actual water thickness is difficult, because neither the surfactant monolayer thickness nor its refraction index are well known), or to approximations made in the theory that could be invalid as discussed earlier in this section. For instance, incorrect fitting of disjoining pressure curves led Yoon *et al* to claim that long range hydrophobic forces were present in soap films [28 29].

The transition between CBFs and NBFs was extensively studied by Exerowa and co-workers. Figure 3 shows the example of films made with SDS solutions containing sodium chloride (NaCl). When the applied pressure is increased, a transition CBF→NBF is obtained for pressures of about 10^5 Pa. The reverse transition NBF→CBF can be also obtained, but when the pressure is considerably lowered. These reversible transitions are observed in an intermediate range of salinity, between about 0.15 and 0.33 M NaCl. At salt concentrations higher than 0.15 M NaCl, NBFs nucleate in the form of black spots in the grey film and are stable, while above 0.33 M NaCl, the electrostatic barrier likely vanishes, only NBFs form, with a constant thickness, as expected for a disjoining pressure dominated by the hydration force.

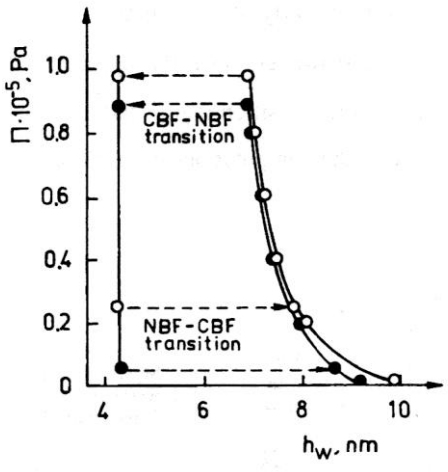


Figure 3. CBF-NBF transitions in films made with 1 mM SDS solutions containing NaCl: open circles 0.165 M NaCl, closed circles 0.180 M NaCl. When the pressure is increased, the CBF transform into a NBF at a high pressure, while the transition back to the CBF occurs at a much lower pressure. The transition pressures decrease with increasing salt until the CBF-NBF transition disappears. Reprinted from ref 1

The time for the CBF-NBF transition can be long, about 30 minutes for 0.28 M NaCl, but decreases to zero at 0.33 M NaCl. This time also decreases when an α irradiation is used. The transition can therefore be obtained in different ways: increasing pressure, increasing salinity and using irradiation with α particles. It therefore bears some similarities with film rupture, which can be also obtained either by increasing the pressure or irradiating the film (section 5.2).

In the absence of salt, CBFs films rupture well below $\Pi_d(h_{max})$. Bergeron proposed that when the applied pressure is increased, thermal fluctuations of surfactant monolayer concentration might help

to overcome the energy barrier [30]. This mechanism could be at the origin of the transition CBF-NBF.

5. Film rupture at large surfactant concentrations

5.1 Black film formation

When $C > C_{bl}$, the films are able to reach an equilibrium thickness and their lifetime increases considerably. Calculations and experiments show that the dimples eventually formed disappear as soon as the thickness becomes comparable to the range of repulsive forces. Figure 4 shows an example of measurements with emulsion films, showing that the film lifetime is simply the thinning time at low surfactant concentration, and the sum of the thinning time and the lifetime of the black film at higher concentration. Figure 4 also reveals an important marginal regeneration when $C < C_{bl}$, while uniform black films form above C_{bl}.

