CURRENT CONCEPTS IN THE THEORY OF FOAMING

By J. A. KITCHENER, D.SC., and C. F. COOPER, PH.D.*

(DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE, LONDON, S.W.7).

Introduction: the problem of foams

IT IS, perhaps, surprising to find in 1958 that no thoroughly satisfactory explanation has yet been given as to why certain liquids foam strongly, others feebly, and many not at all. This situation does not arise from any lack of scientific interest in foams, nor are they without practical importance. On the contrary, the uses or disadvantages of foaming in technical chemistry are too well known to need comment in this Review. It will suffice simply to mention such useful applications as froth-flotation, fire-fighting foams, and foamed rubber on the one hand, and the inconvenience of foams on boilers, rivers, fermentation tanks, and engine oils on the other. The literature contains innumerable papers about foams and several monographs[1a] and reviews[1b] on the subject have appeared in recent years.

A broad survey of this literature suggests several reasons for the confusion of ideas which has prevailed for so long. One is the implicit assumption which many workers have made that there exists one simple explanation for all types of foam under all conditions. But it is surely obvious that a dynamic foam is a complicated physicochemical system. As there is no well-defined physical property of "coefficient of foamability", different experimenters have studied a great variety of systems, including foams in bulk, either static or dynamic, single soap films, single bubbles, pairs of bubbles, bubbles under monolayers, etc., and it is hardly to be expected that one simple factor will explain all the observations.

Another source of confusion has been the multiplicity of isolated, *ad hoc*, experiments which have been carried out and the diversity of materials, often impure, which have been used. (Only quite recently has the great importance of impurities been realised.) Too often the experimenters have ignored the other evidence and unjustifiably generalised their conclusions, with the result that the literature appears to contain several mutually exclusive theories of foaming, each of which explains one group of observations but not the others. A more logical attitude to the data is to suppose that the quantitative properties of foams depend on a number of distinct factors, the relative importance of which varies according to the system chosen for study.

* Carnegie Institute of Technology, Pittsburgh, U.S.A.

¹ (a) J. J. Bikerman, " Foams: Theory and Industrial Applications ", Reinhold, New York, 1953; E. Manegold, " Schaum ", Strassenbau, Heidelberg, 1953; (b) A. J. de Vries, " Foam Stability ", Rubber-Stichting, Delft, 1957; T. G. Jones, K. Durham, W. P. Evans, and M. Camp, " Proceedings of the Second International Congress on Surface Activity ", Butterworths, London, 1957, Vol. I, p. 225. See also ref. 32.

It is significant that a very wide range of foam "persistence" is observed with different materials—in fact, from fractions of a second to years— and there appear to be no sharp transitions from a feebly-foaming to a non-foaming or to a strongly-foaming solution, but only a continuous transition of properties. However, despite chemical differences, there must be certain basic mechanical characteristics common to all strongly-foaming liquids and differentiating them from non-foaming liquids. In this Review an attempt will be made to clarify the problem by first considering this mechanical aspect and then examining the several physico-chemical mechanisms that have been proposed to account for it.

It will be seen that only one important new theory of foam stability has emerged in recent years, namely, the electrical double-layer theory of the eminent Russian colloid scientist, B. V. Derjaguin.† Most of the other concepts still current (and largely valid) date back to the last century, but development of a precise theory of foaming has been excluded by lack of quantitative data to support the qualitative ideas. Consequently, it will be pertinent to include a brief account of certain recent experimental developments in fundamental surface chemistry. The outstanding problem in the theory of foams now seems to be to assess the relative importance of these various physicochemical factors in the different systems.

The occurrence and classification of foams

First, it is well established that pure liquids do not foam. Secondly, the foaming of solutions shows an obvious correlation with surface activity of the solutes. For example, foaming is not pronounced in mixtures of liquids of similar chemical type and surface tension (*e.g.*, benzene + carbon tetrachloride) or in aqueous solutions of highly hydrophilic solutes (*e.g.*, pure glycerol or sucrose): transient foams are obtained with solutes which lower the surface tension moderately (*e.g.*, the short-chain aliphatic alcohols and acids); and really persistent foams arise only with solutes which lower the surface tension strongly in dilute solution (*e.g.*, the soaps, synthetic detergents, proteins, etc.), *i.e.*, the highly surface-active substances.

The onset of foaming on addition of a solute is hard to define experimentally and in fact little reliable evidence can be found in the literature about such borderline systems. The older literature contains many examples of allegedly *feebly-foaming* solutions, but these reports are highly suspect because the experiments were not carried out with sufficiently pure materials. The quantity of a suitable impurity capable of producing a transient foam is often infinitesimal, particularly with water as the solvent, *e.g.*, 0·0002M-sodium cetyl sulphate, or 0·0005% of saponin. In addition, surface films of greasy materials were certainly not avoided by earlier

workers, and it is now known that monolayers containing as little as 10^{-10} mole per cm.^{2} are able to retard the escape of bubbles from water and retain them in the surface for several seconds. Reports of transient foams with solutions of purely inorganic salts such as sodium chloride are almost certainly erroneous; they have never been thoroughly checked‡ with scrupulously purified materials and are contrary to modern theoretical expectations.

Nevertheless, genuine foams are formed with such a great variety of chemical substances that the chemistry of the materials does not provide a useful basis for a classification. The physical chemistry of the surface layers of the solutions is what determines the widely different orders of "stability" observed with different solutions and a rational scheme of classifying foams can be developed on the basis of the order of "stability". The loose term "stability" does not, of course, imply complete thermodynamic stability since foam is a disperse system and contains a higher surface area, and hence higher surface free energy, than would the segregated gas and liquid; consequently, all foams tend to collapse spontaneously. Foams must therefore be either *unstable* structures (*i.e.*, transient, monotonously changing in the direction of decreasing surface area) or, at best, *metastable* (*i.e.*, remaining in a state of suspended transformation). Actually, both types exist and the distinction between them provides a fundamental criterion of classification in the light of which many existing observations begin to fall into place.

Unstable foams are well exemplified by dilute solutions of short-chain aliphatic alcohols or acids (*e.g.*, pentyl alcohol, butyric acid, *m*-cresol, aniline, etc.). These foams are constantly breaking down as the liquid drains from between the bubbles. Their life-time depends on the concentration of the solution, but at best it is only around 20 seconds for aqueous solutions of these non-ionic and weakly surface-active solutes. The life-time of the foams can be considerably extended by adding a second, non-foaming solute such as glycerol to increase the viscosity of the solution and so slow down the drainage of liquid from between the bubbles. In unstable foams there clearly exists a surface force opposing the coalescence of the bubbles; it is too weak to stop the process entirely, but it does retard it considerably.

Metastable foams are characterised by the fact that the process of drainage of liquid from between the bubbles eventually stops and the foam would persist indefinitely if it could be absolutely protected from disturbing influences. "Disturbing influences" include vibration, draughts, evaporation, radiant heat, temperature differences, dust, and other

‡ The Reviewers have, however, carried out enough tests to be sure that the results of Talmud and Suchowolskaja (1931) on the life-time of bubbles on solutions of inorganic salts quoted by Bikerman (ref. 1, p. 51) are worthless. For example, these authors claimed that bubbles on N-potassium sulphate persisted for 40 sec.; but the truth is that, if the salt is first heated to redness in a platinum crucible to destroy dust, etc., bubbles do not persist on the solution for more than 1 sec.

impurities. Dewar's classic experiments (1916) in which he succeeded in preserving horizontal soap films in closed tubes for up to three years are well known. After a certain drainage time such films remain unchanged in thickness. Their eventual breakdown must be ascribed to some uncontrolled disturbance. Such films must undoubtedly have a strong stabilising factor; in other words, in these systems there exists a potential energy barrier, dependent on the structure of the surface layers, which is powerful enough to counterbalance the forces making for collapse, and because of this barrier the system rests at metastable equilibrium.

The class of metastable foams includes, besides the classic soaps, the numerous modern synthetic detergents of the anionic and cationic types and presumably the many proteins and other naturally-occurring macromolecular substances such as the glucoside, saponin, all of which give very persistent foams. The conclusion that these substances (and probably the non-ionic detergents also) give true metastable foams is presumptive and based only on comparison of foam persistence with that of the soaps, but no one seems to have tried to preserve single films of these solutions for very long. A "black" gelatin film§ can certainly be kept for days.

Ordinary three-dimensional foams of these substances generally persist only for a matter of hours in a closed vessel if no special precautions are taken to eliminate all the sources of instability mentioned above. One reason why they do not last for, say, months is that gas slowly diffuses from the small bubbles into the large ones since the pressure and hence the thermodynamic activity of the gas within the bubbles is inversely proportional to the bubble radius. Diffusion of gas eventually leads to a mechanically unstable packing which suddenly rearranges. The shock is sufficient to rupture the extremely thin lamellae in a well-drained metastable foam. It is, of course, a characteristic property of any system in metastable equilibrium that a certain minimum energy is needed to displace it. Drained foams are stable against random molecular fluctuations, but direct experiment shows that the "resilience" of soap films to mechanical shocks decreases as they become thinner.

