

Dynamic Processes in Soap Films

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ABSTRACT Some relations between the two main types of thin liquid films, the water-in-air “soap” films and the invert oil-in-water “lipid” films, are outlined, and several dynamic aspects of film behavior are illustrated and briefly reviewed with reference to more complete treatments. These dynamic processes are important in both types of films, but are easier to study in soap films. The topics include the difference between rigid and mobile films and their interconversion; the origin and measurement of film elasticity; the effect of rate of formation upon film thickness, and the evidence against the existence of thick rigid water layers at the surface; and the kinetics of drainage and the role played in it by viscous flow, marginal regeneration, and intermolecular forces.

There may be considerable question in the reader’s mind—as there is some in mine—about the place of a discussion about soap films in a symposium on biological interfaces. The place of “lipid” films is apparent, since they are widely considered as models for biological membranes. Soap films presumably come in as models for these models. Despite many differences between the two types of films in materials, structures, and forces involved, as well as in experimental methods and in the emphasis of most investigations, there are indeed common methods, such as optical thickness determinations and especially common dynamic processes during the formation and the thinning of a film, and I shall confine my review to some of these. Although common to both systems, these processes are much more easily studied on soap films because of the ease of preparing large films, having areas of several square centimeters or several tens of square centimeters, from pure substances, and the frequently indefinite durability of soap films. It is this greater ease and latitude of experiment which makes soap films valuable models for lipid film studies.

The relation between soap films and invert or lipid films can be illustrated by considering a hydrated lamellar crystal such as is formed under certain conditions of temperature and concentration by most film-forming materials. As shown in Fig. 1, such a crystal is formed by a repetition of layers of water (or, more exactly, an aqueous solution) and of the amphipathic lipid present as double arrays, so that its hydrophilic “heads” are exposed to the adjacent

water layers, whereas the hydrophobic “tails” are relatively protected therefrom. From this succession of layers, we can isolate a repeating bilayer structural unit in two ways. One approach is to cut through the middle of two successive water layers, as indicated in the upper left. In this way, the essential element of lipid films is formed. The other approach is to cut along the middle of two successive lipid layers, as indicated in the upper right. In this way, the basic element of soap films is obtained. There is a secondary difference, in that the lipid film system is obtained by extending the aqueous phase of the

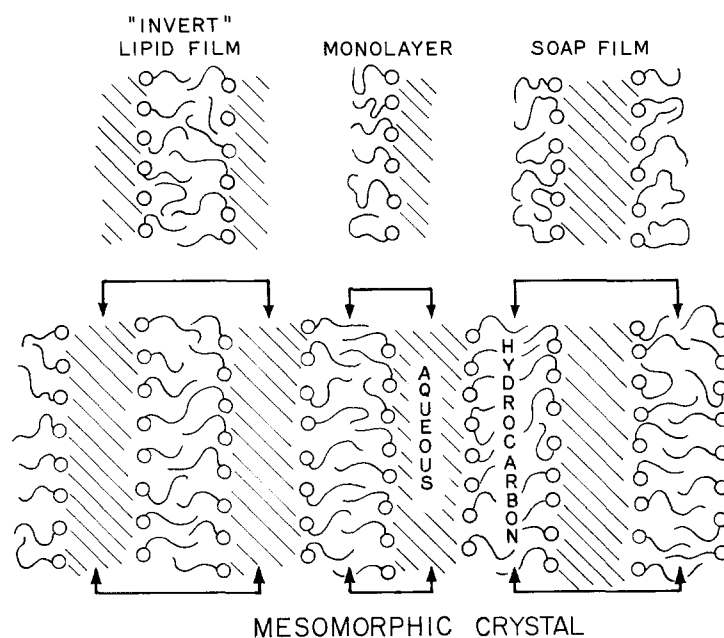


FIGURE 1. The idealized relationship among the structures of liquid crystals, soap films, lipid films, and monolayers formed by amphipathic molecules and water.

bilayer, whereas the soap film is simply surrounded by air saturated with water vapor.