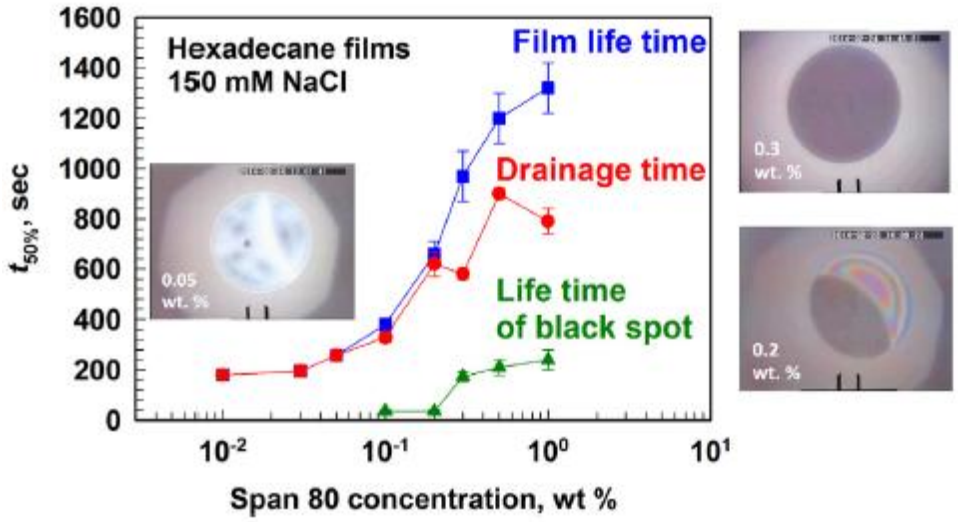


Figure 4. Film lifetime (time required for 50% of films to break after their formation) versus surfactant concentration together with film images. Hexadecane films stabilized by Span 80. The distance between the dark vertical bars is 50 μm. Reprinted with permission from ref [31]

The film thinning time depends on the rheological properties of the film surfaces. Indeed, films thin generally faster than expected from equation 4. In the case of films made with SDS solutions, it was shown that the thinning velocity is controlled by the surface compression elastic modulus E [32]. In principle, the thinning velocity also depends on surface viscosity [33], but this viscosity is very small for SDS solutions and the contribution of the elastic modulus E dominates.

When the bubbles are very small, films form only at the equilibrium thickness and at the difference of larger films that thin while their size remains constant, the small films radius was reported to increase while their thickness remain constant [13].

5.2 Film rupture

In the case of films without repulsive surface forces, the film rupture mechanism is fully deterministic

and now rather well understood (section 3.2). The case of films with repulsive interactions is more difficult to address. One could expect that once the film has reached its equilibrium thickness, it will be indefinitely stable in the absence of mechanical disturbances, such as irradiation. However, when no external perturbation is present, these films can live during long times but always rupture, after a time that varies considerably from one film to another. Figure 5 shows an example of lifetime distribution for a large number of identical films. The large width of the distribution suggests that film rupture is now a stochastic process.

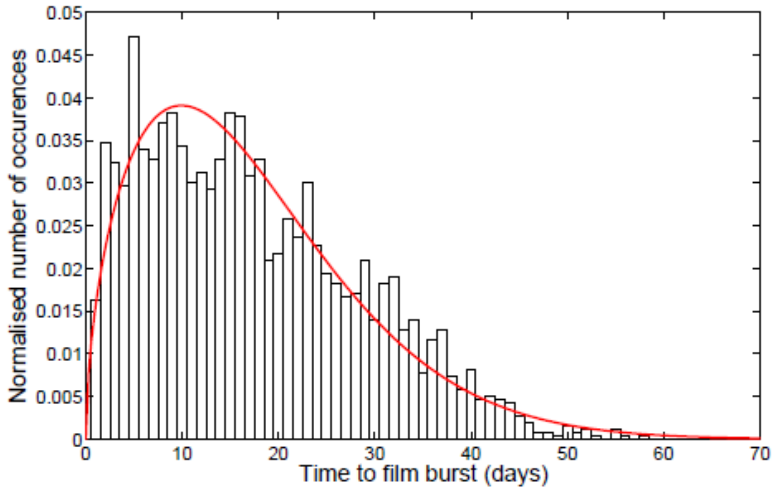


Figure 5 : Film lifetime distribution for a solution of a diswashing detergent. Averages from over 2500 films. Reprinted with permission from [34]

The average film lifetime increases with surfactant concentration once $C > C_{bl}$. Exerowa and coworkers showed that C_{bl} was higher for NBFs than for CBFs. Figure 6 shows that while the *cmc* decreases with increasing salt (about 1.4 mM for 0.1 M NaCl and 0.5 mM for 0.5 M NaCl [35]), C_{bl} is significantly larger for NBFs and is closer to the *cmc*. Furthermore, C_{bl} is less well defined, in this case, it increases with film radius [36].