A clear difference can be seen in the structure of extreme examples of the two types of foam. In unstable foams the bubbles jostle together as an assembly of spheres, only slightly distorted by their neighbours, whereas metastable foams persist long enough for drainage to proceed extensively so that the films of liquid between the bubbles become planar or slightly curved lamellae of practically uniform thickness (Plate 1). Manegold[1] appropriately calls the two structures "kugelschaum" and "polyederschaum", *i.e.*, round-bubble foam and polyhedral foam. However, this observation does not provide a practical criterion for distinguishing fundamentally unstable from fundamentally metastable types since there is a continuous transition from one structure to the other. Some funda-

§ " Black " films are those which are too thin to show nterference colours, *i.e.*, less than about 2×10^{-5} cm.
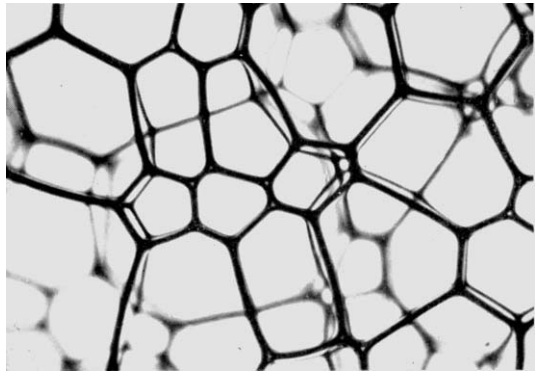
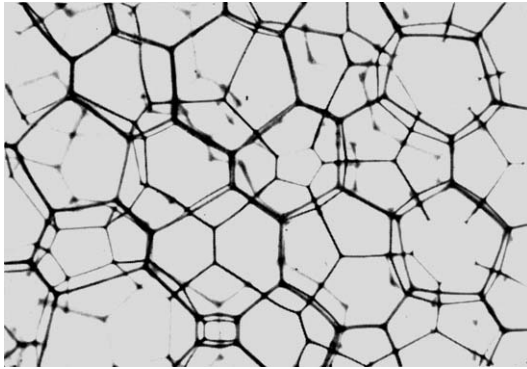*A.* A non-drained spherical-bubble "foam" ("kugelschaum") in a viscous liquid.
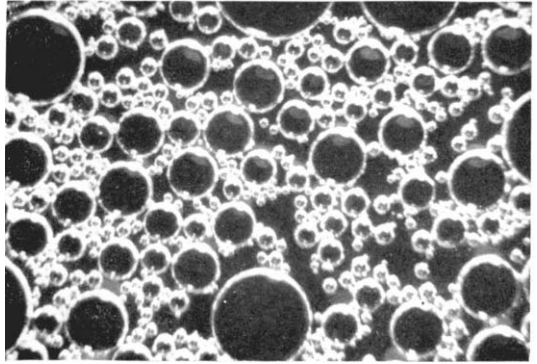
B. A partially-drained foam, showing distortion of bubbles.
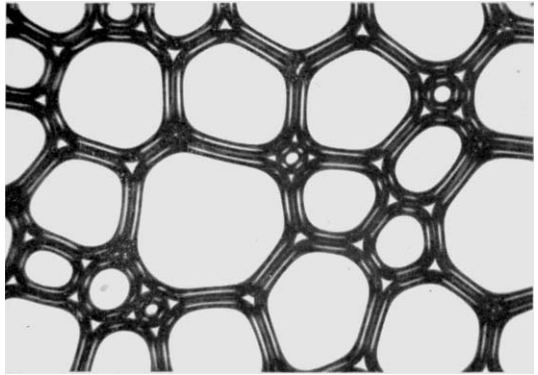
C. After further drainage: the lamellae and Plateau's borders continue to thin. (Note curvature of some bubble walls, owing to unequal internal pressures.)

PLATE 1. *Photomicrographs showing foam structure (contd. overleaf).*

D. A well-drained foam, showing polyhedral cells and very thin Plateau's borders. (In an ideal homo-disperse foam, the bubbles are pentagonal dodecahedra).

E. Solid foam. A section of expanded polystyrene, showing thin membranes and polyhedral cells. (Sample kindly provided by Mr. A. Cooper, Messrs. Expanded Plastics, Ltd.)

PLATE 1 (*contd.*).

mentally unstable foams persist long enough for considerable thinning to take place so that polyhedral faces (though still relatively thick) are formed between bubbles, but nevertheless the lamellae shortly break down. Conversely, a soap foam in its early stages is still practically of the round-bubble type and it remains so for a long time at the bottom because of drainage of liquid from the column above. The question of distinguishing between a spherical-bubble transient foam and a mere mechanical dispersion of bubbles in a liquid will be considered later.

In addition to the well-known foaming substances already mentioned, foaming occurs with certain mixed organic liquids (for example, lubricating oils, particularly those with "additives") and with certain molten glasses and metallurgical slags. As few of these non-aqueous systems have yet been thoroughly studied it can only be assumed that they do not differ fundamentally from aqueous ones. Many solid "foams" (*e.g.*, rubber latex foam) are simply spherical bubbles of gas trapped in a flexible solid, but some of the modern highly expanded "cellular polymers" (*e.g.*, expanded polystyrene) contain as little as 1 % of solid matter and are composed of polyhedral cells with very thin walls like a true, drained foam[2] (Plate 1*E*).

The key questions to be answered therefore reduce to two: (*a*) What is the *physical* factor, common to the great variety of chemically different foaming solutions, which distinguishes them from non-foaming solutions? (*b*) What mechanism (or mechanisms) can account for the metastability of certain liquid lamellae, such as soap films?

When these fundamental questions have been answered it should be possible to explain, at least descriptively, the reactions of different foams to physical and chemical treatments.

The mechanism of thinning and rupture of liquid lamellae

A fruitful approach to the first of the two fundamental problems is to consider the thinning of a liquid film, with and without the addition of a foaming agent, the simplest example being the rise of a single bubble to the surface of a liquid. The sequence of events, as revealed by high-speed cinematography[3] is shown in Fig. 1. On a clean water surface, a bubble bursts within a short time (roughly 10^{-2} sec. from the time its upperside touches the water surface) whereas as little as an incomplete monolayer of insoluble surface film is sufficient to prolong its life to seconds and on a dilute detergent solution single bubbles last for many minutes or even hours. The surface tension, which is a consequence of the intermolecular cohesion, is fully capable of counteracting the buoyancy of the bubble, as is proved by the fact that static equilibrium is achieved by a bubble

[2] A. Cooper, *Trans. Plastics Inst.*, 1958, **26**, 299.
[3] D. M. Newitt, N. Dombrowski, and F. Knelman, *Trans. Inst. Chem. Engrs.*, 1954, **32**, 244.

floating on the surface of a detergent solution (the surface tension of which is lower than that of pure water). The point at issue is therefore why the shell tears in some liquids and not in others.
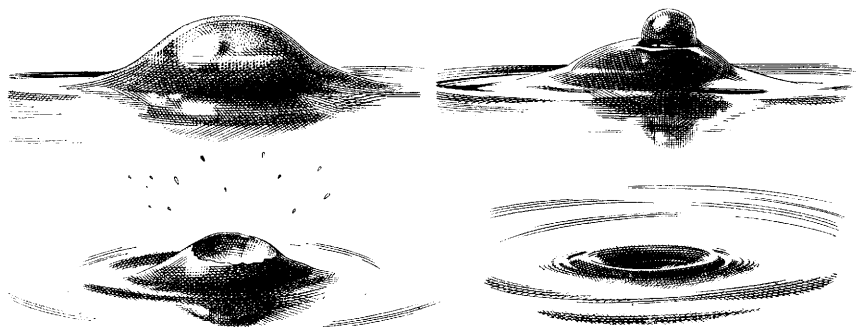

FIG. 1 *Stages in the bursting of a single bubble on the surface of water.* (Drawings by Arthur Smith from the high-speed photographs of Newitt, Dombrowski and Knelman[3].)

Nothing is known for certain about the actual mechanism of rupture of thin liquid films, except that it happens within microseconds. The hypothesis has sometimes been put forward that rupture under the surface tension occurs when a certain critical thickness is reached. Now pure, degassed water in bulk can withstand a static negative pressure of at least 270 atm. without cavitating.[4] The negative pressure tending to tear a static water lamina of thickness d (cm.) and surface tension γ (dyne cm.$^{-1}$) is $2\gamma/d$, and hence the critical thickness for rupture under its own surface tension could be estimated as of the order 10^{-6} cm. Lamellae of this order of thickness are, indeed, observed with carefully stretched "black" films from dilute soap solutions.

