EFFECT OF SURFACE MOBILITY ON THE DYNAMIC BEHAVIOR OF THIN LIQUID FILMS

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Abstract - The role of various factors such as bulk and surface diffusion
of surfactant, surface viscosity and, in the case of emulsions, liquid
flow in the drops, in determining the surface mobility and hence the
velocity of thinning and the lifetime of liquid films are discussed. It
is shown that: 1) With relatively low concentrations of surfactant sol-
uble in the continuous phase surface diffusion plays a dominant role.
2) The velocity of thinning of a plane-parallel emulsion film depends
strongly on the partition coefficient of the surfactant: when the sur-
factant is soluble in the drops rather than in the continuous phase it
has no influence on the surface mobility and the velocity of film thinning
is very high. 3) With surfactant free emulsions or with surfactant sol-
uble in the drops the dissipation of energy in the film is negligible so
that the velocity of thinning does not depend on film viscosity. 4) Sur-
face mobility increases the amplitude of capillary waves in the films but
does not affect the critical thickness of rupture when surface diffusion
and surface viscosity can be neglected; the allowance for the latter two
effects may help in explaining the experimentally observed dependence of
the critical thickness of rupture upon surfactant concentration.

## 1. INTRODUCTION

When two particles (bubbles or drops) in a fluid dispersion (foam or emulsion) come close
enough to each other they will coalesce if the surfactant concentration is low. With higher
surfactant concentration coalescence might not take place. Then the particles may either
rebound or form a (relatively) stable aggregate. Similar phenomena are observed during the
flotation process or when a fluid particle approaches an infinite interface (solid or
fluid). Although the final result of the collision depends on many factors, the hydro-
dynamic behavior of the intervening thin film plays a crucial role in determining the time
scale of the overall process (Ref. 1). Although some authors (Ref. 2) were able to treat
the collision as occurring at arbitrary impact angles, the detailed hydrodynamic descrip-
tion of the thin liquid film seems at present possible only in the case of central colli-
sion, i.e. when the system of two colliding particles has axial symmetry. If such is the
case, the overall process can be conveniently split into five stages: 1) movement of two
single (non-interacting) particles; 2) hydrodynamic interaction of the slightly deformed
particles; 3) strong deformation leading to a bell-shaped formation, called a "dimple";
4) the dimple's gradual disappearance or being pushed out (Ref. 3) and the formation of an
almost plane-parallel film; 5) if the long-range repulsive forces are smaller than the
attractive forces, the appearance at a critical thickness, $h_{cr}$, of a hole or a thinner spot
which subsequently expands until coalescence or equilibrium attachment takes place. If one
defines the life-time of the particles, $\tilde{t}$, as the time elapsed between the moment when they
were set into motion and the moment when coalescence or equilibrium attachment was reached,
it will equal the sum of the durations of all five stages.

The duration of stages 1 and 2 can be estimated using the available theories (Refs. 4 & 5).
Stage 2 starts at $h/R_c \approx 10$ (see Brenner in Ref. 5) and finishes at $h \approx F/2\pi\sigma_0$ (see
Ref. 6), where h is the distance between the interfaces, measured along the line of cen-
ters, $R_c$ is the particle radius, $\sigma_0$ is the interfacial tension and $F$ is the driving (e.g.
buoyancy) force. For particles moved by buoyancy force, $F = (4/3)\pi R_c^3 g\Delta\rho$, (g - gravity
acceleration, $\Delta\rho$ - density difference between the particles and the continuous phase) with
$R_c = 0.1$ cm, $\Delta\rho = 1$ g cm$^{-3}$, and reasonable values of the other parameters, the duration of
either stages 1 or 2 is of the order of $10^{-2}$ sec. Stage 5 can be quite prolonged, in par-