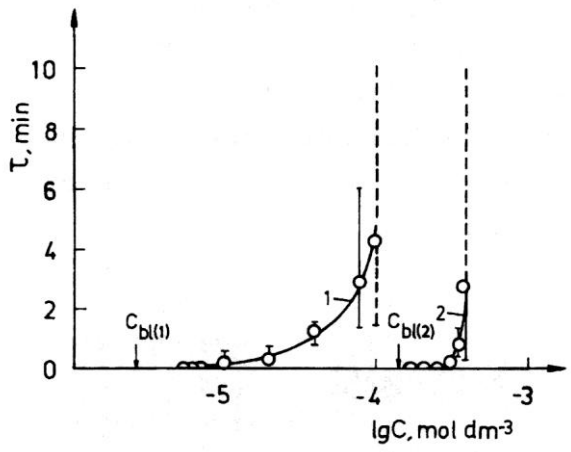


Figure 6. Lifetimes of films made from SDS solutions containing 0.1 M NaCl (curve 1) and 0.5 M NaCl (curve 2).

Film radius 0.1 mm. Reprinted from ref 1

Figure 7 shows the lifetimes of NBFs made with SDS solutions containing large amounts of salt, without and with irradiation. The film stability becomes significant close to 0.2 mM surfactant (not far from the *cmc*, 0.5 mM). Because the lifetimes become rapidly very long, they have been measured at higher surfactant concentrations using α irradiation. The lifetime saturates at the *cmc,* when the surfactant monolayer is expected not to evolve anymore.

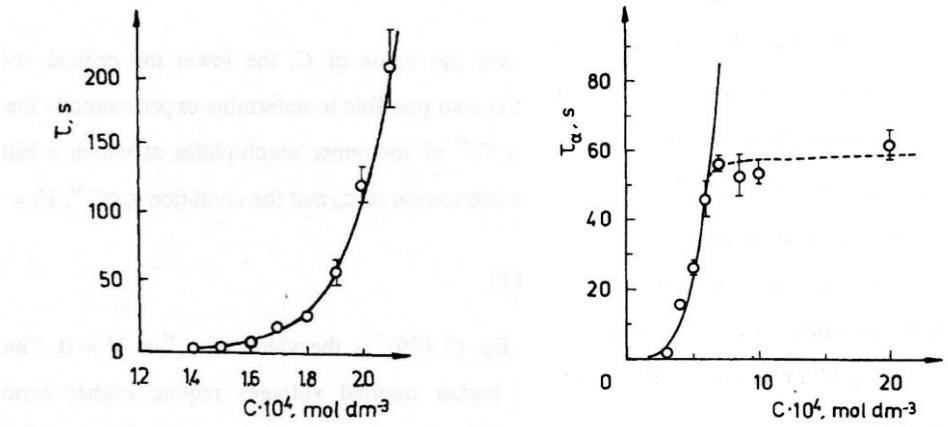


Figure 7 Dependence of the lifetime of NBFs made with SDS solutions versus surfactant concentration; a) 0.5 M NaCl added; b) 0.36 mM NaCl added, irradiated films. The theoretical curves are fits with equation 6. Reprinted from ref 1.

It should be noted that evaporation is also an efficient cause of film rupture, especially in the case of large films left to air, where the film lifetime strongly depends on the air humidity [37]. In the TPFB instruments, a water reservoir is usually kept in the box enclosing the film holder, in order to saturate the air humidity and avoid evaporation of the water of the film.

5.3 Film rupture models

Exerowa and colleagues [1] showed that films made with pure SDS solutions rupture above a critical pressure of about 1000 Pa, well below $\Pi(h_{max})$. Although the electrostatic barrier is lower for 0.15 M NaCl, the critical pressure for rupture is much larger, about 10^5Pa. This suggests that the disjoining pressure has no direct role in film rupture.