If the cut is made through the middle of two adjacent layers—one aqueous, the other lipid—then, as shown in the upper center, an unsymmetrical structure is obtained, which is the basic element of monolayers such as are studied by surface tension methods or on the Langmuir trough. Again, the aqueous side is to be extended and the lipid one exposed to air.

Another aspect of this relationship is shown in Fig. 2. All film-forming solutes are adsorbed, again because of their amphipathic nature, at the corresponding interface—water/oil or water/air—forming a monolayer. If this interface is now pulled into one of the phases, a film may be formed by a thin layer of the other phase between the two monolayers. Depending on which is the thin phase, a lipid or a soap film bilayer is obtained.

Fig. 2 is also a more realistic picture than Fig. 1 because we cannot slice crystals but do indeed generally form films by extending interfaces, be it by blowing a bubble, by wiping over a hole with a brush, or by pulling a frame from a solution. The last is often used in soap film work. Whether a film actually forms when the interface is thus extended, how thin it eventually becomes, and how long it lasts, depend in part at least on forces between the two monolayers as they approach each other and, therefore, on the specific amphipathic compounds.

It may be noted that, whereas lipid films may well thin until the bilayer becomes bimolecular (i.e. not only has two sides but also is only 2 molecules thick), soap films keep a central aqueous core, which is at least about 15A thick (1, 2) except under especially desiccating conditions (3, p. 69), and

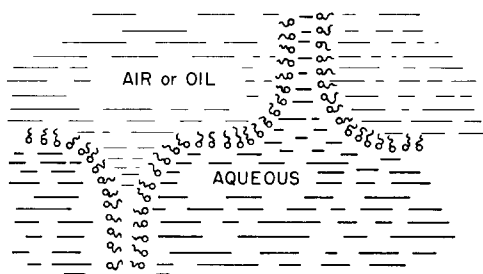


FIGURE 2. Amphipathic molecules accumulate at the interface between water and oil or air. Extension of this interface into one phase or the other generates soap films (upward) or lipid films (downward).

may be many tens or hundreds of angstroms or more in thickness between the two monomolecular surface layers (4–6).

RIGID AND MOBILE SOAP FILMS

The hydrocarbon tails of Figs. 1 and 2 are drawn schematically, but randomly kinked and intertwined as they must be in the common type of soap films such as are formed by sodium dodecyl sulfate solutions, because the surface area occupied by an ion is (7–9) about 40 \AA^2 , almost double the cross-section of a hydrocarbon chain. Since air or water is not likely to be present between the chains, these must form a layer only about 9 \AA thick, despite their extended length of some 17 \AA .

The other type of interface with closely packed extended chains is also known, and its formation requires only the addition of some dodecyl alcohol to a dilute sodium dodecyl sulfate solution (3, p. 10; 10, 11). The two types show markedly different behavior as far as the ability of two neighboring film elements, i.e. neighboring areas of the three-layer sandwich, to slide past each other. In the latter or “rigid” films, this motion is nonexistent or

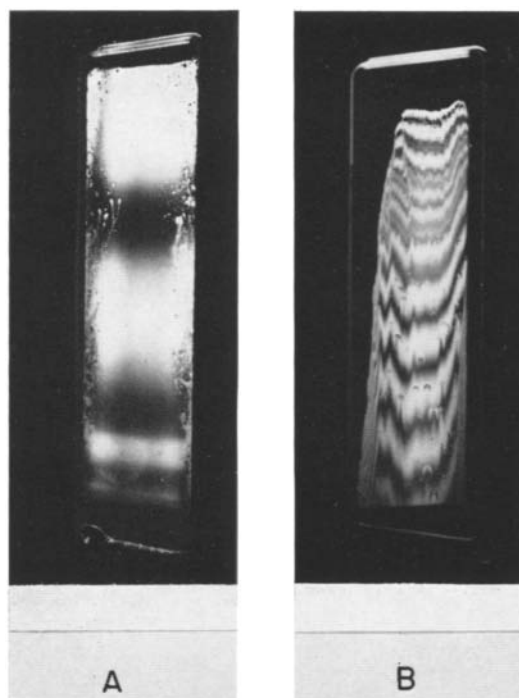


FIGURE 3. Typical appearances of a mobile (*A*) and a rigid (*B*) soap film. Dark and light bands are reproductions of interference colors. Note upward streaming of thinner film elements in mobile film only. Age of mobile film, 70 sec; of rigid film, 50 min. *Figure reproduced from unpublished color slides made by Professor K. Shinoda.*