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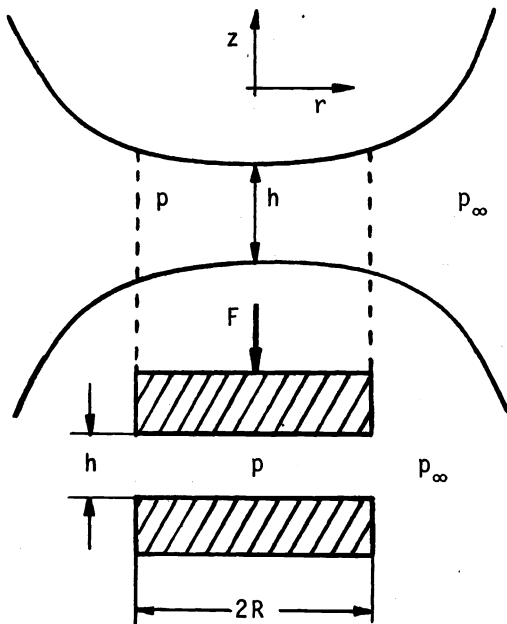*On temporary leave from the University of Sofia.

ticular when leading to equilibrium attachment. However, when the surfactant concentration is low and coalescence takes place (this is precisely the case when surface mobility is very important), this stage lasts for less than $10^{-3}$ sec (Ref. 7). Therefore the overall life-time, which is usually of the order of 1 sec or larger will be determined by stages 3 and/or 4 (see below).

If the disjoining pressure can be neglected, the film shape will be determined by the parameter $\epsilon = F/2\pi\sigma_0 R_c = R_c^2 g\Delta\rho/3\sigma_0$ (Refs. 6 & 8) and the distance $h$ between the surfaces. We were able to show (Ref. 8) that with

$$\epsilon \ll 1 \quad \text{and} \quad h \ll F/2\pi\sigma_0 = \epsilon R_c \tag{1}$$

the film thins without forming a dimple. The central part of the film in this case is almost plane-parallel (Fig. 1) and thins with a velocity only slightly different from the velocity of thinning of a plane-parallel film with suitably defined radius. This conclusion does not depend on whether there has been a dimple in the film before it reached thicknesses meeting the requirement (1). Experimental investigations (Refs. 3, 9 & 10) point out that

Fig. 1. Sketch of a thin film formed between two identical small bubbles or drops. Also shown in the lower part of the figure is a film formed between two parallel discs.



this situation is usually realized with $R_c < 0.1$ cm and $h < 2 \times 10^{-5}$ cm which is in agreement with the criteria (1). The possibility for a film to form and thin without a dimple when the particles are small was also recognized by Buevich and Lipkina as well as by Jones and Wilson (Ref. 11).

The theoretical treatment of the dimple formation and evolution with time (stage 3) is a very difficult problem. Since the early work of Deryaguin and Kussakov (Ref. 11), many efforts have been made to resolve it (Refs. 6 & 11). Since the authors of the various papers use different approximations and assumptions (sometimes difficult to justify, let alone to assess properly), it is impossible to compare those theories quantitatively both among themselves and with the experiment, the latter by itself being often irreproducible. Their common features are that: (i) they all predict, at least qualitatively, the experimentally observed shape of the film, and (ii) they all fail to predict that under certain circumstances the dimple is pushed out of the film which becomes (almost) plane-parallel. It is my belief that this failure is caused by the neglect of inertia effects in the above theories. It prevents them from finding that at a certain thickness the dimple becomes dynamically unstable (Refs. 3 & 10). At what thickness this instability will occur must depend mainly on the particle size, density difference $\Delta\rho$, interfacial tension and surface mobility, the latter being determined by the ratio of the viscosities of the particles and the continuous phase and surfactant properties and concentration.

With small particles this usually happens before the thinnest parts of the film rupture (Refs. 7, 9 & 10). An approximate estimate based on the data in Ref. 10 shows that in this case stage 4 is at least 10 times longer than stage 3; in other words, the overall rate of the process is determined by stage 4 (see also Ref. 12).

All the above arguments, both experimental and theoretical, suggest that life-times calculated using the model of the plane-parallel film can be reasonably close to the real life-times of dispersions containing small particles (droplets or bubbles). Since this model enables one to account in quite detailed form for the role of the surfactant and the liquid flow in the droplets, it thus leads to some interesting predictions for the behavior of dispersions of small particles with low stability, when the surface mobility is of major importance. The numerous effects related to the surfactant and/or liquid flow in the droplets depend strongly on the surfactant concentration and are usually coupled so that even in the rare cases when reliable experimental data are available it is difficult or even impossible to say which one plays the major role.