De Vries proposed that film rupture could proceed via a hole nucleation mechanism with a surface energy penalty [38]. The film lifetime is then: $\tau \sim \exp(W^*/k_BT)$, where W* is the activation energy, k_B the Boltzmann constant and T the absolute temperature. De Gennes [39] related later the energy penalty to the thermal concentration fluctuations in the film surfaces. This process is controlled by compression elasticity rather than by surface tension and disjoining pressure in the models by Sheludko and Vrij. A molecular mechanism similar in spirit was proposed by Helm *et al* for bilayer fusion[40]: once the surfactant layer is less dense at some point, the chains can tilt towards the opposite layer, and the short ranged hydrophobic attraction between opposite surfaces is enhanced. This rupture process could explain why the stability of emulsions and foams frequently appears

correlated with the interfacial compression modulus *E*. De Gennes estimated the film lifetime as [39] [41] [42]:

$$\frac{1}{\tau} = \frac{1}{\tau_0}\frac{A}{A_{hole}}\exp\left(-\frac{\delta\Gamma^2}{\Gamma^2}\,\frac{E\,A_{hole}}{k_B T}\right) \qquad \text{with} \quad W^* = \frac{\delta\Gamma^2}{\Gamma^2}\,\frac{E\,A_{hole}}{k_B T} \tag{5}$$

where τ_0 is a molecular time, A is the film area, A_{hole} the hole area, Γ the surface concentration and $\delta\Gamma$ the change in Γ necessary to suppress the repulsion between film surfaces.

De Gennes also showed that when a film ruptures, the critical radius of the hole r_{hole}^* is half the film thickness [41]. Common black films have thicknesses of the order of a few tens of nanometers, in which case the activation energies are much larger than k_BT. This led de Gennes to say that "with good surfactants the opening of holes is utterly forbidden and intrinsic coalescence is a myth" [39].

In many cases, however, the surfactants are either nonionic or ionic in the presence of added salt. In these cases, the electrostatic repulsion is screened and the disjoining pressure is short ranged (small Debye length for ionic surfactants with salt). Note that if surfactants are present in large quantities, the Debye length in the solution is small and the disjoining pressure is also short ranged. In these cases, the films thicknesses are of the order of a few nanometers. The critical hole radius being half the film thickness, is of the order of the surfactant layer thickness: $r_{hole}^* \sim 2$ nm. Assuming that $\delta\Gamma \sim \Gamma$, i.e. that the hole surfaces are free of surfactant before hole opening, and using equation 5 with E ~ 100 mN/m, one finds an activation barrier W* of the order of 100 k_BT, still quite large. However, it is probably not necessary to have a fully bare surface before film rupture. Indeed, films become stable when the surfactant concentration *C* reaches a value C_{bl}, somewhat below the critical micellar concentration (*cmc*) and close to the point below which the surface concentration starts decreasing appreciably. As discussed earlier, at these concentrations, the repulsive forces likely disappear and no equilibrium film is formed. This means that $\delta\Gamma$ in equation 5 can be smaller than Γ for the hole to nucleate. If we take for instance $\delta\Gamma \sim \Gamma/3$, the energy barrier U* falls to 10 k_BT, for which the film lifetime becomes appreciable.

Exerowa and coworkers introduced a concentration C_e above which there is no driving force for film rupture. They predicted the following dependence of the film lifetime on the surfactant concentration C, when C is below the *cmc* and the films are NBFs [43]:

$$\tau \sim A\, e^{B/\ln(C_e/C)} \tag{6}$$

A and B depending upon various molecular properties. When A, B and C_e are handled as adjustable parameters, the concentration variation of the film lifetime is in very good agreement with experiments as can be seen in figure 7. However, although the film lifetime is very long when C reaches C_e, the films are not indefinitely stable when $C > C_e$ as assumed. Furthermore, E varies in good approximation as ln C below the *cmc*, so equations 5 and 6 predict similar variations of the lifetime with bulk surfactant concentration. The experiments carried out by Exerowa and coworkers are therefore also in agreement with equation 5. Note that equation 6 was established without taking into account the presence of micelles, so it cannot be applied above the *cmc*, while equation 5 should still be valid.