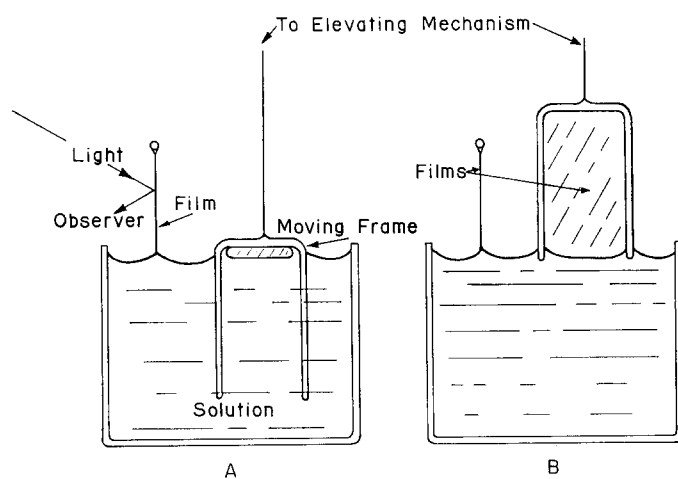


FIGURE 4. Schematic apparatus for observing the effects of rapid extension and contraction of a film. The observed film is shown in cross-section and dips in a solution from which another film may be formed by elevating an inverted-U-shaped frame. Surface tension may be measured simultaneously by suspending the first film from a transducer.

greatly inhibited, as in a tile mosaic. In the former or “mobile” films, it is very free and rapid, somewhat as in one of those children’s puzzles in which blocks slide past each other while always staying in a plane. In mobile films, however, the “blocks” have no rigid shape and deform readily as they flow past one another (3, p. 10).