The purpose of this paper is to give a brief and simplified account of some conclusions we have reached in our studies of the hydrodynamics of thin liquid films with mobile interfaces. I will not attempt any detailed discussion of the mathematical derivations and approximations used (this discussion is available in the papers cited) nor will I give an extensive literature review. Instead, I will try to emphasize only some effects which I believe to be of importance. These effects all stem from the "thinness" of the film; in other words, they are not observed in macroscopic systems built up of the same fluids. This makes them hard to detect experimentally without the appropriate theoretical treatment.

The paper is organized as follows: In the next section a brief formulation of the problem and the methods of solution are given. The results for the velocity of thinning are discussed in Sections 3 (foam films) and 4 (emulsion films). The wetting films (one flat interface solid/liquid) are considered together with the analogous films with two fluid interfaces: in Section 3 when the film is formed between a bubble and a solid surface and in Section 4 when the particle is a droplet. The rupture and the life-time of thin films are the subject of Section 5. Since all these results are derived using the model of the plane-parallel film, it seems pertinent to include some results for films with deformable interfaces which bear out the applicability of this model. This is done in Section 6.

## 2. FORMULATION OF THE PROBLEM

When two fluid particles come close to each other under the action of an external driving force, F, the increased hydrodynamic resistance at the narrowest part of the gap results in a flattening of the particles' surfaces (Fig. 1). As the film thins further, the major part of the energy is dissipated in this flattened region whose radius, R, is of the order of

$$R = (FR_c/2\pi\sigma_o)^{1/2} \qquad (2)$$

(Refs. 6 & 8). For small values of the particles' radii, $R_c$, and thickness at the center (at $r = 0$), h, when conditions (1) are fulfilled, $h^2/R^2 = \varepsilon \ll 1$ so that the fluid flow in the gap is governed by the equations of lubrication theory:

a) $\partial p/\partial r = \mu(\partial^2 v_r/\partial z^2)$

b) $\partial p/\partial z = 0$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)$

c) $(1/r) \, \partial(rv_r)/\partial r + \partial v_z/\partial z = 0$

d) $F = 2\pi \int_0^R (p-p_\infty)r \, dr$

where p is pressure ($p_\infty$ is the pressure in the quiescent liquid), $v_r$ and $v_z$ are fluid velocity components along the coordinates r and z, and $\mu$ is dynamic viscosity. Eq. (3d) expresses the balance of forces acting upon the particles' surface and leads to the sought for dependence of the velocity of thinning on the driving force. These equations were solved by Reynolds (Ref. 13) for a film formed between two rigid discs (see lower part of Fig. 1), with the result:

$$V_{Re} = 2h^3F/3\pi\mu R^4 \qquad (4)$$

When the two discs are very close to each other ($h < 10^{-5}$ cm) one must account for the interaction between them. Then it is advisable to introduce the driving pressure (Refs. 9 & 14):

$$\Delta P = F/\pi R^2 - \Pi \; ; \qquad V_{Re} = 2h^3\Delta P/3\mu R^2 \qquad (5)$$

where $\Pi$ is the film disjoining pressure (for definition of $\Pi$ see Ref. 15), i.e. the force per unit area, stemming from the interaction of the two surfaces. $\Pi$ is positive when it tries to repel the two surfaces.

There are two major assumptions involved in deriving (4): the surfaces are considered as being 1) non-deformable and 2) tangentially immobile ($v_r$ is assumed zero at the discs' surfaces). Neither of them is true under all circumstances for films with fluid/fluid interfaces, nor do these films have well defined radii. It can be shown, however, (Ref. 8) that if an effective radius R is introduced via Eq. (2) and if the conditions (1) are met, the functionality of the velocity of thinning of a deformable film with tangentially immobile surfaces, $V_{immob.} = -dh/dt$, upon F, h, $\mu$ and R is the same as in Eq. (4) and only the numerical coefficient is slightly different (1/2 rather than 2/3). Moreover, it was also shown (Ref. 16) that the effect of the surface mobility on the velocity of thinning in many cases is the same for foam films with deformable and non-deformable surfaces. That is why almost all results hereafter for the velocities of thinning and wave motion are written as ratios of their values for tangentially mobile and immobile film surfaces. These ratios represent mobility factors which presumably depend slightly or not at all on the film shape. Since the mobility factors can be much greater than unity, this effect is by far more important than the deformation of the surfaces.