Apart from those carried out in the group in Sofia, few measurements of film lifetime can be found in the literature. Equation 5 predicts that the film lifetime should depend exponentially on the compression modulus E. It is unfortunately very difficult to determine E, because of the dissolution of

the surfactant in bulk when the surfactant layer is compressed. Only effective values are experimentally accessible and are linked to E by models which validity is frequently questionable [44]. This difficulty is absent when surfactants are irreversibly adsorbed, in which case the determination of E is easier and it has been possible to confirm the exponential variation of film lifetime with E predicted by equation 5 [45] . More experiments are clearly needed to check the validity of equations 5 and 6, in particular their variations with the molecular parameters introduced in these equations.

Another expression for the activation energy W* for hole opening has been proposed by Kabalnov and Wennerstrom[46]. They related W* to surface tension and to the curvature of the surfactant monolayer at the edge of a nucleation hole. They showed that when the surface tension is very small (about 10 μN/m and below), the energy W* is dominated by curvature energy and can drop to values of the order of k_BT. This model is only valid for emulsions with ultralow oil-water surface tension.

As mentioned earlier, a more rapid rupture can be obtained by increasing the pressure above a critical value P^{CR}. None of these existing models consider the role of applied pressure so far. They cannot account for the influence of this pressure and predict a critical pressure for rupture. Very large variations of critical pressures with surfactant chain length were evidenced, while the modulus E does not change significantly, a fact that remains to be explained [30]. Other models assume that films rupture when the pressure is higher than the electrostatic barrier $\Pi_d(h_{max})$, but this assumption cannot apply to NBFs. Furthermore, the pressure of rupture is usually smaller than $\Pi_d(h_{max})$ for ionic surfactants. Finally, even if the electrostatic barrier is overcome, the short range repulsion is still present. It is however possible that the rupture process is made of two steps: first, surface concentration fluctuations lead to a decrease of the electrostatic repulsion barrier and to a CBF -NBF transition. As seen in section 4, the higher the capillary pressure, the easier the transition between CBF and NBF, since smaller fluctuations are needed to overcome the barrier [30]. The second step could be the nucleation of holes, easier in these ultrathin films, the activation energy being not much larger than the thermal energy k_BT. In all cases, the surface compression modulus is expected to play in important role, because surface concentration fluctuations are needed. In turn, the role of the disjoining pressure is probably just to allow for the formation of black films.

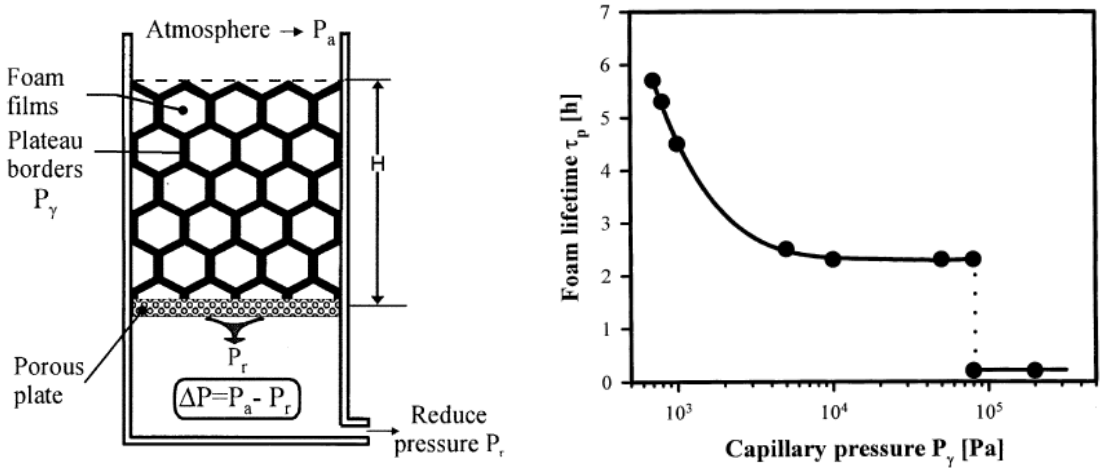
6. Link to foams and emulsion stability

6.1 Foam stability

Foams lose rapidly their liquid because of gravity drainage. When the bubble size is millimetric, foams visually appear as a collection of films. Their stability is therefore closely related to the stability of the foam films. However, because the bubbles are interconnected via a network of Plateau borders (PBs), the analogy is not direct.