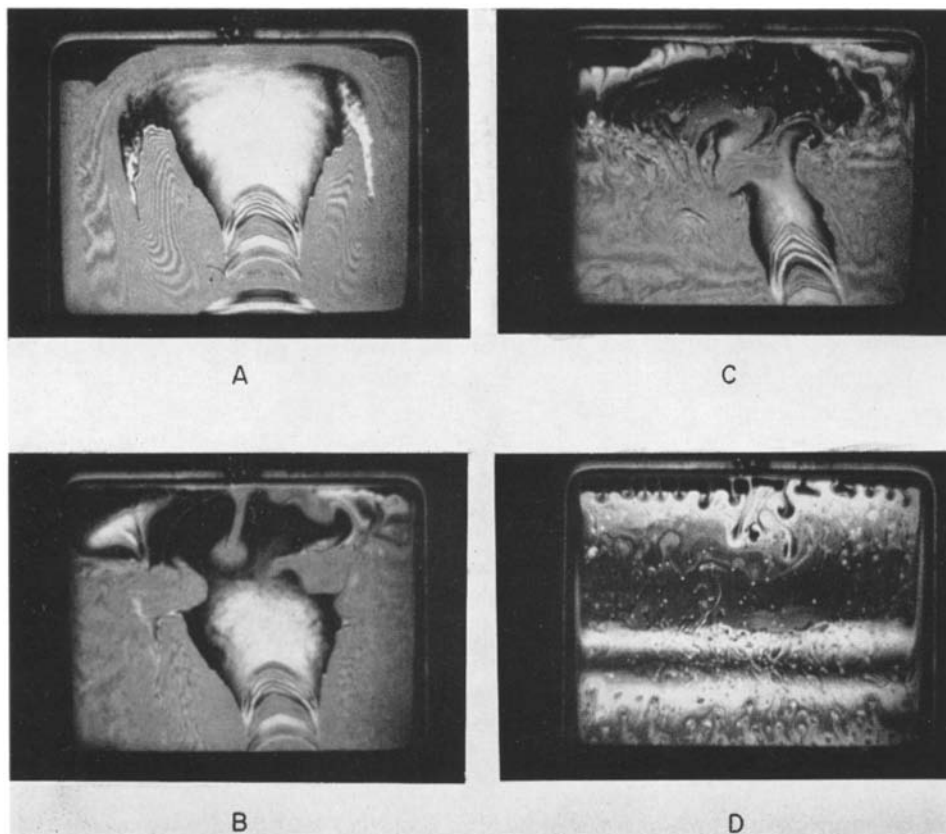


FIGURE 5. The transition from rigid (upper left) to mobile (lower right) film upon rapid extension of the surface in the apparatus of Fig. 4. The “mushroom” in the rigid film is a thinner area formed by marginal regeneration at the lower border. Downward streaming of thick film toward this border is also visible. *Figure reproduced from unpublished color film made by Dr. J. D. Skewis.*

An important consequence of the free motion of film elements in mobile films is that, under the influence of gravity, they tend to arrange themselves according to their weight (per unit surface), i.e. according to thickness. Since each thickness corresponds to an interference color (or Newton ring) in reflected light, this tends to give these films a smoothly horizontally banded aspect, disturbed only by the upward motion of thinner elements (3, pp. 19,

34; 12) as the film drains (Fig. 3 *A*). Rigid films, on the other hand, can resist gravity and have an irregularly, often jaggedly, colored appearance with no rapidly moving parts (Fig. 3 *B*).

As the difference between mobile and rigid films is ascribed to the close packing of hydrocarbon tails in the latter, it is interesting to see the immediate effect of giving the surface molecules of a rigid film more room. Dr. John Skewis and I performed this experiment several years ago (13,¹) by placing a solution of the proper composition (e.g. a 0.2% solution of a mixture of 20 parts of sodium dodecyl sulfate with 1 part of dodecyl alcohol) in a tall jar so as to provide a limited surface for a sufficient volume and making a rigid film by immersing a rectangular frame in the solution and then slowly lifting it.

A second similar frame was then placed in the solution (Fig. 4 *A*) and, when rapidly lifted (Fig. 4 *B*), formed a second film. The formation of this second film rapidly increased the total surface and thus permitted the surface molecules to separate until adsorption of additional ones slowly restored equilibrium. This changed completely the character of the first film from rigid to mobile in a matter of 1–2 sec, as shown by the sequence of photographs of Fig. 5. Of course, a return of the second frame to the immersed condition compressed the molecules in the surface and returned the first film to the rigid condition.

A similar transition between rigid and mobile film occurs very sharply upon heating (10, 11, 14).

FILM ELASTICITY

Expansion of the surface with fewer adsorbed molecules per unit surface corresponds to a lesser lowering of the surface tension (from the high value for pure water), and therefore to an increase in the surface tension of the solution, the so-called Marangoni effect. We may therefore say that, in the above experiment of Fig. 4, the first film was stretched by the increased surface tension of the solution as the second frame was lifted. The question of how much a film extends when thus stretched has been examined by Gibbs (12) and led him to the concept of a film elasticity modulus, E , defined by

$$2 d\gamma = E \frac{ds}{s} \quad (1)$$

where s is the area of the film and γ the surface tension of each of its two sides. Gibbs also explained that for a film, in which adsorption equilibrium is expected to be very rapid, elasticity will be due to the depletion of surfactant within the film as some of it is adsorbed upon the stretching surface. Hence, the equilibrium concentrations, both inside the film and upon its surface,

¹SKEWIS, J. D., and K. J. MYSELS. Presented at the 1960 National Colloid Symposium, Lehigh University.

are lowered, and surface tension increases. It follows that in a thinner film, where less surfactant is available, the same stretching will produce a greater percentage depletion and therefore a bigger change in surface tension and a larger value of the elasticity modulus, E . For a two-component system (e.g. water and a single pure surfactant), Gibbs has also calculated the magnitude of this effect.