Surface mobility affects the velocities of thinning and wave motion through the boundary conditions at the film surface (Ref. 4). As the liquid flows out of the film toward its thicker parts it carries away the surfactant ("convective flux" in Fig. 2), thus perturbing its equilibrium distribution. This generates reverse fluxes, tending to restore the equilibrium distribution: surface diffusive flux and bulk fluxes from the film and the drop (in the case of an emulsion film). The bulk flux can be conveniently split into two subsequent steps: 1) diffusion flux $j_{diff} = \mp D\partial c/\partial z$ up to a layer adjacent to the film surface

BULK FLUX

SURFACE DIFFUSION FLUX
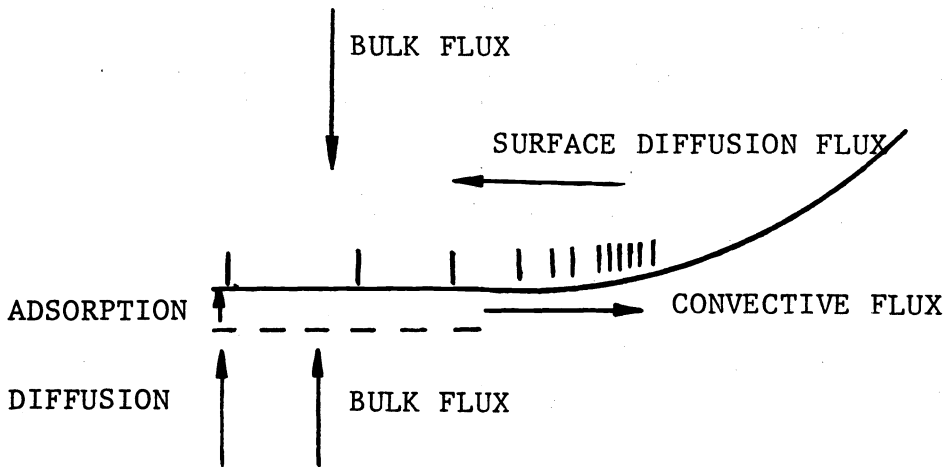
ADSORPTION

CONVECTIVE FLUX

DIFFUSION          BULK FLUX

Fig. 2.  Surfactant mass balance at the film surface.

and 2) adsorption flux $j_{ads} = \alpha(\Gamma_o-\Gamma)$ from this layer onto the surface (for detailed micromechanical formulation of the above concept and Eq. (7) below, see Ref. 18), where c and $\Gamma$ are the surfactant bulk and surface concentrations, D – bulk diffusion coefficient, $\alpha$ – adsorption rate constant, and the subscript "o" denotes equilibrium value. Which one of those two steps will determine the overall rate of the surfactant transfer will depend on the value of the parameter (Refs. 14 & 16):

$$K = \frac{\alpha R(\partial\Gamma_o/\partial c_o)}{D}\frac{R}{h} = \frac{\alpha_o\Gamma_\infty}{a + c_o}\frac{R^2}{Dh} \tag{6}$$

where $\alpha_o$ is the concentration independent factor in the adsorption rate constant (Ref. 4, p. 415, and Ref. 14) and $\Gamma_\infty$ and a are the constants in Langmuir's adsorption isotherm: $\Gamma_o/\Gamma_\infty = c_o/(a + c_o)$; the second equation (6) is valid only for surfactants obeying Langmuir's adsorption model. With K >> 1 the process is diffusion-controlled and in the opposite case, adsorption controlled. Note that because of the factor R/h >> 1 in Eq. (6)

