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**PHYSICS AND PHYSICAL CHEMISTRY OF
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Soap Films as a Central Theme in Detergent Research*

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SOMMAIRE

L'attention est attirée sur le fait qu'en ce qui concerne la détergence et l'usage des détergents pour stabiliser les mousses, les émulsions et les suspensions, le facteur critique est le comportement de la dernière lame mince d'eau séparant deux bulles de mousse, deux gouttes d'émulsion, deux particules en suspension, la salissure et l'objet sali. Les films de savon constituent des systèmes presque idéaux pour l'étude de ces lames minces. La couleur et la réflexion de la lumière fournissent des renseignements exacts sur l'épaisseur des films de savon. On s'explique relativement bien leur structure ainsi que le mécanisme de leur écoulement. On réalise des «films noirs» dont l'épaisseur est déterminée par l'action combinée des forces de Van der Waals, et de la répulsion électrostatique entre les doubles couches électriques et éventuellement d'autres forces dont la portée est du même ordre. On peut utiliser les films noirs pour obtenir des renseignements sur ces forces, soit en faisant varier la charge de surface et la teneur électrolytique des films de savon ou plus directement, en mesurant la diffusion de lumière dans ces films. Jusqu'ici, on ne s'explique que partiellement la stabilité finale des films de savon, c'est-à-dire leur résistance à la rupture. Il est essentiel de poursuivre la recherche sur ce point non seulement pour réussir à comprendre la structure des films de savon, mais aussi pour l'interprétation de la détergence et de la stabilité des émulsions et des suspensions.

ZUSAMMENFASSUNG

Es wird darauf hingewiesen, daß in der Detergenzie und im Gebrauch von Detergentien zur Stabilisierung von Schäumen, Emulsionen und Suspensionen der kritische Faktor das Verhalten der letzten, dünnen Wasserschicht ist, die zwei Seifenblasen, Emulsionstropfen, suspendierte Teilchen oder Schmutz und verschmutzter Gegenstand trennt. Seifenfilme sind beinahe ideale Systeme, um diese dünnen Schichten zu untersuchen.

Farbe und Lichtreflektion geben genaue Information über die Dicke von Seifenfilmen; ihre Struktur und der Mechanismus des Wasserabflusses sind verhältnismäßig gut durchschaubar. „Schwarze Filme“ werden gebildet, und ihre Dicke wird bestimmt durch das Wechselspiel von van der Waals Kräften, elektrostatischer Abstoßung zwischen elektrischen Doppelschichten und möglicherweise anderer Kräfte mit einer Reichweite in der gleichen Größenordnung. Schwarze Filme können benutzt werden, um Informationen über

* Plenary lecture delivered in Brussels, on Thursday 10th September 1964.

diese Kräfte zu erhalten, entweder durch Veränderung der Oberflächenladung und des Elektrolytgehalts von Seifenfilmen oder auf eine direktere Art und Weise durch Messung der Lichtzerstreuung durch diese Filme. Die Bruchfestigkeit von Seifenfilmen ist erst teilweise geklärt. Eine weitere Untersuchung dieses Punktes ist wesentlich nicht nur für das Verständnis von Seifenfilmen, sondern auch für die Interpretation der Detergencie und der Stabilität von Emulsionen und Suspensionen.

SUMMARY

It is pointed out that in detergency and in the use of detergents for stabilizing foams, emulsions and suspensions, the critical factor is the behaviour of the last thin layer of water separating two foam bubbles, emulsion droplets, suspended particles or soil and soiled object. Soap films are nearly ideal systems for studying these thin layers. Colour and reflection of light give accurate information about the thickness of soap films; their structure and the mechanisms of their drainage are relatively well understood. "Black films" are produced and their thickness is determined by the interplay of Van der Waals forces, electrostatic repulsion between electrical double layers and possibly other forces with a range of the same order. Black films can be used to obtain information about these forces, either by manipulating the surface charge and electrolyte content of soap films or more directly by measuring the scattering of light by these films. The ultimate stability of soap films i.e. their resistance against breaking is as yet only partially understood. Further research on this point is essential, not only for the understanding of soap films, but also for the interpretation of detergency and of the stability of emulsions and suspensions.

Introduction

Detergency means cleaning, removing of soil and dirt from fabrics, the skin and other objects. Detergents are surface active substances, which promote this process by aiding water to penetrate between the dirt and the soiled objects, by peptizing the dirt particles, and by keeping them in suspension, so as to allow their removal in the form of more or less stable suspensions or emulsions. In the wetting process contact angles are of importance, but the critical stage in detergency is the formation of a thin layer of water between, say, the fabric and the dirt particle, and the prevention of breaking of this layer in later collisions.

The use of detergents as stabilizers for foams, emulsions and suspensions of various nature is wide-spread. Here also the stabilizing action ultimately reduces to the prevention of breaking of the last water film between two particles, drops or gas bubbles.

Consequently the study of these thin water layers is of central importance for many applications involving detergents, not only for the cleansing processes, but also for the use of detergents in stabilizing suspensions, emulsions and foams.

These thin layers of water can be investigated with particular ease in the form of soap films*. They can be studied individually or in foams. They can be obtained as water films, in air or between layers of oil or mercury, and in the inverse form as oil films between water layers. Their colour or rather the interference of light reflected from them gives detailed information on their thickness. By following the colour changes, the mechanism of their thinning can be studied until eventually the films break.

Colour of Soap Films

Light falling on a soap film is reflected at the two sides of the film with the same amplitude, but with a phase difference, composed of a reversal of phase at the reflection at the front face plus the phase difference connected with travelling twice through the film, as illustrated schematically in Fig. 1.