On the other hand, nothing approaching this degree of attenuation can be observed with pure liquids such as water, for, if attempts are made to form very thin lamellae of water, the sheets disintegrate within microseconds at a stage when their average thickness is still in the range 10^{-3}—10^{-4} cm. Experiments of this kind were carried out by Dombrowski and Fraser[5] in which expanding sheets of liquid issuing from a slit orifice were photographed by a flash method. However, in these experiments the cause of rupture of the laminae was not simply the gradual thinning of the sheet as it expanded radially from the orifice, but the growth of transverse waves which subjected the sheet to rapid local thinning[6]. It is perhaps significant that cavitation occurs in water containing dissolved air at a negative pressure of only 1 atm. in an acoustical field.[4] Thus, a liquid under tension breaks by nucleation of gas bubbles if the stress is applied

[4] L. J. Briggs, *J. Appl. Phys.*, 1950, **21**, 721.
[5] N. Dombrowski and R. P. Fraser, *Phil. Trans.*, 1954, **247**, *A*, 101.
[6] N. Dombrowski, personal communication.

so rapidly that the supersaturated gas cannot diffuse out. It seems reasonable to conclude that an expanding bubble of water probably tears by nucleation of dissolved gas or vapour at a thickness of the order of 10^{-4}—10^{-5} cm. and that waves of microscopic amplitude probably play a part in causing rapid local thinning to this extent.

The *slow* thinning of horizontal liquid films between two gas bubbles was investigated by Derjaguin and his co-workers.[7] These experiments are so important at the present stage of development of the theory of foams that they deserve closer examination. The apparatus used is shown in Fig. 2. The two small bubbles are formed on the cups *a* and *b*, and as they are in direct communication *via* the tube *c*, the gas pressure within the bubbles is equal and the small lamina separating them is planar over an area of about 1 mm.². There is therefore no difference of hydrostatic pressure across the gas–liquid boundary (as there is at a curved surface) and a little consideration shows that the easily measured pressure difference Δh (see Fig. 2) is equal to the pressure forcing the liquid from between bubbles (which Derjaguin calls the "disjoining pressure").
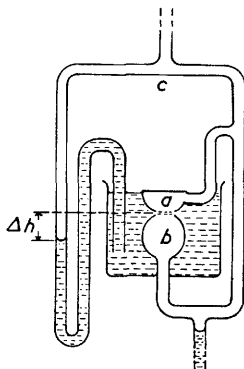

FIG. 2   *Principle of the experiments of Derjaguin and Titijevskaya[7] (diagrammatic) for determining the " disjoining pressure " between two bubbles.*

The more elaborate part of the apparatus, not shown, is an optical arrangement for determining the thickness, *d*, of the horizontal lamella of liquid. This is obtained from a precise measurement of the intensity of monochromatic light reflected from it, the apparatus consisting of a microscope with microphotometer attachment. By adjusting the head of liquid in the connecting tubes, one can gradually force the bubbles together and simultaneously measure the thickness of the lamella and the hydrostatic pressure acting on it.

The qualitative results obtained with this apparatus were described by Derjaguin as follows: "As might be expected, the observation of films of

[7] B. V. Derjaguin and A. S. Titijevskaya, " Proceedings of the Second International Congress on Surface Activity ", Butterworths, London, 1957, Vol. I, p. 210.

pure water is impossible. Even with the most careful approach of the lower bubble to the upper (with the aid of a micromanipulator), the break occurred imperceptibly rapidly at the first instant of contact between the bubbles without any detectable flattening. However, a high degree of purity is needed to obtain this result. The bubble holders must be of silica, as with glass holders . . . after a waiting period of about 1 minute the life-time of the film is of the order of 1—2 seconds.

"In presence of surface monolayers of organic compounds, the picture changes. The effect of alcohols of the aliphatic series dissolved in water was first studied. At the first instant of compression of the bubbles a film of apparently uniform thickness is formed, but this gradually and steadily becomes thinner, generally remains uniform, and bursts after becoming almost black. The thinning process is well reproducible as regards duration and evidently occurs according to a definite law as a function of time. The initial thickness of the film is about 0.1μ. The life-time of the film falls with increase of pressure, P.

"We then studied the effect of fatty acids. The addition of 0.2 mole/litre of acetic acid to water gave films which became thinner and broke after 16 seconds. . . . A solution of 0.00025M-octanoic acid gave a film of constant thickness (0.11μ at $P = 560$ dyne/cm.²) . . . Thus, soluble fatty acids differ sharply from soluble alcohols in their capacity to form films of a thickness which is quite stable with time; apparently, this property is due to the formation of a soap." (The quantitative results obtained by Derjaguin for the film thickness in different solutions will be considered later.)

These experiments point clearly to the property which distinguishes foaming from non-foaming liquids. It is simply the ability to *resist excessive localised thinning* of a membrane of liquid, while a controlled general thinning proceeds. Under these conditions a thin lamella of fluid can be formed, though, when formed, the lamella may subsequently prove to be either transient or persistent. To show such special rheological properties, the fluid must possess a special form of *elasticity* such that any applied stresses which tend towards local thinning are rapidly opposed and counterbalanced by restoring forces generated during the initial displacements of the material. The restoring force of what may be called "film-elasticity" must increase with displacement, like that in a stretched rubber membrane, though it may not necessarily follow Hooke's law; in other words, the thinner the film becomes, the greater becomes its tension. Pure liquids are completely lacking in the property of elasticity because their surface tension is independent of extension.

By analogy with other types of elasticity, Gibbs defined surface elasticity, E, as the stress divided by the strain per unit area. The tension in a lamella is 2γ dynes/cm., and therefore if an extension of the area (A) by an amount dA causes a rise of surface tension of $d\gamma$, $E = 2A \, (d\gamma/dA) = 2 \, (d\gamma/d \ln A)$. It is easy to demonstrate experimentally the increase of tension with

extension in a soap film by means of the Dupré frame apparatus; if the film is rapidly extended at one end, coloured bands further along the film will move outwards in the same direction, showing that a gradient of tension has been established. Similarly, Gibbs pointed out that the tension near the top of a vertical soap film must be greater than that at the bottom because of the weight of the film. But it is not easy to measure the changes of tension with extension and thus determine the modulus of surface elasticity.

Numerous tests of the effect of thickness on the surface tension of soap films have been made and are reviewed by Bikerman,[1a] but these are static experiments in which the film is allowed to thin by draining. No detectable change of surface tension ($< 1 \%$) then occurs, even down to about 100 Å. Derjaguin's experiments are a much more sensitive method of detecting any static effect of thickness on properties. The results (Fig. 3) show that a
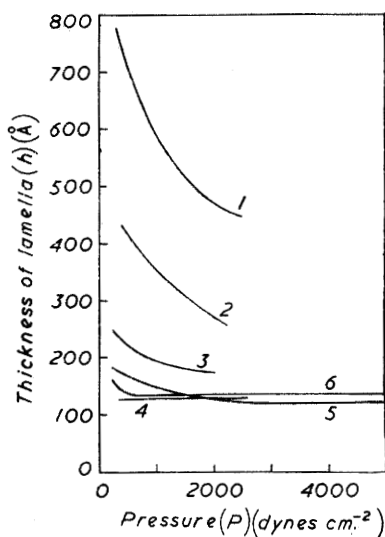

FIG. 3   *Typical results of the experiments of Derjaguin and Titijevskaya, showing the thickness of lamella (h) as a function of " disjoining pressure " (P), for various solutions.* 1—4. 10^{-3}N-Sodium oleate containing sodium chloride at 1, 10^{-4}N; 2, 10^{-3}N; 3, 10^{-2}N; 4, 10^{-1}N; 5, 0.3% " Aerosol OT " $+ 10^{-2}$N-sodium chloride. 6, 0.1% Saponin $+ 10^{-1}$N-sodium chloride.

detectable force opposing thinning can be measured with certain very thin films but the effect on surface tension would be negligibly small. Furthermore, since such forces were absent from foamable solutions of alcohols they cannot account for the dynamic elasticity of thick films of such solutions.

It is not established at what lamina thickness the restoring forces of film elasticity first come into action. Soap films when first formed are too

thick to show interference colours (say 5×10^{-4} cm.) so presumably elasticity develops already by this stage. From a thermodynamic point of view, the important quantity for protection of a lamina against shocks is the work of displacement, measured by the restoring force multiplied by the distance of displacement, since it is this work which must be capable of cancelling the kinetic energy of possible disturbances before a dangerously thin spot (100—500 Å) is produced. A good shock-absorbing film must therefore be capable of providing a large work of displacement before rupture. Of major importance for securing resilience is the capacity of a film to suffer large *displacements* without rupturing. This is the distinction between an "elastic" material and a brittle one, not the value of the modulus of elasticity. Hence, for example, a thick soap film is more robust than a thin one of the same surface tension because it contains more reserve material, permitting considerable extension before the critical thinness is reached.
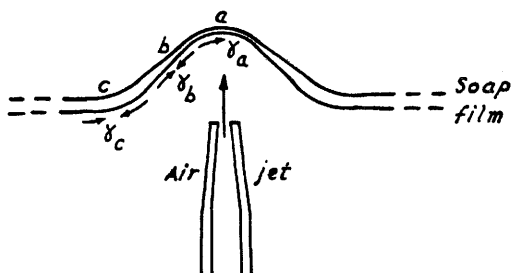

FIG. 4   *Local thinning of a soap film under the impact of a gas jet (see text).*

The mechanism of film-elasticity can be illustrated by an imaginary experiment in which a narrow jet of air suddenly impinges on a soap film; Fig. 4 shows schematically the state of affairs a moment after the jet is switched on and while the bubble is still expanding. It is thinnest at the apex, a, and thickest at c. If the theory is correct that the local, instantaneous surface tension, γ, of a foamable liquid increases with extension, then $\gamma_a > \gamma_b > \gamma_c$. Such a gradient of surface tension along the line abc means that each section of liquid will be subject to a net force towards a and the liquid will therefore stream outwards and feed the expanding bubble from its edges. The same mechanism on a microscopic scale would explain the resistance of thin soap films to rupture under the action of disturbances; a thinning spot automatically draws liquid from its perimeter.