Foam drainage proceeds essentially through the network of PBs, the loss of water of the films being only a very minor contribution. The surfactant can exchange freely between surfactant layers and the water of the PBs, so the surface tension is constant. This is quite different from the case of film thinning, during which the surfactant is entrained towards film borders, and since there is not enough surfactant in the film to replenish its surfaces, large surface tension gradients develop. These gradients are quantified by the elastic modulus E, explaining why the thinning velocity strongly depends on the value of E. The velocity of foam drainage depends rather on the surfactant layer viscosity. Experiments with foams made with SDS solutions that lead to mobile surfaces (small

surface viscosity) confirmed that drainage was faster than with mixed dodecanol-SDS solutions, leading to immobile surfaces (large surface viscosity) [47].



a) b)

Figure 8. a) device used to apply a fixed capillary pressure to the foam: the foam is separated from the liquid by a porous plate and the liquid is sucked out in the bottom opening in order to increase the pressure; b) foam lifetime versus applied capillary pressure for a foam made with a solution containing 1 mM SDS and 0.5 M NaCl with an average film radius of 2.5 mm. Reprinted with permission from [48]

At the end of drainage, an equilibrium liquid fraction vertical profile is established, in which the osmotic pressure is equilibrated by the hydrostatic pressure [49]. The foam can then be stable for long period of times. After reaching hydrostatic equilibrium, typically after 10 minutes (longer if the foam is made of very small bubbles), the bubbles grow slowly because of Ostwald ripening. During this process, the bubble assemblies undergo reorganizations in the foam, a process that can lead to film rupture: either the liquid in the Plateau borders is not sufficient to allow the reorganization [50], or the films that have to be created during the reorganization are not sufficiently covered by surfactant and break[51]. In other cases, ripening continues without film ruptures, but when the bubbles reach a certain size, the foam usually collapses [52].

In most cases, the capillary pressures in foams are not very high, especially when the foam height is small. Exerowa and coworkers used a device allowing applying larger pressures to a foam (figure 8a). They showed that the foam lifetime decreases with increasing pressure (figure 8b). The critical pressure for film rupture and foam collapse are similar, provided films of same size are used in the measurements (Figure 9). They also showed that the critical pressure for films and foams decreases when the film size increases (Figure 9). Similar results were found for emulsions, where the existence of a critical pressure that decreases when the drop size increases was also evidenced [53].

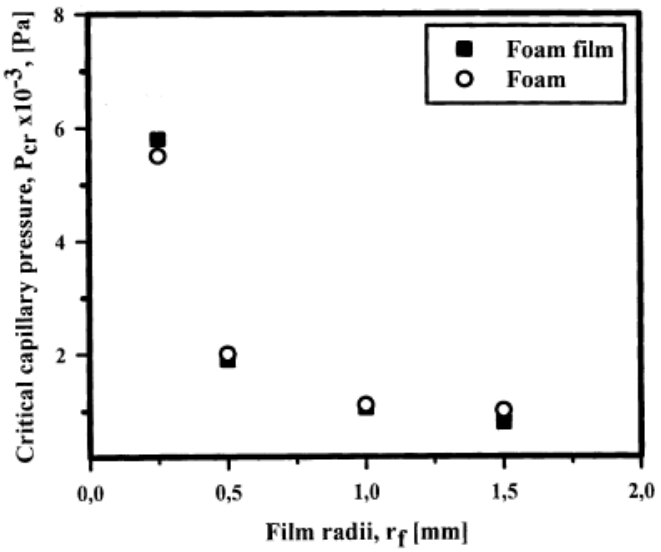


Figure 9. Critical pressure of rupture of single foam films and films in foams versus average film radius. Surfactant is 70 μM symperonic 85. Reprinted with permission from [48]

It is well recognized that the stability of foams is not correlated with the surface tension. Typical surface tensions of surfactant solutions are similar, between 30 and 40 mN/m in general. The important parameter seems to be the surface modulus E. However, surfactants with monolayers with high E do not necessarily give rise to stable foams. This is related to their solubility in water as shown by Garrett and Moore in a study of alkyl benzene sulfonate surfactants of increasing chain length.[54] Surfactants of small chain length are too soluble in water and do not form compact monolayers, whereas surfactants of long chain lengths are not soluble enough in water and are rapidly consumed during foam formation.