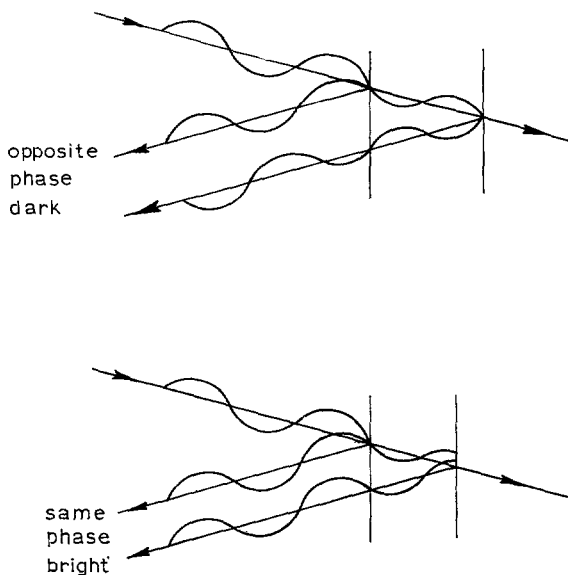


Fig. 1. Depending on thickness of film, light is reflected with minimal or maximal intensity.

If white light is reflected at a film, some of the wave lengths are extinguished or weakened by interference, and in the reflected light the complementary colour is particularly strong. The colour of the reflected

* The term soap film is used here for any thin film stabilized by soap or by an other detergent.

light is quite a good and reasonably accurate indication for the thickness of the film, provided this thickness is between about 1000 Å (1st order white, or silver) and about 10,000 Å, when the colours become weak shades of red and green. Figures 2 and 3 illustrate this for light reflected from a soap film in a vertical frame, which, under the influence of gravity is stratified in horizontal layers, increasing in thickness from top to bottom*. In Fig. 3 the top part of the soap film appears black, i.e. it does not reflect any wavelength, indicating that the film is extremely thin, so that the phase difference between the two reflected beams arises almost completely from the 180° phase shift at the frontal surface.

Actually the reflection is not completely zero. The film is gray rather than black and the intensity of the reflected light can be used to calculate the thickness of the film from the equation:⁽¹⁾

$$I_{\text{refl}} = 4I_0 \left(\frac{n-1}{n+1} \right)^2 \sin^2 \frac{2\pi nd \cos \theta}{\lambda_{\text{vac}}} \quad (1)$$

in which

- I_0 = intensity of incident light
- I_{refl} = intensity of reflected light
- n = refractive index of the film
- $(n-1)/(n+1)$ = Fresnel reflection coefficient
- d = thickness of the film
- θ = angle between light beam *in* the film and the normal
- λ_{vac} = wavelength of light *in vacuo*

The occurrence of black spots in soap films was already known to Hooke,⁽²⁾ who in 1672 gave a communication to the Royal Society entitled "On holes in soap bubbles". Isaac Newton⁽³⁾ also studied these "holes" and observed that several black films of different thickness could coexist in the same bubble, a subject which was taken up later by Jean Perrin,⁽⁴⁾ A. S. C. Lawrence⁽⁵⁾ and others. Other famous investigators, who occupied themselves with soap bubbles are J. Plateau⁽⁶⁾ the eminent Belgian scientist, who although blind, conceived and described a number of very pertinent experiments on the behaviour of soap films, and C. V. Boys⁽⁷⁾ whose rightly famous lectures on "Soap bubbles and the forces which mould them" are fortunately again easily accessible in modern reprints.

* More accurate values for the film thickness can be obtained by the use of monochromatic light.

Structure of Soap Films

In soap solutions the partly hydrophobic nature of the soap molecules leads to their accumulation at the surface, as indicated by the corresponding lowering of the surface tension. A soap film therefore is a thin layer of soap solution covered on both sides by a layer of adsorbed soap molecules. Marangoni⁽⁸⁾ and Gibbs⁽⁹⁾ pointed out that this adsorption of soap

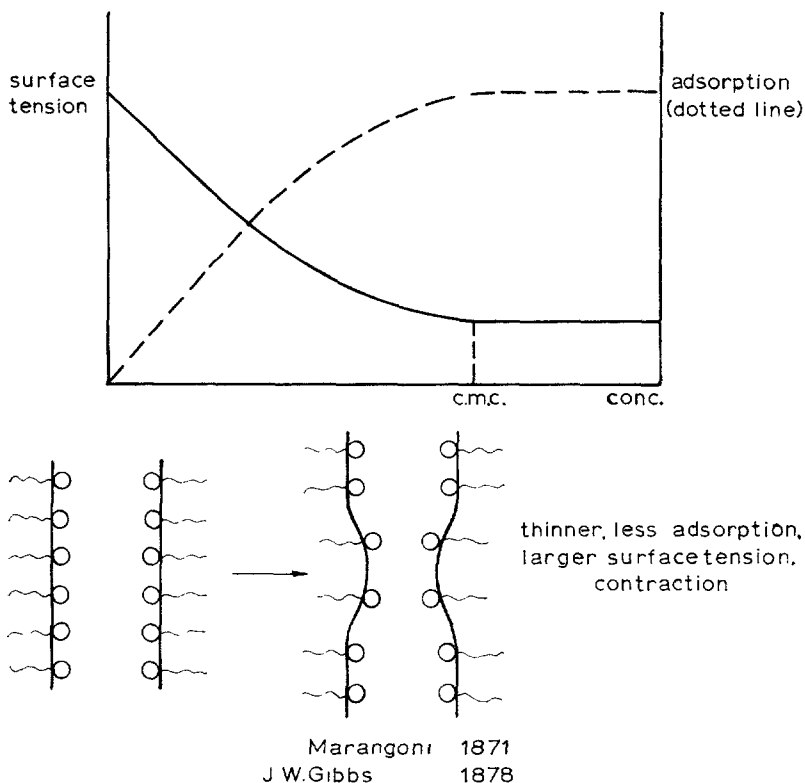


Fig. 4. Illustration of Gibbs-Marangoni effect in stabilizing soap films.

molecules is one of the essential prerequisites for the stability of films. If such a film were extended locally, the local amount adsorbed per unit area would decrease, the surface tension would increase as illustrated in Fig. 4 and contraction of the extended part would follow, thus preventing thinning by extension, which would ultimately lead to breaking of the film.