It follows, therefore, that any liquid that shows a positive value of the coefficient $d\gamma/dA$ under dynamic conditions should be capable of foaming to some extent. The great variations in foaming power of different solutions are then probably related to differences in the effective value of $d\gamma/dA$ under practical conditions, although, in addition, the relative rates

of the local displacement, the flow of the liquid and the relaxation of surface tension changes are certainly important (see later).

There are at least four distinct theories, proposed by Gibbs (1878), Marangoni (1865), Plateau (1873), and Derjaguin (1953) to account for film elasticity. They are complementary rather than mutually exclusive mechanisms and are probably all operative, though generally in different circumstances. These theories will be considered in turn in the subsequent sections. Before leaving the general aspects of film elasticity, however, it is of interest to note the formal analogy between this property and the rheological property of "spinnability", the capacity shown by certain melts and solutions of long-chain substances to be drawn out into fibres. In that case the "flow elasticity" (or "elastico-viscosity") of the liquid is due to orientation and extension of the molecular chains along the direction of flow. In film formation the liquid is flowing in two dimensions. It is therefore conceivable that a spinnable fluid would also show film elasticity and thus form a polyhedral foam. Expanded polystyrene seems to provide an example of this class, in which elastico-viscosity gives the necessary protection against local over-thinning of the expanding lamellae. If this suggestion is correct, such systems form an entirely distinct class of foams and have only the film elasticity in common with the usual foaming liquids.

Gibbs's surface-elasticity theory

Gibbs showed that if a thin film of a solution of a surface-active solute (*e.g.*, a soap) is subjected to local stretching, the surface tension of that part increases because the solute is positively absorbed in the surface and any increase of surface area therefore leads to a decrease of average solute concentration within the film and hence a rise of equilibrium surface tension. This effect is clearly significant only with rather thin films where the amount of solute absorbed on the surface is comparable with that contained within the film. Further, it is more important with strongly absorbed solutes than weakly absorbed ones, and for solutions of low rather than high concentration.

The operation of Gibbs elasticity in thin stretched films can scarcely be doubted but there seems to have been no direct test of the theory. Its magnitude can be calculated from thermodynamical formulae as shown from the following example. Fig. 5(*a*) shows the equilibrium surface tension of solutions of pure sodium dodecyl sulphate as a function of concentration.[8] The quantity of the solute which is adsorbed per cm.[2] of surface (Γ) can be calculated from these results by use of the well-known Gibbs adsorption equation which, for a 1:1 electrolyte, takes the form

$$\Gamma = \frac{1}{2RT} \frac{d\gamma}{d \ln cf_{\pm}}$$

(where c is the concentration of sodium dodecyl sulphate in moles per

[8] E. J. Clayfield and J. B. Matthews, ref. 7, p. 172.

cm.[3] and $f_{\pm}$ is a mean ion. activity coefficient for the detergent at this concentration). Results so calculated[8] show that the adsorbed monolayer behaves substantially as a two-dimensional vapour. Suppose now that a quantity of the solution is expanded without change of overall composition into the form of a sheet of thickness d cm. A quantity $(2\Gamma'/d)$ moles of solute would be removed from each cm.[3] of the liquid to bring it to adsorption equilibrium with the remaining solution which would have the reduced bulk concentration of $(c-2\Gamma'/d)$ moles/cm.[3]. By simultaneous solution of the conditions of conservation of solute with the Gibbs equation one obtains the required values for the surface tension of solutions
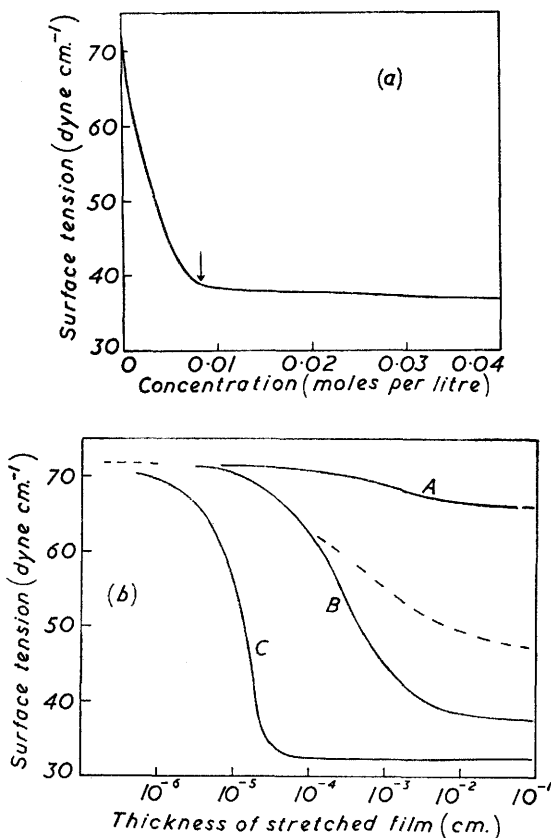
FIG. 5   *Surface activity and the Gibbs effect in solutions of sodium dodecyl sulphate.* (*a*) Surface tension as a function of concentration.[8] The arrow represents the critical micelle concentration (0·008M).   (*b*) Calculated surface tension of *A*, 0·001M; *B*, 0·01M-(static); and *C*, 0·1M-solutions when extended as thin sheets of thickness *d* cm. [calc. from results in (*a*)].   (The surface elasticities are proportional to the slopes of these graphs.)   The broken line is the hypothetical curve for the conditions of *B* with $t = 0·01$ sec.

expanded to various thicknesses. Some approximate results so calculated for sodium dodecyl sulphate at three initial concentrations are shown in Fig. 5(b).

Consider, for example, the 0·01M-solution. If the film were stretched to 10^{-3} cm. thickness, the surface tension would rise from *ca.* 38 to *ca.* 45 dynes cm.$^{-1}$. This solution would have a well-developed elasticity over the range 10^{-2}—10^{-5} mm. thickness. The restoring forces developed are less than 0·01% of the strength of those in a sheet of rubber of the same thickness, but they are nevertheless significant in relation to the mass of liquid—for example, 10^3—10^4 dynes per g. of film, which would impart accelerations of 10^3—10^4 cm. sec.$^{-2}$ to the portions of liquid. Although these calculations are crude it is evident that the Gibbs effect provides a plausible source of surface elasticity.

Fig. 5(b) shows also that the range of film thickness over which the Gibbs effect operates depends on the concentration of the solution. With 0·001M-sodium dodecyl sulphate the total reduction of γ is too small to provide a strong elasticity at any thickness. With 0·1M-sodium dodecyl sulphate negligible elasticity develops above 10^{-4} cm., partly because of the small dependence of γ on c above the critical micelle concentration and partly because of the large reserves of solute present in the solution. Around 10^{-5} cm. elasticity is strong, and it persists down to 10^{-6} cm., so that this solution should provide very thin lamellae. Nothing is to be gained by attempting to press the Gibbs elasticity theory further because it is based on a static model.

Marangoni's surface-elasticity theory

Gibbs was well aware that the surface elasticity of solutions under dynamic conditions would be *greater* than that calculated by the above, static, theory, since a rapidly expanding surface would have a tension greater and a compressed surface less than the equilibrium value. This had been pointed out a decade earlier by Marangoni. But at that time no quantitative data were available about the difference between dynamic and equilibrium tensions. Since then a good deal of evidence has been forthcoming. The oldest observation is apparently that of Dupré (1869) who deduced from the height of rise of fine vertical jets of solution that the apparent tension of a soap solution was similar to that of water in these experiments. Then came the introduction by Rayleigh (1879) of the oscillating-jet method of determining dynamic surface tension. Rayleigh showed in 1890 that a freshly formed surface of a soap solution has a surface tension close to that of pure water for periods less than 0·01 second provided that the concentration is low ($< 0·04$M). Sutherland[9] has given a useful review of work on dynamic tensions.

[9] K. L. Sutherland, (a) *Rev. Pure Appl. Chem. (Australia)*, 1951, **1**, 35; (b) *Austral. J. Sci. Res.*, 1952, *A*, **5**, 683. See also R. Defay, and J. Hommelen, *Ind. chim. belge*, 1958, **23**, 597.