We have succeeded (15) in measuring Gibbs' film elasticity by an experiment similar to that of Fig. 4, in which the first frame was suspended from a sensitive transducer to give a direct measure of the force which was stretching the film. The extent of stretching was deduced from the observed and re-

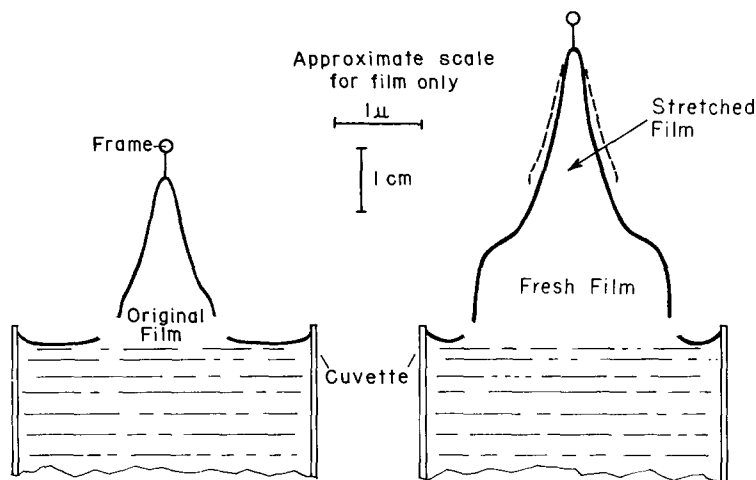


FIGURE 6. Schematic of the method of Prins, Arcuri, and van den Tempel (16) for measuring film elasticity. The dashed cross-section is that of the film on the left, which was then stretched by the weight of the additional film pulled out of the solution.

corded motion of interference fringes. As expected, rigid films showed a much higher modulus than mobile films.

Recently, Prins, Arcuri, and van den Tempel (16) devised a simpler method, shown schematically in Fig. 6. A film is formed by lifting the frame, allowing it to drain for a short time, and the frame is then lifted further so that additional film is formed. The weight of the new film stretches the original one, and both this weight and the stretching are obtained from a continuous thickness record. By using this procedure, quite good agreement with the theory has been obtained.

It may be noted that, as the film stretches, it also thins. The interference fringes which give the thickness record are like contour lines in a map, and move on the surface as the thickness changes. Hence, to obtain the stretching of the surface, one has to go through a somewhat complicated procedure (15) involving integration of the thickness to obtain the position of points corresponding to equal volumes of film.

THE FORMATION OF FILMS

When a frame is lifted from a solution, the film is formed essentially because the surface layers cling to the top of the frame, and are thus lifted, and some solution is entrained between them. The faster the lifting, the more solution is

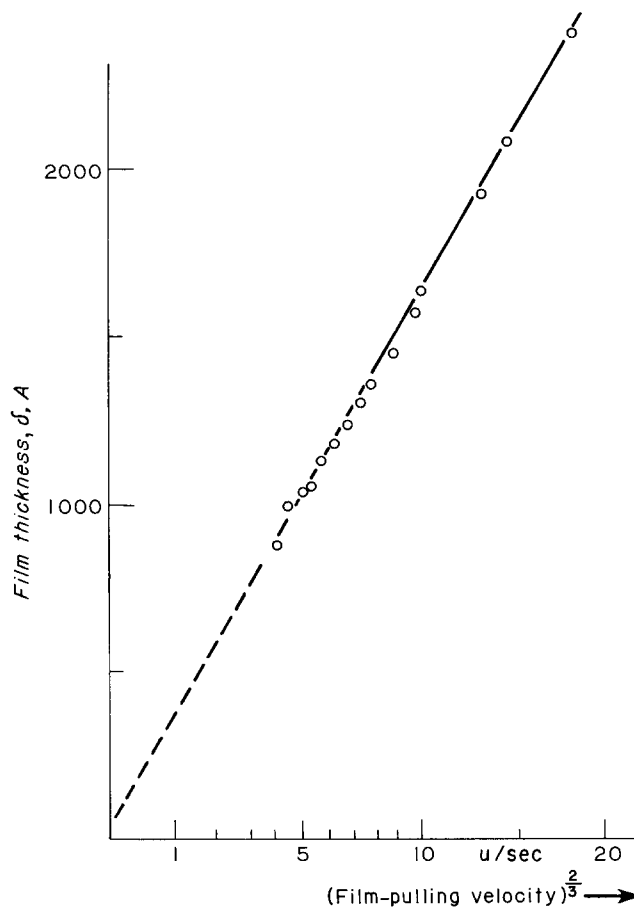


FIGURE 7. The thickness of a film as a function of the rate at which it is pulled out from bulk solution. Data from reference 18. The least squares line shown has a near zero intercept and a slope in agreement with equation 2.