the surfactant transfer in the film is much more likely to be diffusion controlled than is
a similar process taking place at the interface between two bulk phases. In the most inter-
esting region of low surfactant concentrations, $c_o \ll a$, one has $K = \alpha_o \Gamma_\infty R^2 / aDh$. If
$\Gamma_\infty / a = 10^{-3}$ cm, $R = 10^{-2}$ cm, $D = 10^{-5}$ cm$^2$sec$^{-1}$ and $h = 10^{-5}$ cm, then $K = 10^3 \alpha_o$ so
that in most cases the surfactant transfer is diffusion controlled ($K \gg 1$). Adsorption
will be slow enough to be the rate-determining process only if $\alpha_o \ll 10^{-3}$ sec$^{-1}$ (see
Note a). In the opposite case, $c_o \gg a$, as the diffusion flux increases $K$ decreases
and adsorption has more chances to be the rate-determining process.

I will confine myself now only with the more probable mechanism of diffusion controlled sur-
factant transfer (although the other case has also been treated in Refs. 14, 16 & 19). In
this case local equilibrium between the surface and the adjacent liquid layer is assumed;
in other words, the surface concentration is calculated from the bulk concentration at the
film surface ($z = h/2$ for the upper surface) using the equilibrium adsorption isotherm.
The surfactant mass balance at the film surface reads

$$\frac{\Gamma_o}{r} \frac{\partial (r v_r)}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} \left( D_s r \frac{\partial \Gamma}{\partial r} \right) = -D \frac{\partial c}{\partial z} + D^d \frac{\partial c^d}{\partial z} \qquad (7)$$

where superscript "d" denotes quantities pertaining to the drop and $D_s$ is surface diffu-
sivity. In formulating (7) it was assumed that the perturbation of the surfactant distri-
bution is small, i.e. $(\Gamma_o - \Gamma)/\Gamma_o \ll 1$ (Ref. 4), which for a thinning film is tantamount to
$\mu V R^2 / h^2 \Gamma_o (\partial \sigma_o / \partial \Gamma_o) \ll 1$ (Ref. 14). The surfactant distribution is calculated from the
diffusion equation, by neglecting the convective mass transport in the film and assuming the
presence of a diffusion boundary layer in the drop (Ref. 20).

The second important boundary condition affected by the surface mobility is the surface
tangential stress balance (Fig. 3). The non-uniform surfactant distribution leads to sur-
face flow, which in turn gives rise to surface stresses. The difference in surface concen-
tration along the surface results in difference of the local values of the surface tension,
$\sigma$, which produces a surface force (equal per unit length to the gradient of the surface
tension) opposite to the liquid flow. On the other hand, during its motion, the surfactant
monolayer may undergo dilating and shearing deformations which also produce surface stresses.
The sum of the above surface stresses and the tangential bulk stress from the liquid in the
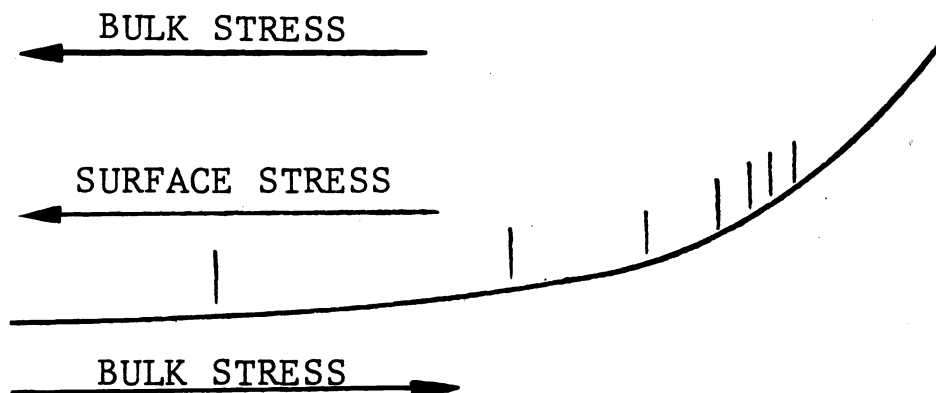


Fig. 3. Tangential stress balance at the film surface.