The same effect occurs in the thin layer between two neighbouring oil droplets in an emulsion and counteracts coalescence. Analogous effects, viz an energy barrier against desorption of adsorbed surface layers are active in stabilizing suspensions.

The destructive influence of certain foam breakers (e.g. octyl alcohol) is closely related to this Gibbs-Marangoni effect. Octyl alcohol is surface active and when it hits the surface, decreases the surface tension locally thus leading to thinning of the contaminated spot and eventually to breaking of the lamella.

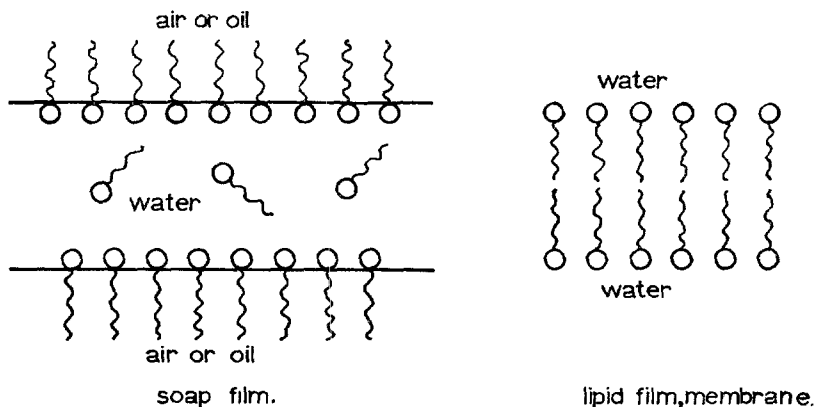


Fig. 5. Schematic picture of soap film and lipid membranes.

Just as aqueous soap films can be obtained between oil layers, it is possible to prepare oil films between water layers. They can be considered as models for studying the stability of water in oil emulsions, and if allowed to drain until nothing but the two layers of amphipolar substances are left, they form interesting models for biological membranes,⁽¹⁰⁾ which have their hydrocarbon layers inside and the polar groups outside, cf. Fig. 5.

Recent Revival of Interest in Soap Films

Although, as you have seen, soap films were considered worthy objects of research by some of the greatest scientists, this field has been badly neglected in the first half of the present century. Colloid chemists, although classifying foams as "dispersions of gas in liquid" presumably considered the size of foam bubbles hardly as "colloidal". Surface chemists were so much interested in insoluble monolayers and in adsorption of gases on solids that they neglected the field of adsorption at liquid-gas boundaries and the study of soap films.

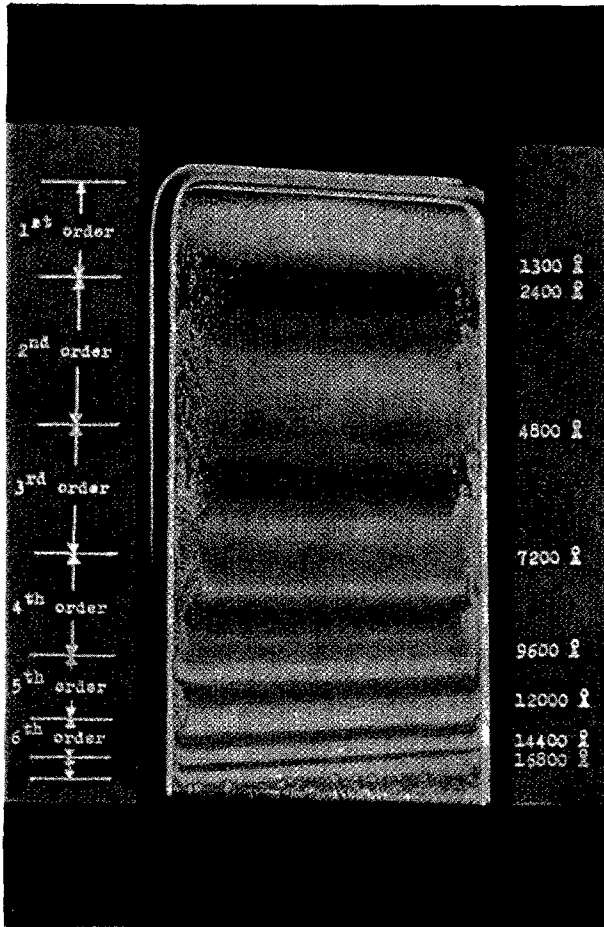


Fig. 2. Colours reflected from a soap film illuminated by white light. Scale of thicknesses.