entrained, because it has less time to escape at the bottom of the film before being entrapped between the parallel surfaces of the film. The hydrodynamics of this process can be analyzed in detail and lead to Frankel's law (3, p. 55; 17):

$$T = 1.88 v^{2/3} \eta^{2/3} / \gamma^{1/6} (\rho g)^{1/2} \quad (2)$$

which states that the thickness T is proportional to the $\frac{2}{3}$ power of the velocity, v , at which the film is pulled out, with the surface tension, γ , the density, ρ , and viscosity, η , of the solution, and the gravitation accelera-

tion, g , entering into the proportionality constant. The numerical constant 1.88 is not empirical, but results from the computer solution of the basic differential equation.

Experimental agreement with Frankel's law is very good (17, 18), and, for rather slow pullouts ($5\text{--}20\ \mu/\text{sec}$) and corresponding thicknesses of $800\text{--}2000\ \text{A}$, the results are precise enough (Fig. 7) to show that, whereas the surface monolayers are rigid, the solution between them has the bulk viscosity, η ,

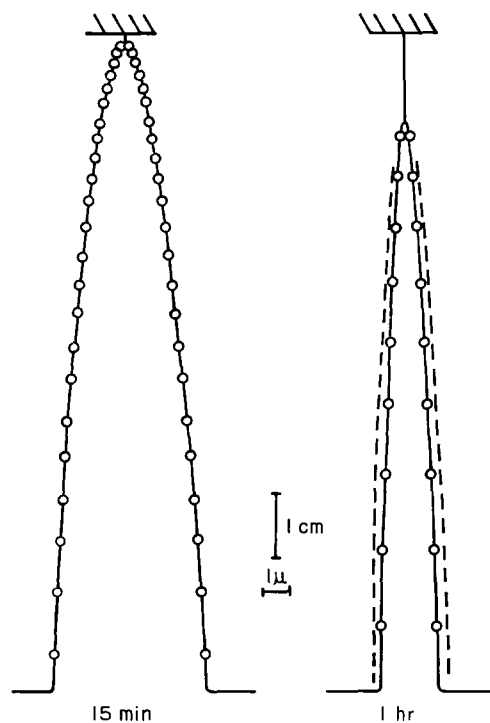


FIGURE 8. Cross-sections of a rigid film. The points are experimental, the lines are parabolas, and the dashed parabola is theoretically predicted. The small deviation is probably due to evaporation. *Figure reprinted by permission from Soap Films—Studies of Their Thinning and a Bibliography, Pergamon Press, New York, 1959, p. 29*

within the experimental error, which is equivalent to a rigid layer of less than $10\ \text{A}$ on each interface. This experiment shows that rigid water structures play no significant role in the dynamics of these films. For a discussion of the bearing of this evidence on the more general question of rigid surface layers of liquids, the reader is referred to comments by Overbeek (19), Derjaguin (20), and Scholten (21).

DRAINAGE OF RIGID FILMS

A rigid film is essentially a sandwich of aqueous solution between two unyielding surface monolayers. Thinning of the film occurs by removal of this solution, and this may be due to evaporation or to viscous flow downward under the influence of gravity. Evaporation leads rapidly to bursting, and we try to reduce or eliminate it as much as possible. The viscous flow can then be observed, and leads to a very slow thinning of the film. The reason for this

slowness is that, whereas the solution has essentially the viscosity of water, the two film surfaces are so close together that they form a capillary conduit of extreme narrowness measured in microns or less. A hydrodynamic analysis, also due to Frankel, shows that the film should rapidly acquire a parabolic cross-section and then thin at each point linearly with the square root of time (3, p. 26). Fig. 8 shows an experimental verification. It should be noted that, even after 1 hr of thinning, the film is over 1μ in thickness at the base. Another point to which we will return shortly is that the position of the top of the parabola has shifted downward during the 45 min separating the two film profiles shown.