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drop must counterbalance the tangential bulk stress from the film liquid, which causes the surface flow. General formulation of the respective boundary condition can be found else-where (Ref. 21). In the framework of the model and approximations used here, the stress balance at the upper film surface is:

$$\mu \frac{\partial v_r}{\partial z} = \mu^d \frac{\partial v_r^d}{\partial z} + \frac{\partial \sigma}{\partial r} + \mu_s \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial (r v_r)}{\partial r} \right) \tag{8}$$

where the surface viscosity, $\mu_s$, for the present axisymmetric system is the sum of the dilatational and shear surface viscosities. If there were no surfactant diffusion, the liquid flow would initially stretch the surfactant monolayer until a steady distribution is established, at which the surface tension gradient is sufficiently large to stop the flow at the surface. Indeed, Eq. (7) with $D_s = D = D^b = 0$ leads to $v_r = 0$ at the surface. Because of the diffusion fluxes, however, this never happens; the stretching of the surfactant mono-layer is always smaller than required for immobility and the velocity of film thinning is consequently higher. This effect was pointed out in Ref. 7 (see also Ref. 43).

The last term in Eq. (8) complicates very much the solution because it involves the second derivative of $v_r$ and thus requires the formulation of one more boundary condition at the film perimeter. Two attempts to account for the influence of the surface viscosity on the film thinning have been published thus far (Refs. 22 & 23), but it is not yet clear to what extent the boundary conditions used there were realistic. More troublesome is the very mean-ing of the surface viscosity term. Surface viscosity, similar to surface excess, $\Gamma$, is formulated as an excess quantity (Ref. 24) and may therefore depend on the system's parame-ters, in the particular case of a thin film on its thickness (Ref. 25). If such is the case, the value of $\mu_s$ to be used in Eq. (8) may differ significantly from the value measured experimentally for the same surfactant at the interface between two bulk phases. Fortunately, the contribution of this term is usually small as far as film thinning is con-cerned: its ratio to the term on the left hand side of Eq. (8) is of the order of $\mu_s h / \mu R^2$ (for more precise estimate, see Ref. 20) and with $\mu = 10^{-2}$ g cm$^{-1}$sec$^{-1}$ it becomes sizable only at large surface viscosities, $\mu_s > 0.1$ s.p. That is why it may be of importance only for the wave motion, where the radial length scale (the wave length) is much shorter. In order to calculate the shear stress exerted on the surface by the liquid in the drop, one must also solve the respective set of Navier-Stokes equations (the method of solution is described in Ref. 26).

These are the main equations needed to solve the problem, which reflect the physical effects involved. Some additional effects related to the wave motion will be discussed in Section 5. More detailed mathematical formulation of the problem, including all equations and boundary conditions used, can be found in Refs. 27 & 28. I now proceed with the discussion of the results so derived.

### 3. FOAM FILMS

Because of the low viscosity of the gas in the bubble, in this case the term with $\mu^d$ in Eq. (8) can be dropped. Since the surfactant is soluble only in the continuous phase, the term with $c^d$ in Eq. (7) is also zero. Then

$$V/V_{Re} = 1 + 1/\varepsilon^f = 1 + b + h_s/h \tag{9}$$

where the quantities

$$b = - \frac{3\mu D}{\Gamma_o (\partial \sigma_o / \partial c_o)} \quad ; \qquad h_s = - \frac{6\mu D_s (\partial \Gamma_o / \partial c_o)}{\Gamma_o (\partial \sigma_o / \partial c_o)} \tag{10}$$

account for the bulk and surface diffusion, respectively. In the case of Langmuir's adsorp-tion, using Gibbs adsorption isotherm, one can write

$$b = \frac{3\mu D (a + c_o)^2}{\Gamma_\infty^2 kT c_o} \quad ; \qquad h_s = \frac{6\mu D_s a}{\Gamma_\infty kT c_o} \tag{11}$$

where k is Boltzmann's constant and T - absolute temperature.