With *extremely* dilute solutions of highly surface-active agents such as soaps, the surface tension falls steadily during many seconds, corresponding to the time required for the molecules to travel, chiefly by diffusion, to the surface from the interior of the solution. These changes can be followed easily by the Wilhelmy plate method or the drop-shape method. In addition, many authors have recorded much slower ageing effects, extending to minutes, hours, or even days; but these are now known to be due to traces of impurities (for example, multivalent metallic ions) from the glass or water or trace amounts of agents which form condensed mixed films with the principal detergent. Slow ageing with detergents largely disappears on purification.[10] Similarly, the slow ageing of surfaces of protein solutions, saponin, etc., is partly due to the slowness of diffusion from dilute solutions and partly to irreversible "denaturation" processes which some of these substances suffer when adsorbed at an interface.

In any case, such very slow surface changes have little relevance to the problem of foams, as surface elasticity must come into operation in very short periods of time if it is to protect a thinning lamella against breakage. The precise time-scale concerned in the development of foam lamellae seems never to have received attention; but judging by the times concerned in various experiments involving expanding films and jets of water one can guess that the order of magnitude of time during which surface elasticity must come into effect is around 10^{-3} to 10^{-2} second.

Unfortunately, it is not possible at present to carry out calculations of the magnitude of the Marangoni effect in, say, an expanding lamella of solution because of the complicated hydrodynamics. Even the interpretation of experimental studies of dynamic surface tension is obscured by convection effects in the liquid, as it seems to be impossible to devise an experiment in which a fresh surface is formed without some disturbance. Sutherland,[9b] for example, has shown that the oscillating-jet method gives different results for the ageing of solutions according to the size of jet used. The rate at which solute arrives at a surface depends on (*a*) the rate of diffusion to the surface, (*b*) convective transport, (*c*) possible electrical repulsion in the case of a surface-active electrolyte, and (*d*) possible steric hindrance to the entrance of large molecules into an already fairly crowded monolayer. Factors (*c*) and (*d*) are probably unimportant for the foaming of fairly dilute solutions, being relevant chiefly to the slow processes. Most of the work with the oscillating-jet technique has been concerned with the soluble aliphatic alcohols and for these the "half-time" for the adsorption is of the order of 0·01 sec. (*e.g.*, for 0·005M-heptyl alcohol). Sutherland[9a] and others have shown that adsorption occurs somewhat more rapidly than can be accounted for by diffusion alone; the discrepancy is greater the narrower the jet. There seems no doubt that transport to the surface is partly convective and this is true even for the plate method.[9b] Consequently a precise treatment of the Marangoni effect is impossible without

[10] See, *e.g.*, A. P. Brady, *J. Phys. Chem.*, 1949, **53**, 56.

more knowledge of the flow which occurs when bubbles are pressed together.

Data on dynamic tensions in solutions of ionized detergents in the time interval 10^{-3}—10^{-2} sec. are sparse. Much discussion has centred round the slower processes commonly observed with slightly impure materials and hydrolyzable soaps and at one time the opinion was widely held that electrical or steric energy barriers must exist to account for these slow rates. But, in fact, with well purified detergents,[10,11] using the oscillating-jet method, Burcik[12] has obtained results for sodium laurate, sodium dodecyl sulphate, and sodium oleate which show rates of change of surface tension closely similar to those found for non-ionic agents, *i.e.*, the order of magnitude of 0·01 sec. for about half the final change of tension to occur with a solution about 0·001M. Fig. 6 shows a rough comparison of ionic and non-ionic materials. Burcik's results with detergents (*e.g.*, curve *C* in Fig. 6) seem to show a fast process followed by a much slower
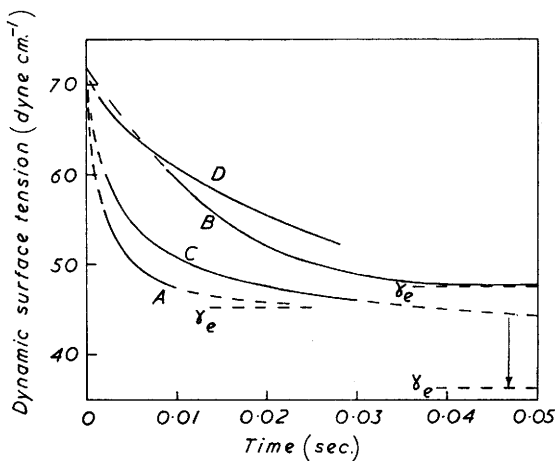

FIG. 6 *Typical examples of the surface tension of solutions under dynamic conditions: surface tension as a function of surface age.*
A, 0·005M-Heptyl alcohol, with jet diam. 0·035 cm.:[9] *B*, as *A*, ditto, with jet diam. 0·1 cm. (Addison): *C*, 0·005M-sodium dodecyl sulphate:[12] *D*, 0·1% "Tween" (polyoxyethylene sorbitan monolaurate.[12] γ_e marks equilibrium tension; for curve *D* it is 36·7 dynes cm.$^{-1}$).

one. The rate is naturally faster the more concentrated the solution and *vice versa*.[12] Thus with 10^{-4}M-"Aerosol OT" (sodium dioctyl sulphosuccinate) Padday[13] found ageing in the range 0·1—1 sec. Burcik showed that addition of sodium chloride increases the rate of adsorption of ionic detergents but not of a non-ionic detergent, "Tween 20" (polyoxyethylene

[11] G. D. Miles and L. Shedlovsky, *J. Phys. Chem.*, 1944, **48**, 57.
[12] E. J. Burcik, *J. Colloid Sci.*, 1950, **5**, 421; 1953, **8**, 520.
[13] J. F. Padday, ref. 7, p. 1.

sorbitan monolaurate). These observations might be supposed to support the theory that diffusion in the former is opposed by an electrical potential and this might also account for the slower process mentioned. However, there is also the common-ion effect of sodium chloride on the thermodynamic activity of these surface-active electrolytes. The added salt enhances the lowering of surface tension as well as its rate of change, and a knowledge of the effect of sodium chloride on the diffusion coefficient of the detergent ion would also be needed before the effect on the rate of adsorption could be fully analysed.

The above evidence being reviewed, it is clear, despite the incomplete experimental data, that solutions of all types of surface-active solute show marked time effects in the range 10^{-3}—10^{-2} sec., which provides strong support for Marangoni's theory. The Marangoni effect operates on any expanding surface carrying an adsorbed layer, irrespective of the thickness of underlying liquid, and provides a restoring force tending to protect a film against local thinning. It operates even on a deep pool of solution, opposing local displacements and therefore damping capillary waves. This effect of soluble detergents (as distinct from insoluble oil films) was recorded by Brown.[14] It is easily demonstrated by adding a drop of detergent solution to a trough of water on which ripples are being produced by a vibrating plate: a film "flashes" across the trough at the rate of about 30 cm./sec. and greatly reduces the amplitude and extent of the ripples until, in a few seconds, the surface film dissolves in the substrate. Such damping of capillary waves may well be an auxiliary factor in foam stabilisation by the Marangoni effect, operating even on thick films and therefore promoting smooth thinning of the liquid between bubbles.

The surface transport theory

The rapid movement of liquid monolayers in a surface-tension gradient has been suggested by Ewers and Sutherland[15] as the basis of a theory of foam stability and foam-breaking. Their paper cites many interesting points in favour of the idea. A spreading monolayer, dragging with it significant quantities of the underlying solution, would rapidly repair thinning spots in a lamella. This phenomenon of "surface transport" is well established. It was first studied by Schulman and Teorell[16] who showed that a monolayer of oleic acid, spreading at the rate of 5 cm./sec., carried with it a water layer effectively 0·03 mm. thick. The work was continued later by Crisp[17] and recently Blank and La Mer[18] found, by using a dye solution, that liquid can even be raised against gravity by the surface transport of a film of, e.g., cyclohexyl myristate from one trough to another

[14] R. C. Brown, *Proc. Phys. Soc.*, 1936, **48**, 312.

[15] W. E. Ewers and K. L. Sutherland, *Austral. J. Sci. Res.*, 1952, *A*, **5**, 697; cf. L. T. Shearer and W. W. Akers, *J. Phys. Chem.*, 1958, **62**, 1264.

[16] J. H. Schulman and T. Teorell, *Trans. Faraday Soc.*, 1938, **34**, 1337.

[17] D. J. Crisp, *Trans. Faraday Soc.*, 1946, **42**, 619.

[18] M. Blank and V. K. La Mer, ref. 7, p. 102.

at a slightly higher level. The effect does not imply any special structure or viscosity of the film or adjoining water layer and it arises simply from the viscous drag of the expanding monolayer on the water and can readily be calculated.[19]

The surface transport theory can be regarded as an extension of the Marangoni effect, from which it differs only in specifying a mechanism for the movement of solution once a gradient of tension has been established. The classical explanation of the "healing" effect of a local increase of tension focused attention on the restoring forces opposing displacement or thinning, *i.e.*, the modulus of elasticity. The surface transport theory advances the idea a stage further by pointing out that a gradient of surface tension (such as that envisaged in Fig. 4) will first lead to a *surface flow* and this, in turn, will move adjoining liquid layers. The speed of response will therefore be much greater than if the force were thought of as operating over the whole of the liquid lamella. It would be interesting to determine the velocity at which a sudden relaxation of tension is transmitted by a monolayer. Here again, absence of quantitative data prevents further development and testing of a qualitatively attractive theory.