MARGINAL REGENERATION

In striking contrast to rigid films, the mobile ones thin to an equilibrium thickness in a matter of minutes instead of hours. Thus, viscous flow cannot be an important factor, and other, more efficient mechanisms must be present. Elasticity measurements show that a stretching of the film surface cannot be significant either. Close observation, especially of horizontal films formed on a loop of wire or, better, on the mouth of a funnel (3, p. 37; 22), indicates that the main thinning mechanism is an exchange (3, p. 21; 13) of thick film elements for thin ones at the boundary of the film. It is within this thicker boundary, the so-called Plateau border, that the liquid can rapidly flow downward, and hydrostatic suction is therefore operative. Thicker film is therefore sucked into the border, but, because of the elasticity of the surface, it has to be replaced by a film of equal area. This replacement film is drawn out of the border and, according to Frankel's law (equation 2), has a thickness depending on the rate of its formation. This whole process, which we called "marginal regeneration," is spontaneous, since more force is exerted by a given suction upon a thicker film than upon a thinner one, and it is self-regulating, since acceleration would generate thicker film and thus reduce this difference in forces. Again, a detailed hydrodynamic analysis has been made and predicts a greater difference between the two thicknesses than observed (3, p. 63). Hence, it is likely that additional factors, such as gravitational forces and perhaps Marangoni effects, are also involved.

Once formed by marginal regeneration, the thinner film elements rise under the influence of gravity as explained above, and soon reach the level and, therefore, the color of their own thickness, to disappear from view as separate entities.

Although most important in the thinning of mobile films, marginal regeneration is also operating in rigid films. Here, however, the resistance to movement of film elements past each other is much greater; only large areas with large thickness differences are able to overcome this obstacle, and the motions are much slower. Fig. 5 A shows the result of marginal regeneration at the bottom of a rigid film with thin film formed in the middle and thick

films disappearing along both sides. The displacement of the origin of the parabola in Fig. 7 is due to the fact that the thick film at the bottom was being sucked into bulk solution as very thin film was being slowly pulled out at the top of the frame.

EFFECT OF ATTRACTIVE FORCES

Attractive forces between individual molecules have the same kind of effect as attractive forces between the two surfaces. This is because, in an intermediate region between thick and thin films, intermolecular forces result in a stronger attraction (and therefore a motion) toward the more numerous

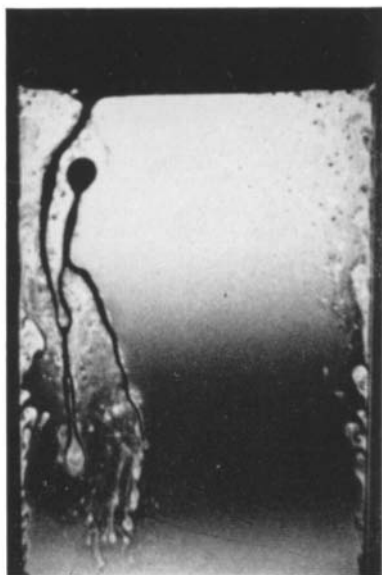


FIGURE 9. Rapid consumption of thick film by black film with welt formation. Note the rising "bubble" of black film and the right streamer of black film weighted down by the thick welts. The left streamer is weighted by a drop-shaped island of thick film. *Figure reproduced from an unpublished color slide made by Dr. P. C. Scholten.*

molecules of the thicker film and away from the less numerous ones of the thinner film. The result is therefore the same as if the two surfaces were attracted more toward each other as the film became thinner and solution molecules were squeezed out toward the thicker film (13, 23). Thus, the thicker film tends to become still thicker—to form a welt—at its boundary with the thinner film, and, at the same time the area of the thinner one grows, that of the thicker one is reduced. The thinner one "consumes" the thicker one, with the excess liquid pressed out and collecting at the boundary. The different thicknesses lead, of course, to further movements by gravity, and, when the process is energetic enough, it culminates in a very complicated appearance and extremely rapid thinning, which may be complete in a matter of seconds. This has been called irregular behavior (3, p. 12) or critical fall (24, 25). Fig. 9 shows an example of rather energetic thinning by such a mechanism, with the result that the thicker welts at the boundary of the very thin black film are able to pull it down into the thicker film.