The relative contribution of the bulk and surface diffusion depends on the thickness and the ratio $h_s/b$ which at $c_o \ll a$ and $D_s/D \sim 10$ (see below) equals $2 D_s \Gamma_\infty / Da \sim 10^{-2}$ cm. Since $h \sim 10^{-5}$ cm, at low surfactant concentrations the mobility ratio, $V/V_{Re}$, is entirely controlled by the surface diffusion. In this case the velocity of thinning depends only on the surface properties of the surfactant so that the mechanism of its supply onto the sur-face (diffusion or adsorption controlled) is immaterial. With lower concentrations, $h_s$

is larger and the film thins faster. Note also that this effect depends strongly on the thickness. Indeed, with $\Gamma_\infty kT \sim 10$ and $c_0/a \sim 0.1$, $h_s \sim 10^{-5}$ cm; therefore, at $h > 10^{-5}$ cm the film can behave like one without surface mobility and still have at $h < 10^{-5}$ cm velocity of thinning significantly larger than $V_{Re}$. That is why conclusions about the role of the surface mobility based on investigations of the velocity of rising of <u>single</u> bubbles might be irrelevant to the film thinning.
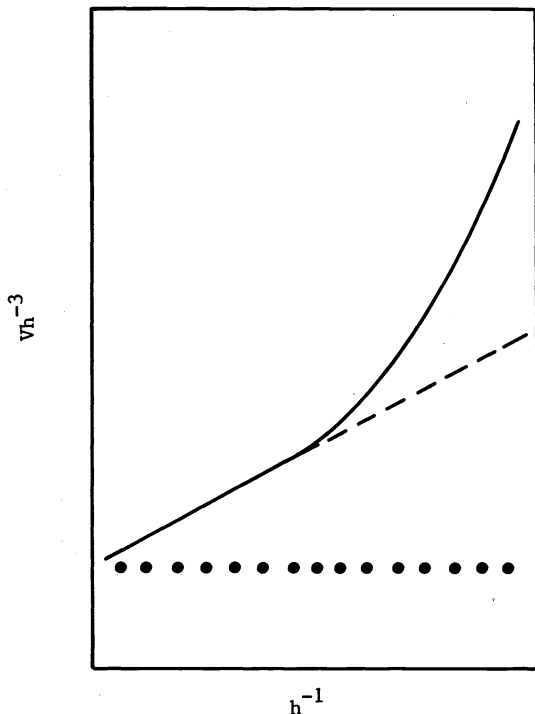
The surface diffusion effect steadily decreases with increasing concentration, whereas b increases at $c_0 > a$. That is why the velocity ratio, $V/V_{Re}$, exhibits a minimum at $c_0^* = a(1 + 2D_s\Gamma_\infty/aDh)^{1/2}$. At $c_0 > c_0^*$ bulk diffusion is operative in controlling the surfactant transfer. This case is of lesser interest, however, since bulk diffusion is less efficient in promoting surface mobility. Recall also that with $c_0 > a$ the process may be adsorption controlled. The above considerations will still be valid when the mechanism of adsorption is not Langmuirian, but then the general expressions (10) must be used. The surface mobility effect may be then even higher, especially in the cases when the adsorption isotherm does not reach saturation.

The neglect of the surface diffusion when analyzing bubbles' coalescence phenomena may lead to a serious overestimate of the effect of the disjoining pressure, $\Pi$. This can be best demonstrated by considering the way $\Pi$ is calculated from the measured velocity of film thinning in the dynamic method of Scheludko (Ref. 9). If one assumes that the film thinning is governed by Reynolds' equation (4) and write this equation in the form (see also (5)) $V/h^3 = \beta(1 + f)$ ($\beta$ is a factor comprising all thickness independent quantities and $f(h) = -\pi R^2\Pi(h)/F$), one is able to conclude that $V/h^3$ vs. h should be a constant, $\beta$, as long as $f \ll 1$. From the deviation of $V/h^3$ from $\beta$ at lower thicknesses, one calculates the disjoining pressure. (To avoid differentiation of the experimental data for the thickness vs. time, usually $h^{-2}$ is plotted vs. time, which is essentially the same.) If, however, the thinning is governed by Eq. (9) rather than by (4), one has