Surface viscosity and bulk viscosity

Plateau was responsible for the concept of surface viscosity which, indeed, he believed to be the chief factor in the development of foam lamellae. His own experimental measurements were inadequate, but his main contentions have since been fully proved; thus, weakly-foaming alcohol solutions have little surface viscosity, soaps a moderate amount, and some solutions of proteins, saponin, etc., a high surface viscosity even amounting to surface rigidity.

In recent years several different instruments have been developed for measuring surface viscosity. This property is the exact 2-dimensional analogue of ordinary viscosity and its coefficient is analogously defined and determined. The coefficient of surface viscosity, η_s is the force (in dynes) which must be applied per cm. of length along a surface to maintain a gradient of surface flow (between two parallel lines 1 cm. apart) of 1 cm. sec.$^{-1}$. The unit is the surface poise, having dimensions MT^{-1}. The simplest instrument for detecting surface viscosity is the oscillating-disc viscometer, the logarithmic decrement of its torsional oscillations being determined with and without the surface film. However, as the damping due to the water alone is relatively large with a disc, it is better to use a ring or the edge of a cylinder. For insoluble monolayers the canal method is well founded on theory[19] and is accepted as a standard. For monolayers showing non-Newtonian flow, a sensitive rotating-disc surface viscometer has recently been described by de Bernard[20] (who also gives references to other instruments).

[19] W. D. Harkins and J. G. Kirkwood, *J. Chem. Phys.*, 1938, 6. 53, 298.
[20] L. de Bernard, ref. 7, p. 1.

The limitations of these viscometers for use with soluble films were pointed out by Ewers and Sack[21] who devised a very sensitive instrument, based on the canal model, but in which the underlying liquid was caused to flow and the rate of movement of the surface was determined by floating graphite particles. The theory was worked out so that the instrument gives absolute results for the surface monolayer. A similar idea was used in a new viscometer described recently by Davies,[22] but here a circular canal was used and the liquid was moved by rotation on a turntable. This instrument was calibrated by means of insoluble monolayers of well-established surface viscosity. There is some confusion in the literature as to whether "surface viscosity" includes the drag due to the water below the monolayer. Ewers and Sack[21] and Davies[22] point out that in the canal methods this drag is allowed for theoretically, so the true viscosity due to the monolayer alone is obtained, whereas with the oscillating visco-meter[23] a much higher apparent viscosity (η_s') is recorded because no correction is (or can be) made.

Some typical results for surface viscosity are collected in Table 1 which also illustrates the two kinds of "surface viscosity". It is seen that very dilute solutions of alcohols or soaps have a scarcely detectable surface viscosity, even with solutions which foam appreciably. On addition of a small amount of lauryl alcohol to sodium dodecyl sulphate the foaming increases greatly[23] and the surface viscosity increases ten-fold. Proteins give yet higher viscosities, and on concentrated solutions the films behave as non-Newtonian pastes with a definite yield point and structural viscosity.[24] According to Trapeznikov[25] the surface layers of saponin solutions show visco-elasticity.

The great problem to be settled is what contribution surface viscosity makes to foam stabilization. Some authors have claimed for it a major importance while others have considered it of quite secondary value. It is generally conceded that (a) there is a strong correlation between foam stability and surface viscosity, but (b) actual rigidity (as in solid, "brittle" monolayers such as that of stearate monolayers on hard water) is detri-mental to foam life. This is probably because of the very short range of areas over which such films show elasticity. A viscous, fluid, but elastic layer is required.

The most important function of enhanced viscosity is to retard *drainage* of liquid from between the bubbles. This factor has been studied particu-larly by Miles, Ross, and Shedlovsky[26] who determined the rate of thinning of vertical soap lamellae by observing their interference colours and proved that this corresponded closely with the rate of drainage of liquid from

[21] W. E. Ewers and R. A. Sack, *Austral. J. Chem.*, 1954, **7**, 40.
[22] J. T. Davies, ref. 7, p. 220.
[23] A. G. Brown, W. C. Thuman, and J. W. McBain, *J. Colloid Sci.*, 1953, **8**, 491.
[24] *E.g.*, S. C. Ellis, A. F. Lanham, and K. G. A. Pankhurst, *J. Sci. Instr.*, 1955, **32**, 70.
[25] A. A. Trapeznikov, ref. 7, p. 242.
[26] G. D. Miles, J. Ross, and L. Shedlovsky, *J. Phys. Chem.*, 1945, **49**, 93.

columns of the foam, a process which can be distinguished from actual breakdown of foam, at least with the more stable systems. It is clear that partial or complete immobilisation of the outer surfaces of lamellae will have an increasingly strong effect in retarding flow the closer the sides come together. Consequently, high surface viscosity favours the development of lamellae, since the liquid can drain much more rapidly from thick regions than from thin. Miles *et al.* also discovered interesting phase

TABLE 1. *Typical values for true* (η_s) *and apparent* (η_s') *surface viscosities* (*g. sec.*$^{-1}$) *of monolayers.*

	η_s (*absolute*)	η_s (*apparent*)	*Ref.*
Pure water..	0	0	
Stearic acid monolayer at 20 Å²/ molecule	6×10^{-4}	—	22
Octadecyl alcohol monolayer at 20 Å²/molecule	4×10^{-3}	—	22
n-Octanol ($3 \cdot 8 \times 10^{-4}$M) ..	0	—	21
,, ($7 \cdot 7 \times 10^{-4}$M) ..	1×10^{-4}	—	21
Sodium dodecyl sulphate ($3 \cdot 5 \times 10^{-3}$M)	3×10^{-4}	2×10^{-3}	21, 23
Sodium dodecyl sulphate ($3 \cdot 5 \times 10^{-3}$M)+lauryl alcohol ..	30×10^{-4}	40×10^{-3}	21, 23
Sodium laurate ($0 \cdot 1 \%$, pH 10) ..	1×10^{-4}	1×10^{-3}	21, 23
Serum albumin monolayer (3 dynes/cm.)*	—	2×10^{-2}	24
Serum albumin monolayer (6 dynes/cm.)†	—	(1×10^{-1})	24
Serum albumin monolayer (10 dynes/cm.)†	—	(3×10^{-1})	24

* Newtonian fluid.   † Plastic, with structural viscosity decreasing with increasing rate of shear.

changes occurring at definite temperatures with certain mixed films: above the transition temperature the films were fast-draining and below it slow-draining, corresponding closely to low and high viscosities and, conversely, high and low foam persistence[27]. These experiments seem clear enough, but Burcik and Newman[28] also showed that those mixtures, such as sodium dodecyl sulphate + lauryl alcohol, which give viscous mixed films also show a slower rate of adsorption (despite a lower final tension)

[27] M. B. Epstein, J. Ross, and C. W. Jakob, *J. Colloid Sci.*, 1954, **9**, 50.
[28] E. J. Burcik and R. C. Newman, *J. Colloid Sci.*, 1954, **9**, 498.

than pure sodium dodecyl sulphate (probably because of formation of complexes in solution). Hence, the Marangoni effect would be stronger with them. This is another example of the great difficulty of "separating the variables" in research on foaming.

However, there is no real doubt in this case, since viscosity of any sort retards coalescence of bubbles. Even in the absence of added surface-active solutes, a spherical-bubble "foam" can be built up by injecting a sufficiently dense stream of small enough bubbles into any viscous liquid. The rate of coalescence of the bubbles decreases with decreasing bubble size and with increasing viscosity. The reviewers have confirmed that the rate of collapse of a column of this kind of "foam" depends predominantly on the rate of drainage. This was proved by comparing the rates with "pure" liquids such as glycerol, medicinal paraffin, and silicone fluids. By using multiple jets, a foam of bubbles of uniform and controlled size was built up and its rate of collapse was then determined at several temperatures. The rate of collapse was the same with different liquids if they were compared at temperatures such that their viscosities were equal. Their surface tensions were different, showing that surface properties are largely irrelevant in these "foams".

Further, in agreement with Brady and Ross,[29] the rate of collapse of such foams was found to be proportional to the viscosity; in paraffin foams the activation energy for collapse was the same as that for viscous flow. The addition of a detergent to glycerol, of course, enhances the persistence of the foam. Thus the presence of a foam-stabilising factor can be detected even in viscous liquids such as certain molten silicates by comparison with a pure liquid of similar viscosity.

It can be concluded, therefore, that true foaming requires film elasticity, but the lifetime of a practical foam can be greatly extended by viscosity, either of the liquid as a whole or of the surface layer only. The question whether a liquid with surface viscosity only would foam is hypothetical since surface viscosity does not occur without surface activity.