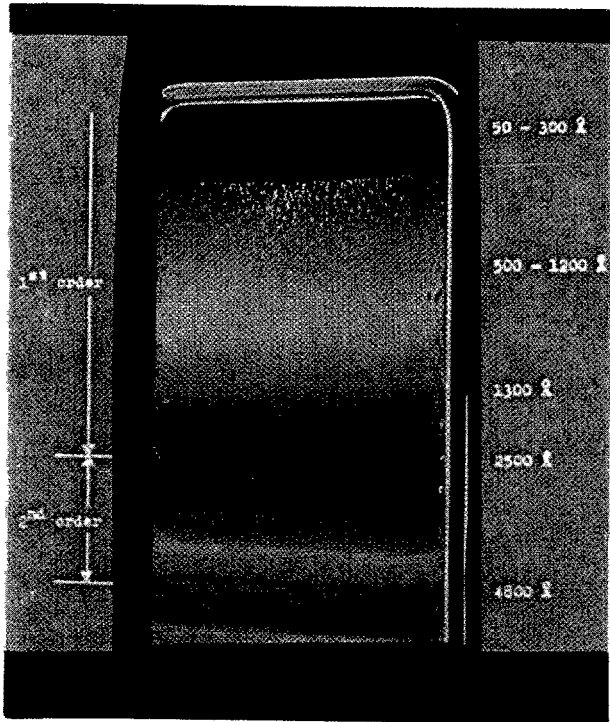
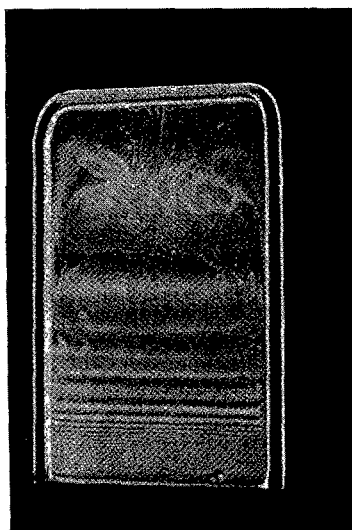


Fig. 3. The same film as in Fig. 2 at a later stage.



Figs. 9a and 9b. Turbulent motion in marginal regeneration. (Fig.9a reprinted from *Soap Films*, Mysels, Shinoda and Frankel with permission from Pergamon Press Ltd.).

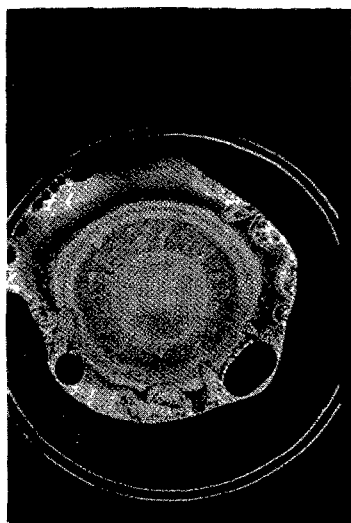


Fig. 11. Horizontal film. Discontinuous transition between black and coloured film. Taken from Mysels et al. ref.11, p.62 plate III, (with permission from Pergamon Press Ltd.).

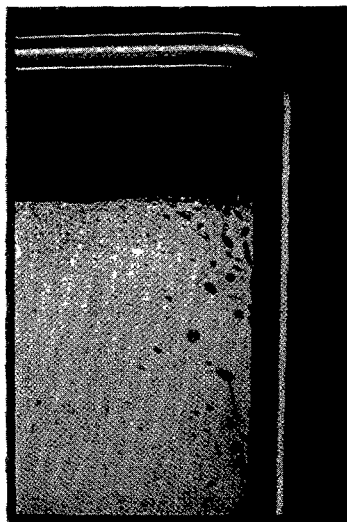


Fig. 12. At the boundary black-silver a thicker rim is formed which shows in the form of yellow droplets. (Reprinted from *Soap Films*, Mysels, Shinoda and Frankel with permission from Pergamon Press Ltd.).



Fig. 13. Critical fall which causes a rapid increase of the black area.

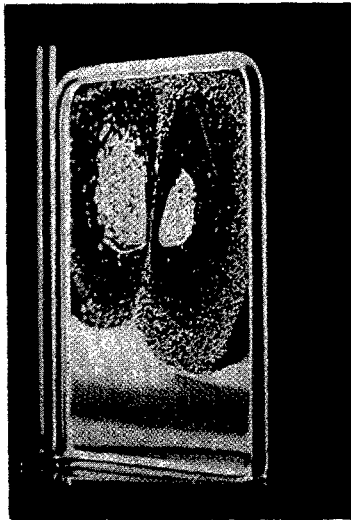


Fig. 20. Soap film, set in rapid circulating motion by an air current directed upward between and slightly below the "eyes".

Fortunately more recently interest in soap films has revived, based on an increased importance of foams and on the recognition that soap films are excellent models for many phenomena in surface and colloid chemistry.

Mysels and his coworkers⁽¹¹⁾ made a very thorough study of drainage mechanisms. Derjaguin and Titijevskaja⁽¹²⁾ used black soap films to demonstrate the "disjoining pressure" caused by the mutual repulsion of the electric double layers formed by the soap ions and their counterions. De Vries,⁽¹³⁾ in a study of foams and foam stability was the first to recognize the importance of Van der Waals forces in the formation of black spots in soap films.

Indeed in the last-named effects we encounter the reason why research on black films may be so valuable. The range of the Van der Waals forces and of the electrostatic forces is just of comparable order to the thickness of black films and this is not accidentally so, but a fundamental property, because the interplay of these forces just determines the thickness of the film. We return later to this point.

Drainage of Soap Films

We have seen already that, according to Gibbs and Marangoni, thinning of soap films does not in general occur by stretching, and must therefore be due to drainage. The most simple form of drainage would be viscous flow between quasi solid soap layers, as shown in Fig. 6.

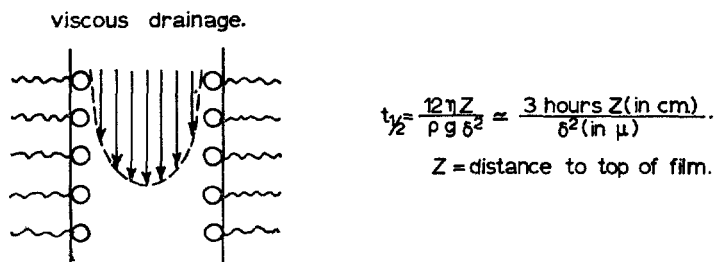


Fig. 6. Viscous drainage of soap film.