It is difficult to distinguish which is the important parameter in foam rupture: pressure, bubble radius or liquid fraction, because in general, these parameters cannot be varied independently. A recent experiment was performed using a layer of bubbles (two-dimensional foams) with a device allowing varying independently the different parameters. The control parameter for foam collapse was found to be the bubble radius [55]. This result is in agreement with equation 5 that predicts that the lifetime is inversely proportional to film area. However, the experiments were made at very low capillary pressures. It is therefore possible that other mechanisms operate at higher pressures.

6.2 Emulsion stability

The behavior of emulsions is similar, although due to the small density difference between oil and water, gravity has much less influence, and creaming (or sedimentation) is very slow. But at some stage, the creamed emulsions reach equilibrium with a drop volume fraction rather homogeneous, again because of small density differences. The drops then grow because of Ostwald ripening, and coalesce when they reach a certain critical size, as bubbles in foams. The critical size depends on the elastic modulus E, as expected from equation 5 [56].

In situations where the surfactant is equally soluble in oil and water, for instance in the oil-water-surfactant systems leading to ultralow interfacial tensions, the surfactant monolayers are very compact because the surface pressure of the monolayers is high, since it almost compensates the

bare oil-water interfacial tension. However, these systems give rise to notoriously unstable emulsions. The explanation is in fact simple: when the surfactant monolayers are compressed or extended during the approach of emulsion drops, the surface tension gradients vanish because the surfactant can rapidly exchange with the interior of the drops (the surfactant is partitioned equally between oil and water in these systems, while it is more soluble either in oil or in water in usual emulsions). Everything happens as if the surfactant were absent and as if the emulsions were made with pure oil and water[57].

7. Conclusions

After the pioneering studies of the Sofia's group, a considerable knowledge has been accumulated on small liquid films, of size comparable to bubbles in foams and even drops in emulsions with the miniaturized devices. The surface forces have been measured and found to be in semi-quantitative agreement with DLVO predictions at large film thickness. At small film thickness, the force is a hard-wall repulsion, as expected for a hydration force. The film lifetime studies opened the way to a better understanding of foam and emulsion stability. Together with studies by other groups, the research field remains very active today.

Exerowa defined a surfactant concentration C_{bl} above which black films form. This concentration separates two regions in which the mechanisms of film rupture are different. At low surfactant concentration, when two drops/bubbles approach, their surfaces deform. If the velocity of approach is large, the deformation may become non axisymmetric. When the surfaces come closer, coalescence readily occurs. Hydrodynamic models now allow predicting with accuracy the coalescence time, at least in the case of axisymmetric deformations. The coalescence time is essentially the film thinning time which is rapid (typically < 1 min). The corresponding emulsions and foams are therefore unstable.

At large surfactant concentrations, repulsive surface forces appear, flat films form, and the film lifetime becomes much longer. In addition, the film rupture is stochastic, whereas it is deterministic at small surfactant concentration. Film rupture models are still in a preliminary stage. It is however clear that the role of surface forces is mainly to allow the formation of black films and that their role in film rupture is limited. In turn, the influence of the surface compression modulus in the film lifetime is predicted to be important, but experiments are needed to confirm the predictions. The rupture mechanism above the critical pressure might be different and remains to be clarified.

At the difference of experiments on isolated films, experiments on foams readily provide averages over many films and avoid tedious repetition of film measurements (about 100 rupture events are necessary to obtain a significant determination of black film lifetime). However, foam stability depends on the other elements of structure such as Plateau borders. For instance film thinning is mainly related to E, while foam drainage is rather related to surface viscosity. Furthermore, the foam stability does not solely depend on bubble coalescence, but is coupled to liquid drainage and ripening. Correlations of studies of foam films and foams, as well as parallel studies with emulsions could however help to progress in the understanding of film rupture.

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