Electrical double-layer repulsion (Derjaguin)

The preceding paragraphs have been chiefly concerned with the formation of foam lamellae under dynamic conditions. Turning now to the forces responsible for metastability of lamellae under static conditions, we think it worth quoting the words of Gibbs himself: "That which is most difficult to account for in the formation of black spots is the arrest of the process by which the film grows thinner. It seems most natural to account for this, if possible, by passive resistance to motion due to a very viscous or gelatinous condition of the film."

The "viscous or gelatinous condition" is essentially Plateau's theory and it undoubtedly operates in certain systems (as already mentioned).

[29] A. P. Brady and S. Ross, *J. Amer. Chem. Soc.*, 1944, **66**, 1348.

However, the recent work has shown that many metastable foams do *not* possess great surface viscosity; the adsorbed layer on pure detergent solutions is gaseous or a mobile liquid. Derjaguin has put forward the theory that the very thin metastable "black" films owe their stability chiefly to electrical repulsions between the ionic double-layers which are formed by adsorption on two sides of the lamellae. The existence of such layers not only follows from the well-established orientation of surface-active electrolytes but is also indicated by high electrical conductivity of thin soap lamellae and the migration of liquid through them under the influence of an electric current, both of which are doubtless due to electro-osmosis.

Derjaguin and Titievskaya's experiments on solutions of undecanoic acid in water, dilute hydrochloric acid, and potassium chloride showed that the equilibrium thickness of these thin films is very much dependent on the electrolyte. In 10^{-3}N-hydrochloric acid the lamellae thin slowly but eventually collapse (as do those of solutions of short-chain alcohols). But on water and 10^{-3}N-potassium chloride an equilibrium thickness is reached, depending on the concentration of the carboxylic acid and inversely on the applied hydrostatic pressure. With increase of concentration of potassium chloride the equilibrium thickness is reduced and collapse sets in at 10^{-2}N. Sodium oleate films could be studied in up to 0·1N-sodium chloride, with results shown in Fig. 3.

Such results point clearly to electrical double-layer effects. (A similar pointer is given by older work on the effect of salts in reducing the stability of foams of soaps but these observations were not certain proof because of the effect of salts on the adsorption of the soaps.) The results were shown by Derjaguin and Titievskaya to be interpretable in terms of the Gouy–Chapman theory of flat double-layers. The theory of the interaction (repulsion) of double-layers was worked out previously by Derjaguin and his co-workers in their important contributions to the theory of stability of colloids.[7] Essentially equivalent treatments have been developed independently by Verwey and Overbeek, whose well-known monograph[30] provides the only full account of this theory in English.

The relationships between h, the distance between the double layers, and P, the repulsive force per cm.[2], is simple only if the double-layer potential is small (*e.g.*, <25 mv) when it takes the form (Derjaguin, 1937),

$$P = \frac{2\pi\sigma^2}{D\sinh^2(\kappa h/2)} = \frac{D\psi_0^2}{8\pi\kappa^2\cosh^2(\kappa h/2)}.$$

where σ is the surface charge density of ions, ψ_0 the surface potential, D the dielectric constant of the medium in the double-layers and κ the reciprocal thickness of the double-layer (as employed also in the Debye–Hückel theory). For high potentials more elaborate formulae are available.

[30] E. J. W. Verwey and J. T. G. Overbeek, " Theory of the Stability of Lyophobic Colloids ", Elsevier, New York, 1948.

With the more dilute salt solutions the results with sodium oleate were well represented by assuming a nominal charge density in the double layers of 160 e.s.u. per cm.^{2}, which corresponds to only a fraction of the actual soap molecules in the monolayer. Full agreement with the results for sodium oleate could be obtained only by introducing certain additional assumptions, amounting to a rigid "hydration" layer 60 Å thick because the film thickness at the higher salt concentrations did not decrease as much as the double-layer theory would predict.

If correct, these results are obviously of great importance. They have not yet been confirmed by any other experimenters for films between gas bubbles, but van den Tempel[31] has recently carried out very similar experiments with oil droplets in 0·01M-sodium dodecyl sulphate + sodium chloride and has come to very similar conclusions, namely, that the lamella thickness does not decrease with increasing salt concentration in the region of 0·01M as much as the double-layer theory predicts. He concludes that "the experimental results suggest the presence of still other repulsive forces which become operative at distances between the interfaces smaller than about 125 Å". It seems, therefore, that the old ideas of "steric hindrance" or "solvation sheaths" may yet have to be revived in colloid chemistry for very close approach to surfaces, though more evidence is needed. The evidence for electrical double-layer repulsions in the range of h between 100 and 800 Å is strong.

The influence of other factors on foam persistence

(*a*) **Concentration of Solute.**—Many studies have been reported of the effect of the concentration of the active solute on foaming, and it is generally found that foaming passes through a maximum at intermediate concentrations. This conclusion applies to soluble alcohols, fatty acids, soaps, synthetic detergents and even insoluble monolayers. It is observed with very different methods of test such as those depending on the life-time of single bubbles, the dynamic foam height, or the persistence of a column of foam, although these different tests do not always give the "optimum" at exactly the same concentration. Numerous examples are quoted in Bikerman's monograph.[1] With sparingly soluble agents such as octyl alcohol and pine oil, the foaming drops to zero when the solution becomes saturated.

It is generally considered that these observations support the surface elasticity theory of foaming. Too dilute a solution gives a small range of surface tension for the effects to range over, while too concentrated a solution carries too large a reserve of solute which can diffuse to the surface and restore a low tension during the thinning of a lamella. (This applies theoretically to both the Gibbs effect and the Marangoni effect and careful experiments with a favourable system might help to decide which of these is the more important.)

[31] M. van den Tempel, *J. Colloid Sci.*, 1958, **13**, 125.

Dervichian[32] emphasises another aspect of this phenomenon: the compressibility of the adsorbed monolayer. By reference to experiments on the persistence of bubbles under insoluble monolayers, he concludes that the adsorption layer should be neither a "gaseous" monolayer nor a rigid condensed film; for optimum stabilisation it should be a compressible two-dimensional fluid such as the "liquid expanded" type of monolayer. Such a film can respond appropriately with moderate changes of tension to both expansion and compression of area, whereas a gaseous monolayer needs large changes of area to give comparable changes of tension and a "solid" monolayer crumples on compression and has only a short range of expansion over which a changing tension is operative.

(b) **Temperature.**—Change of temperature has a relatively greater effect on viscosity than it has on surface tension Nevertheless, local differences of temperature cause gradients of surface tension and Plateau observed that a warmed spot in a soap film becomes thinner. (The fact that it does not continue to thin to breaking point under the greater tension of the surrounding, cooler, foam shows again that the tension increases with decrease of film thickness.) In a column of bubbles in a viscous pure liquid quite small differences of temperature cause rapid collapse. Particularly with solvents like glycerol, oils, and silicate slags, rise of temperature has a marked effect in increasing the rate of drainage of foams, owing to reduction of the bulk viscosity. An interesting special effect has been studied by Epstein and his co-workers[27,33] who found that certain mixed adsorbed films such as sodium dodecyl sulphate+lauryl alcohol have a sharp transition temperature, below which they are two-dimensional solids (and hence give slow-draining foams) and above which they are fluid (and hence give fast-draining foams).

(c) **Mixed Surface-active Agents.**—Numerous examples have been recorded of the co-sorption of two or more agents, often producing stronger foaming than either separately. Other examples besides sodium dodecyl sulphate+lauryl alcohol (or lauric acid) are alkyl arylsulphonate detergent +NN-bis-2-hydroxyethyl-lauramide and sodium stearate+stearic acid (resulting from hydrolysis or the action of carbon dioxide). Some of these mixed films are "plastic", i.e., solid films.[34]

Such surface "complexes" seem to depend on the convenient packing of the non-ionic agents between the chains of the ionic ones, thus causing condensation of a monolayer which would otherwise be "expanded" on account of electrostatic repulsion between the head groups. Crystalline intermolecular adducts containing two sulphate molecules to one alcohol molecule can be prepared in some of these systems.

Certain pairs of surface-active agents are mutually antagonistic as

[32] D. G. Dervichian, *Bull. Soc. chim. France*, 1956, 15.
[33] M. B. Epstein, A. Wilson, C. W. Jakob, L. E. Couroy, and J. Ross, *J. Phys. Chem.*, 1954, **58**, 860; cf. G. D. Miles, J. Ross, and L. Shedlovsky, *J. Amer. Oil Chemists' Soc.*, 1950, **27**, 268.
[34] E. J. Burcik and R. C. Newman, *J. Colloid Sci.*, 1957, **12**, 10.

regards foaming.[35] For example, stearates spoil the performance of oleates for soap-bubbles and small amounts of sodium palmitate or stearate in the presence of calcium salt render the foam of sodium *p*-dodecylbenzene-sulphonate unstable.[36] These all appear to be cases where the two agents are structurally unable to pack well together. Perhaps the adsorbed layers separate into two phases; heterogeneity of structure would account for the ready disintegration of lamellae since local tensions would be unbalanced under dynamic conditions. These effects are fairly specific: sodium laurate or oleate renders the foam of sodium *p*-dodecylbenzenesulphonate *more* stable, as does calcium palmitate with straight-chain detergents.