This flow has a parabolic profile and will give rise to a more or less parabolic cross section of the (vertical) soap film. Assuming the viscosity of the flowing liquid to be equal to the bulk viscosity, η , the time in which the film has halved its thickness is given by

$$t_{\frac{1}{2}} = \frac{12\eta z}{\rho g \delta^2} = \frac{3z(\text{in cm})}{\delta^2(\text{in } \mu)} \text{ hours} \quad (2)$$

in which g is the acceleration by gravity, z is the distance to the top of the film, δ its thickness, and ρ its density.

Films in which the soap layers have quasi rigid properties indeed show this kind of drainage, as illustrated in Fig.7, taken from Mysels et al.*

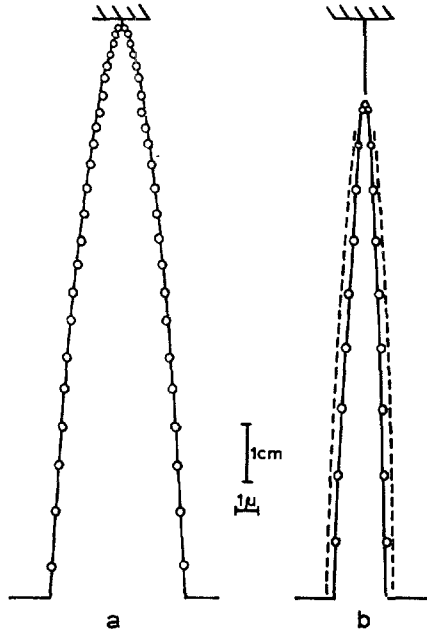


Fig. 7. Thinning of rigid soap film The dotted shape is calculated on the basis of the viscous drainage mechanism (eq. 2). The circles with the drawn lines are based on observations 15 minutes (a) and 1 hour (b) after drawing the film. (Reprinted from *Soap Films*, Mysels, Shinoda and Frankel with permission from Pergamon Press Ltd.)

However, this is an extremely slow drainage process and in most films, viz. those in which the soap layers behave more like two-dimensional liquids (mobile films), most of the drainage is due to an exchange of thick against thin film at all loci where the film is attached to a bulkier liquid. Citing Willard Gibbs† we read “At such an edge we generally find a liquid mass, continuous in phase with the interior of the film, which is bounded by concave surfaces, and in which the pressure is therefore less than in the

* ref. 11, p. 29.

† ref. 9, p. 309.

interior of the film. This liquid mass therefore exerts a strong suction upon the interior of the film, by which its thickness is rapidly reduced. This effect is best seen when a film which has been formed in a ring is held in a vertical position. Unless the film is very viscous, its diminished thickness near the edge causes a rapid upward current on each side, while the central portion slowly descends. Also at the bottom of the film... portions which have become thinned escape from their position of unstable equilibrium beneath heavier portions, and pass upwards, ... By these processes, the whole film is rapidly reduced in thickness”.

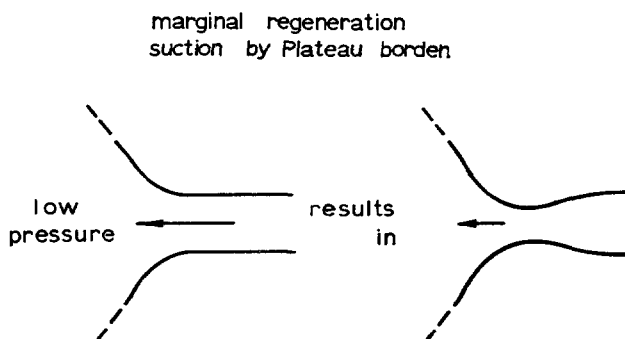


Fig. 8.

Obviously Gibbs, the great theoretician, was a very careful observer and experimenter as well. Figure 8 illustrates the thinning of the film near an edge (Plateau border). This process, called “marginal regeneration” by Mysels, is the cause of strongly turbulent motions in soap bubbles and is shown in a vertical film in Fig. 9.

Just to illustrate how much more rapidly this drainage mechanism works than viscous flow, we show in Figure 10 that a mobile film loses its thickness in minutes rather than in hours.

The mechanism of drainage is a factor of great importance in the stability of foams and emulsions. It is obvious that a film cannot break without first becoming very thin. If the soap layers are rigid (not mobile), thus preventing the type of flow necessary for marginal regeneration, this will decrease the rate of thinning and thus postpone the moment at which the film eventually reaches a critical thickness, at which it may break. This same effect also explains why in general emulsions formed from viscous oils are more stable than those containing more fluid oil drops, because a high viscosity of the oil will prevent rapid (turbulent) drainage of

water from between two oil drops. With suspensions of solid particles, and in detergency, marginal regeneration is not possible and drainage is thus exclusively due to viscous flow.

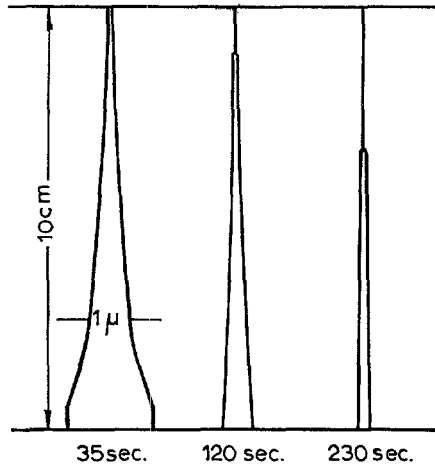


Fig. 10. Profile of mobile soap film as a function of time.* (Reprinted from *Soap Films*, Mysels, Shinoda and Frankel with permission from Pergamon Press Ltd.).