CONCLUSION

By logical extension, the various thinning mechanisms listed above should reduce the film thickness to zero. If this happens at any one spot, the film bursts and disappears in 1 msec or so. Bursting is an interesting dynamic process in itself, and we are making some progress in studying it (26), but that is a very different story. The observations described in this paper were possible solely because the film does not thin out to zero, but only to an equilibrium value. This means, of course, that in addition to the thinning forces there are others which tend to keep its two surfaces apart and come into effect when the film is thin enough. Electric interaction—the double-layer repulsion—is one such well-documented mechanism (2, 4–6, 22). Steric interaction of adsorbed surfactants may well be another (27). The resultant equilibrium condition is in itself of great interest, but this is also another story, clearly not included in the dynamic processes with which this paper has dealt.

REFERENCES

1. JONES, M. N., K. J. MYSELS, and P. C. SCHOLTEN. 1966. *Trans. Faraday Soc.* **62**:1336.
2. MYSELS, K. J., and M. N. JONES. 1967. *Discussions Faraday Soc.* **42**:42.
3. MYSELS, K. J., K. SHINODA, and S. FRANKEL. 1959. *Soap Films—Studies of Their Thinning and a Bibliography*. Pergamon Press, London.
4. LYKLEMA, J., and K. J. MYSELS. 1965. *J. Am. Chem. Soc.* **87**:2539.
5. SCHELUDKO, A., and D. EXEROWA. 1960. *Kolloid-Z.* **168**:24.
6. SCHELUDKO, A. 1960. *Konink. Ned. Akad. Wetenschap., Proc., Ser. B.* **65**:76, 87.
7. NILSSON, G. 1957. *J. Phys. Chem.* **61**:1135.
8. WILSON, A., M. B. EPSTEIN, and J. ROSS. 1957. *Colloid Sci.* **12**:345.
9. WEIL, I. 1966. *J. Phys. Chem.* **70**:133.
10. MILES, G. D., J. ROSS, and L. SHEDLOVSKY. 1950. *J. Am. Oil Chemists' Soc.* **27**:268.
11. EPSTEIN, M. B., A. WILSON, C. W. JACOB, L. E. CONROY, and J. ROSS. 1959. *J. Phys. Chem.* **58**:860.
12. GIBBS, J. W. 1931. *Collected Works*. Longmans Green, London. **I**:309.
13. MYSELS, K. J. 1964. *J. Phys. Chem.* **68**:3441.
14. BECHER, P., and J. DEL VECCHIO. 1964. *J. Phys. Chem.* **68**:3511.
15. MYSELS, K. J., M. C. COX, and J. D. SKEWIS. 1961. *J. Phys. Chem.* **65**:1107.
16. PRINS, A., C. ARCURI, and M. VAN DEN TEMPEL. 1967. *J. Colloid Interface Sci.* **24**:84.
17. MYSELS, K. J., and M. C. COX. 1962. *J. Colloid Sci.* **17**:136.
18. LYKLEMA, J., P. C. SCHOLTEN, and K. J. MYSELS. 1965. *J. Phys. Chem.* **69**:116.
19. OVERBEEK, J. T. G. 1966. *Discussions Faraday Soc.* **42**:12.
20. DERJAGUIN, B. V. 1966. *Discussions Faraday Soc.* **42**:137.
21. SCHOLTEN, P. C. 1966. *Discussions Faraday Soc.* **42**:136.
22. OVERBEEK, J. T. G. 1960. *J. Phys. Chem.* **64**:1178.
23. SCHELUDKO, A., and D. EXEROWA. 1960. *Kolloid-Z.* **168**:24.
24. DEWAR, J. 1923. *Proc. Roy. Inst. G. Brit.* **24**:197. 1927. *Collected Papers*. Cambridge. 1343.
25. LAWRENCE, A. S. C. 1929. *Soap Films*. G. Bell & Sons, Ltd., London.
26. Papers presented at the 151st and 155th National Meetings of the American Chemical Society. In press.
27. DUYVIS, E. M., and J. T. G. OVERBEEK, 1962. *Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B.* **65**:26.