(*d*) **Miscellaneous Factors.**—Amongst other factors not mentioned that may affect foaming are: (i) evaporation (which can increase or decrease film life in different circumstances), (ii) solid particles (which can also act in either manner, according to their size and wetting characteristics), and (iii) the layer structure in "black" soap films. It is well known that "black" films become thinner in discrete steps which are supposed to correspond to double layers of soap molecules oriented end-to-end, but there seems to have been no progress on this problem in recent years. It is not clear whether the films showing these effects are concentrated enough to consist throughout of oriented liquid crystalline phases or whether multi-molecular surface micelles are formed by adsorption. Little reliable information is available about adsorption at the surface of detergent solutions above the critical micelle concentration. (According to Clayfield and Matthews,[8] phase transitions occur with sodium dodecyl sulphate.) The surface chemistry of protein solutions is even more nebulous at present, and foaming of highly purified proteins seems not to have been investigated. Schütz[35] and others have demonstrated how bile acids and various other substances of biological origin can be fractionated by foaming.

Antifoam agents

The technical literature contains many examples of substances which are claimed to prevent foaming or destroy foams; but different agents are recommended for different foams and they seem to have been developed largely empirically. It is evident from the above discussion of the mechanism of foaming that the most important action of a completely effective antifoam agent must be to eliminate surface elasticity, *i.e.*, to produce a surface which has substantially constant tension when subjected to expansion. To do this, it must displace any foam stabiliser that may be present. Hence, it must have a low intrinsic tension in the pure state and be able to *spread* when applied to the foam lamella. Further, it must be present in sufficient quantity to maintain a high surface concentration even under dynamic conditions: low solubility is therefore an advantage. Many antifoams are insoluble "spreading" oils.

[35] F. Schütz, *Trans. Faraday Soc.*, 1946, **42**, 437.
[36] H. Peper, *J. Colloid Sci.*, 1958, **13**, 199.

There are two types of antifoam agent, namely, *foam-breakers* and *foam-inhibitors*. As is well known, many foams can be made to collapse rapidly by applying a few drops of ether, octyl alcohol, etc. Even the vapour is sufficient. Ether has an exceptionally low surface tension and therefore if local regions of a foam lamella receive ether, these regions are rapidly pulled out by the higher tension of the surrounding parts of the film. Now ether is not itself a foaming agent, being only weakly surface-active. Hence, the ether-bearing region tears on being stretched by tension from the sides. Ether has no foam-breaking action if the foaming solution is previously saturated with ether. Evidently, further reduction of tension cannot then occur on adding more ether, but an original powerful foaming agent present can still be responsible for a positive $d\gamma/dA$ factor during stretching.

Certain moderately surface-active substances, which alone in dilute solution are actually foamers, though feeble ones (*e.g.*, pentyl alcohol), act as foam-breakers when applied neat to soap foams and also to foams formed from their own dilute solutions. But pentyl alcohol in excess will neither foam itself nor permit a dilute soap solution to do so; it is then a foam inhibitor. This is a case of swamping the surface with a high concentration of rapidly-diffusing molecules so that any transient rise of tension on stretching is rapidly annulled. (Pentyl alcohol will also inhibit foams on *concentrated* detergent solutions, but large quantities are needed, probably because of solubilisation of the pentyl alcohol in the detergent micelles.)

Generally more effective and more versatile than any soluble antifoam agents are materials such as the silicone fluids which are insoluble in water and have tensions as low as 20 dynes cm.$^{-1}$. As foam-inhibitors, they are applied as emulsions or with a diluent, so that every bubble rising to the surface of the liquid catches enough silicone to spread over the air–liquid interface as a "duplex" film or a monolayer with excess of liquid as lenses.[37] Quantities of the order of 1—60 p.p.m. are said to prevent foaming of adhesives, dyebaths, fermentation vats, sewage tanks, tars, and even engine oils. (Pure hydrocarbons do not form true foams, but compounded engine lubricants do.) Polyfluorinated hydrocarbons also seem likely to be useful antifoams for oils as they have even lower surface tensions, around 10 dynes cm.$^{-1}$.

All the above examples of antifoam action seem to depend on eliminating the surface elasticity, but S. Ross and his co-workers[38] have shown that while some commercial antifoam agents (*e.g.*, 1,3-dimethylbutyl alcohol) do indeed cause the rupture of thick lamellae before drainage can occur, others (*e.g.*, tributyl phosphate) act by promoting drainage in the early

---

[37] L. T. Shearer and W. W. Akers, *J. Phys. Chem.*, 1958, **62**, 1264.
[38] (*a*) S. Ross, *J. Phys. Colloid Chem.*, 1950, **54**, 429; (*b*) S. Ross and G. J. Young, *Ind. Eng. Chem.*, 1951, **43**, 2520; (*c*) S. Ross and M. J. Cutillas *J. Phys. Chem.*, 1955, **59**, 863; (*d*) S. Ross and J. N. Butler, *ibid.*, 1956, **60**, 1255; (*d*) S. Ross and R. M. Haak, *ibid.*, 1958, **62**, 1260.

stages of a foam's history and so shorten its life-time. Viscous surface layers were found to assume practically the viscosity of water on the addition of traces of tributyl phosphate, and formation of a plastic surface film on (impure?) sodium lauryl sulphate solutions was inhibited. Similarly, 0·001 % of an unspecified substance used to prevent foaming of egg white during dehydration completely inhibited formation of the normal gelatinous film on 0·01 % egg albumin solution,[38d] and dimethyl-silicone, used as a foam inhibitor for hydrocarbons, has been reported to remove surface viscosity of oils.[39] Silicones may therefore have a dual action. In a recent paper Ross and Haak[38e] have shown by the oscillating jet technique that foam inhibitors may also accelerate the rate of change of dynamic surface tension with time, thus possibly reducing the Marangoni effect in another way. Finally, to complete the series, one may note that the other possible contribution to stability, the electrical double-layer repulsion, may be reduced by increase of the concentration of indifferent electrolytes.

Summary of conclusions

On the basis of the evidence which has been reviewed here, the following main conclusions have been drawn:

1. Dispersion of gases in liquids can be divided into two classes: (A) Spherical-bubble dispersions, the life-time of which depends only on viscous drainage of liquid from between the bubbles; (B) True foams, having longer life-times than comparable dispersions of class A.

2. True foams can be sub-divided into (a) transient, (b) metastable, and (c) solidified foams.

Transient foams form polyhedral bubbles with relatively thick walls which subsequently become thin and collapse at some definite stage (typical example: pine oil foam). Metastable foams form lamellae which become thin to the "black" state and then remain at a definite thickness until they are destroyed by external disturbances (typical example: soap film). Solidified foams may start as either type (a) or (b) in the liquid state, but the lamellae are preserved by solidification (e.g., of a plastic) or possibly by drying.

3. The *primary requirement* for true foaming is a rheological property which may be called "film-elasticity". If a lamella has this property, a restoring force is produced under the action of any stress that tends to pull out the film to greater areas; conversely, a reduction of area induces a restoring force opposing thickening. This elastic property may have a relaxation time as short as a fraction of a second (in transient foams) or it may be much longer and may include also a static component, as in metastable foams.

4. Exceptionally, the restoring force of film elasticity can arise from

[39] D. W. Criddle and A. L. Meader, *J. Appl. Phys.*, 1955, **26**, 840.

flow elasticity ("elastico-viscosity") of the homogeneous fluid itself (as in the production of expanded polystyrene); but in the majority of foamable solutions it is due to *surface elasticity*, caused by depletion of an adsorption layer. Both the Gibbs effect and the Marangoni effect should contribute to surface elasticity, but their relative importance is not clearly established. A contributory effect of surface elasticity is probably the damping of ripples which would otherwise cause dangerous local thinning.

5.   The mechanism by which liquid is drawn towards a thinning spot in a lamella is probably surface flow of the adsorption layer under the action of a gradient of surface pressure and the simultaneous dragging along of some of the underlying liquid. This is the "surface transport" theory of Ewers and Sutherland.

6.   The life-time of foams is increased by increase of fluid viscosity or by the presence of surface viscosity or surface plasticity; these factors prolong the drainage process and perhaps also help to reduce ripples.

7.   Metastable, "black" soap films depend for their persistence largely on an electrical double-layer repulsion between the opposite sides of the lamellae. In addition, there is some evidence to suggest that steric effects, possibly due to hydration layers, may also be involved with extremely thin films.

8.   Foaming may be either enhanced or reduced by addition of a second surface-active agent according to whether or not the two agents can pack together in a mixed adsorption layer. The most effective anti-foam agents are spreading, insoluble liquids.

9.   Several other subsidiary factors affect the properties of foams in practice, *e.g.*, diffusion of gas from small to large bubbles, the presence of any suspended particles, evaporation, temperature gradients, or slow ageing processes.

It is evident that further progress in the understanding of foaming requires more precise, quantitative studies of the flow process and of the magnitude of the restoring forces in thinning lamellae.