Black Films

As mentioned in the beginning of this lecture soap films develop black parts, "holes", and from some of the figures already shown and the following Fig. 11 it is clear that the black film is separated by a sharp (nearly) discontinuous transition from thicker coloured film. Gibbs[†] already remarked... "the thinnest parts tending to become still more thin (apart from any external cause) very much as if there were an attraction between the surfaces of the film insensible at greater distance, but becoming sensible when the thickness of the film is sufficiently reduced". He continues a little further on "that in the formation of these black spots a separation of different substances takes place, and not simply an extension of a part of the film, is shown by the fact that the film is made thicker at the edge of these spots".

This observation is nicely illustrated in Fig. 12 in which yellow spots between the black and the silver film show a colour which really belongs to a

* ref. 11, p. 34.

† ref. 9, p. 311

lower, hence thicker part of the film. These thicker “drops” flow down from the rim between black and silver film and under favourable circumstances (high soap concentration) may do this so rapidly that they carry a wake of black film after them, which increases the length of the black/silver border and thus strongly accelerates the formation of black film, accompanied by turbulent motions called “critical fall” by Dewar.⁽¹⁴⁾ See Fig. 13.

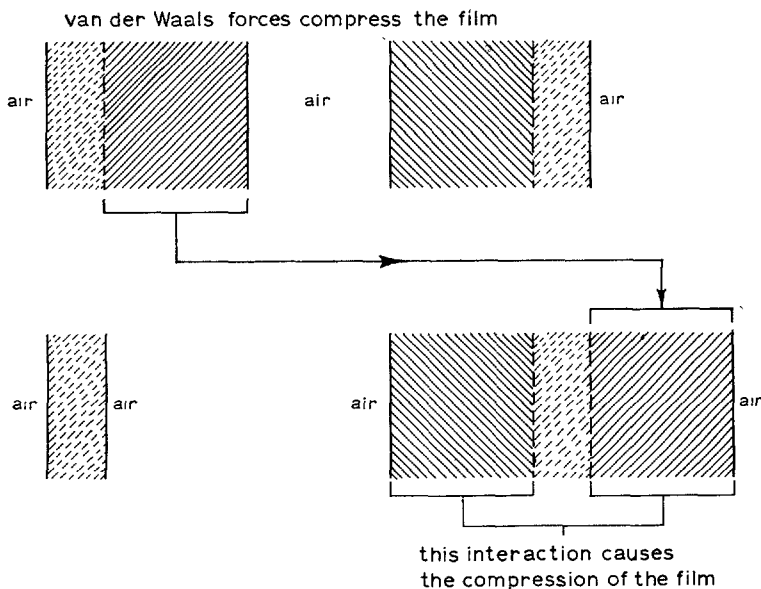


Fig. 14. Van der Waals forces.

De Vries⁽¹³⁾ has suggested that the “attraction between the surfaces of the film” invoked by Gibbs is really due to the ever-present Van der Waals forces. The phenomenon of surface tension is explained by the fact that molecules near the surface are at a higher level of potential energy than those in the bulk of the liquid, because they are insufficiently surrounded by molecules to which they are attracted. If a film becomes sufficiently thin, molecules in the middle of it will “feel” the lack of attraction at both sides. By moving to thicker parts of the system these molecules will reach a more favourable position (of lower energy). Figure 14 illustrates in a different way that Van der Waals attraction favours a disproportionation of a film and points the way to finding a quantitative expression for this “compressing effect”.

Considering all energies of interaction in the lower and upper parts of this figure one finds that all are the same except that in the lower figure the attraction between the parts with heavy cross-hatching is present. This attraction lowers the energy of the whole system by an amount equal to

$$V_{\text{attr}} = -\frac{A}{12\pi d^2} \quad (3)$$

where A is the Hamaker⁽¹⁵⁾ constant related to the London attraction constant λ by the equation: $A = \pi^2 q^2 \lambda$, where q is the number of molecules per cm^3 and λ = London energy between two molecules multiplied by the sixth power of the distance between them.

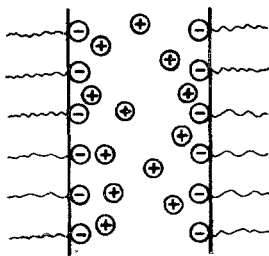


Fig. 15. Schematic picture of soap film, with anionic soap, and overlapping electric double layers.

Although we understand in this way why soap films after they have thinned to a certain extent will develop thinner (black) parts, it is (I cite again W. Gibbs*) “most difficult to account for in the formation of the black spots is the arrest of the process by which the film grows thinner”. Considering the stability of these thin films and foams, the stability of emulsions and suspensions, and detergency itself, “the arrest of this process” is of course of the utmost importance. For films prepared with ionic detergents, the thinning process is counteracted and finally stopped by the electrostatic repulsion between the two layers of soap ions, repulsion which is attenuated by the presence of a diffuse electric double layer of small ions as illustrated in Fig. 15.

This electrostatic repulsion had already been considered in the explanations of Schiller layers⁽¹⁶⁾ and of the stability of colloids.⁽¹⁷⁾ The application to soap films was first suggested by Derjaguin and Titijskaja.⁽¹²⁾ Considering the ions as point charges, subjected to a distri-

* ref. 9, p. 312.

bution according to the Boltzmann principle, and the surface charge as being completely smeared out, the energy of repulsion per unit area can be calculated and is given approximately by:⁽¹⁸⁾

$$V_R = \frac{64cRT}{\kappa} \tanh^2 \left(\frac{zF\psi}{2RT} \right) \cdot \exp(-\kappa d)$$

$$\kappa = \sqrt{\frac{8\pi cz^2 F^2}{\epsilon RT}}$$
(4)

in which c is the concentration of (symmetrical) electrolyte in moles/cm³, $1/\kappa$ is the Debye-Hückel length, z the valence of the ions, F the charge of a monovalent gramion, ψ the surface potential, ϵ the dielectric constant of the solution, R the gas constant and T the absolute temperature.

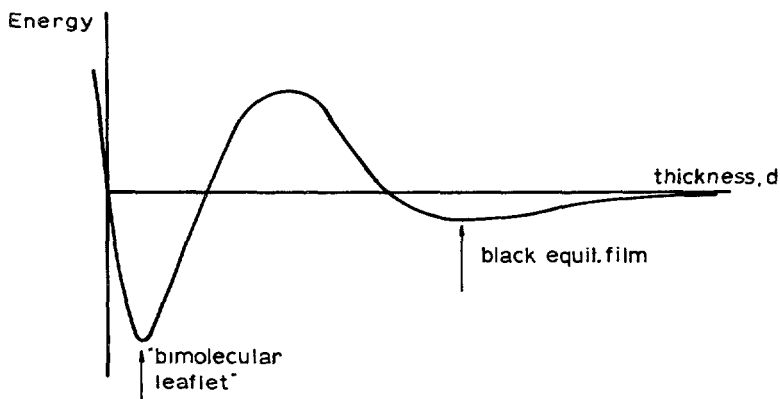


Fig. 16. Energy vs. thickness curve for Van der Waals attraction, electrostatic repulsion and Born repulsion.

If these two contributions to the energy of the film are taken together the resulting energy vs. thickness curve reflects the fact that the attraction is an inverse power of the thickness, whereas the repulsion is an exponential function. This means that for great thicknesses the Van der Waals attraction is always the main term and compression results; for very small thicknesses the Van der Waals term is again the more important one, but for intermediate thicknesses repulsion may prevail, as illustrated in Fig. 16, where in addition the Born repulsion between the soap molecules (for extremely thin films) is taken into account.

If the detergent is non-ionic, the long range electrostatic repulsion is replaced by a shorter range, but steeper repulsion due to the interaction between the wriggling hydrophilic tails (entropic interaction⁽¹⁹⁾) or the Born repulsion between the hydrophilic parts of the non-ionic detergent. It has been suggested by Derjaguin,⁽²⁰⁾ that in addition to electrostatic repulsion, repulsion may be due to oriented water layers.

One of the aspects of the interaction curve of Fig. 16 is that it presents two minima corresponding to two more or less stable thin films. The thicker of the two films will be rather stable and not subject to breaking. Any local thinning of this film would be opposed by an increase in surface tension. Whether the thinner film will be stable or not depends on details in its structure. If it contains very little solvent, the Gibbs-Marangoni effect is absent or weak, and the film may be too rigid or brittle for stability.

The so-called "stratified" black soap films in which black films of more than two different thicknesses coexist, had already been observed by Newton,⁽³⁾ and have been studied extensively by Johonnot,⁽²¹⁾ Perrin,⁽²²⁾ Lawrence⁽²³⁾ and others.

They are probably multiple layers of essentially bimolecular leaflets, and may correspond to liquid crystals with an increasing number of layers.

Except for the thinnest of these, which corresponds to the thin minimum of Fig. 16, they are not represented on this curve.

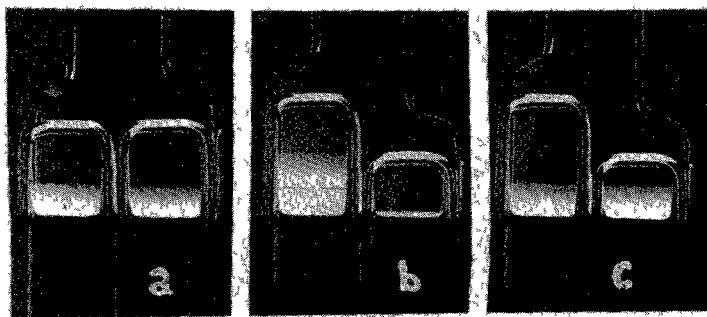


Fig. 17. Equilibrium between two types of black (gray) film.
a. initial equilibrium; *b.* left hand frame pulled out, right hand frame pushed down;
c. after a few hours the separation line has returned to its original level.

As the same or similar interaction curves determine the collision behaviour of emulsion droplets and suspended particles, and the interaction between dirt and fibre or skin, research on soap films gives access to the most central aspects of stabilization⁽²⁴⁾ and detergent action.

Duyvis⁽²⁵⁾ has found an actual case, in which the two minima occur in equilibrium with one another, an equilibrium which depends on gravity. This is illustrated in Fig. 17, where a represents a vertical soap film (the "soap" consisting of a large part of non-ionic detergent, with a small addition of an ionic one, leading to a weak but far-reaching repulsion. The two black films (the lower one is rather grey) are in equilibrium at a height of about 3 mm above the bulk solution level and this equilibrium can be reached both from below and from above, as illustrated in Figs. 17b and c.

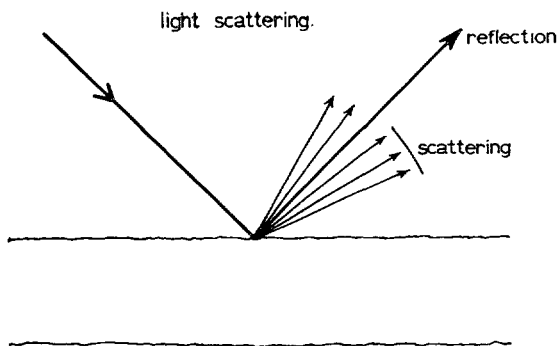


Fig. 18. Light is scattered by surface corrugations.

It is not possible to change the Van der Waals force to any great extent, without strongly altering the composition of the system, but the electrostatic repulsion can be manipulated quite easily by using mixtures of ionic and non-ionic detergent, which changes the charge per unit area and by changing the electrolyte content, which changes κ and therewith the range of the electrostatic forces.

Recently one of my coworkers Dr. A. Vrij⁽²⁶⁾ developed a new tool for investigating the forces in thin films. Such films not only reflect light, they also scatter it as a consequence of the thermal corrugations of the surfaces. The corrugations are counteracted by the surface tension and they are coupled, i.e. brought more or less in phase with one another, by the molecular forces which reach across the thin film. A study of light scattering will therefore give direct information on the forces in the film.

Stability of thin films

We return now to our original problem, the stability of thin films, i.e. their resistance to breaking. In the first place the presence of a surface active substance is necessary to prevent catastrophic local thinning (Gibbs-

Marangoni effect). High viscosity or rigidity of at least one of the media, or rigidity of the surface layer, slows down drainage and prolongs the life of the thin film. The interplay of electrical and other forces determines whether or not there is a metastable "equilibrium film". But we should not forget that the actual breaking of a film is a discontinuous transition, not represented on energy curves like those of Fig. 16.

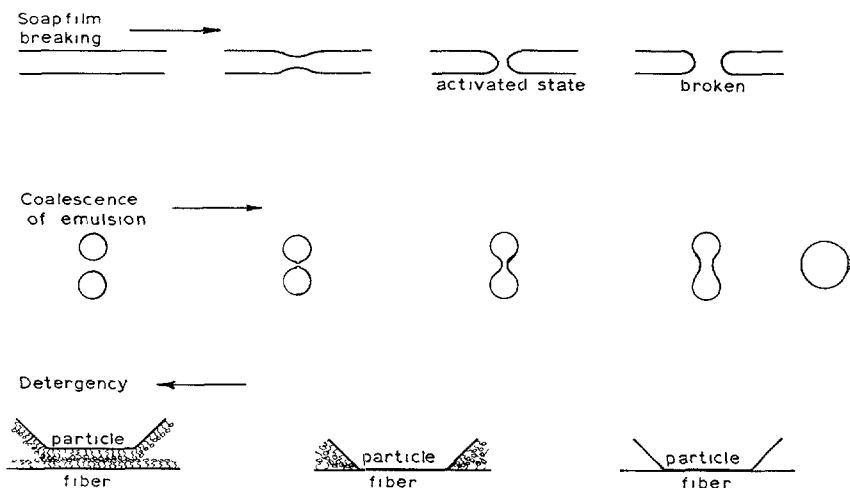


Fig. 19.

So far there is comparatively little experimental work on the breaking of individual thin films and particularly little work on the breaking of soap films. A tendency exists of course either to work with very labile films which break rapidly, or to use stable films with a life so long that breaking does not seem to occur. But as the breaking presumably is due to a "Brownian" accident, experiments in the middle range of moderate stability appear badly reproducible and are avoided. Nevertheless here is an important and interesting field of research.

I want to draw attention to two more theoretical aspects of the breaking. Scheludko⁽²⁷⁾ has pointed out that at and below a certain critical thickness a film is unstable with respect to a small local disturbance, because in a small thinning the gain of Van der Waals energy is more than the increase of energy due to the enlarged surface area. This occurs for films of a thickness of about 300 Å. In such a case the film will thin out further, until it breaks or until a stable black film is formed.

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De Vries⁽¹³⁾ has shown that the formation of a small hole in a plane parallel film is a process which requires energy, because the total surface area of the film with the small hole is larger than that of the intact film. Only when the radius of the hole is larger than the film thickness, will the hole grow spontaneously. The maximum energy of the system corresponding to the activation energy for breaking is only small enough to allow spontaneous breaking ($10-20 kT$) when the film is about 20 \AA or thinner. Consequently the film corresponding to the right hand minimum of Fig. 16 will not break, but the very thin film corresponding to the left hand minimum may be unstable. The model used by de Vries is of course very simple and it would be valuable to develop this theory for a more realistic model of the formation of a critical hole in a soap film. This is especially important since the thinnest black film may well contain a water layer of only 10 \AA thickness or even less, with two layers of soap molecules, and this is far removed from a film of homogeneous composition.

In Fig. 19 we show once more the parallelism between breaking of a soap film, coalescence of two emulsion droplets, and the process of detergency.

Conclusion

In soap films all the characteristic features which are necessary for understanding the stability of the systems in which we are interested in detergency, are present and can be investigated in a very pure and neat way. That is the reason why I want to "propagandize" soap film research as a method of obtaining more fundamental understanding of many aspects of detergent action. The main, but not the only interest will be in the properties of black films. But before obtaining these, one has to pass the stage of the coloured film, which apart from its scientific interest can give aesthetic satisfaction as well. I want therefore to end my lecture by showing a few short scenes from a film on soap films, in which you will see the set-up in which the films and photographs have been obtained, some examples of marginal regeneration, the critical fall, and finally a demonstration of the strength of soap films. In this demonstration a current of air is blown against the film and sets it in violent motion, which can be sustained even by the black film as shown in the last figure (Fig. 20).

At the end of the lecture a film was shown entitled "Drainage of soap films", which had been prepared by the Foundation Film and Science, University Film, at Utrecht.

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