$$V/h^3 = \beta(1 + b + h_s/h) + \beta(1 + b + h_s/h)f(h) \qquad (12)$$

Therefore, the appropriate processing of the experimental data would be to plot $V/h^3$ vs. $h^{-1}$ (see Fig. 4) to determine $\beta b$ and $\beta h_s$ from the linear part of the curve (at $h^{-1} \to 0$) and to use these values to deduce $f(h)$ and hence $\Pi$ from the deviation from linearity at higher values of $h^{-1}$. If the same data (the solid line) were processed according to the original version of the dynamic method (Ref. 9), i.e. by using Reynolds' equation, all the deviation of the solid line from the horizontal dotted line would have been attributed to the disjoining pressure. The latter might result in its gross overestimate.



Fig. 4. A schematic plot of $V/h^3$ vs. $h^{-1}$ for a film with tangentially mobile surfaces (solid line). The broken lines are for zero disjoining pressure: the dotted line ($\cdots\cdots$) corresponds to $h_s = 0$ and the dashed line ($- - - - -$) to $h_s > 0$.

The dynamic method has been extensively applied to the measurement of the van der Waals disjoining pressure in non-aqueous liquid films (see the references in Ref. 9) when no other method can be used. The deduced values were $5 \div 7$ times higher than the ones theoretically calculated (Ref. 29). With water films both static (with equilibrium, non-thinning films) and dynamic measurements are possible. The static results coincide reasonably well with the theoretical estimates whereas the dynamic values are nearly 2 times higher.

All these facts find their natural explanation if allowance is made for the surface diffusion. The surface activity, $\Gamma_\infty/a$, in non-aqueous solutions is normally lower than in water, $D_s$ is probably higher, and $h_s$ should be accordingly higher (see Eq. (11)). That is why the effect of the surface diffusion will be more pronounced and hence the overestimate of $\Pi$ larger in non-aqueous solutions. A similar situation should exist with emulsion films.
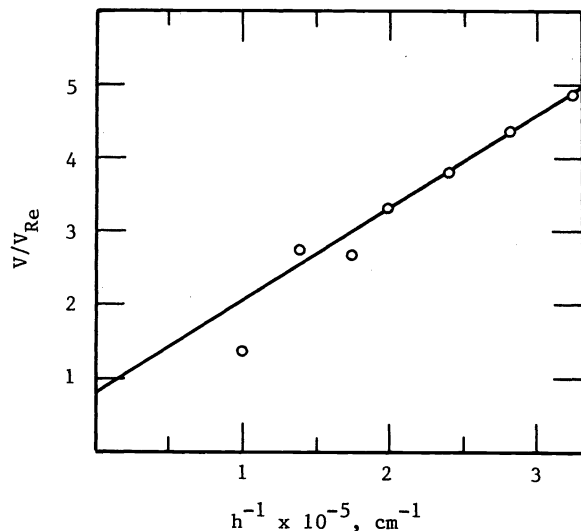
If surface diffusion is neglected, not only the numerical values of $\Pi$, but the deduced functionality on $h$ may be wrong. To illustrate this let us assume the simplest possible case, when the Hamaker function, $A$, is a constant and the real (presumably known) isotherm is $\Pi = -A/6\pi h^3$. By inserting this in (12) one can calculate $V/h^3$ as a function of $h$. Let us assume now that this is the experimental curve $V/h^3$ vs. $h$ and try to process these data by neglecting surface diffusion. Simple calculations lead to the following relationship between the "measured" (in this way) Hamaker function, $A_m$, and its "real" value, $A$:

$$A_m = A + (Ah_s/h)(1 + 6Fh^3/AR^2)$$

Therefore, we would discover in this way an apparent dependence of the "measured" Hamaker function on the film thickness.

Eq. (9) was applied by Manev (Ref. 30) to the experimental data for the velocity of thinning, $V$, of aniline films containing dodecanol. When $V_{Re}$ was calculated using the theoretical values for $\Pi$ (calculated by the method from Ref. 29) a linear dependence of $V/V_{Re}$ on $h^{-1}$ was found (Fig. 5) which is an indication of strong surface diffusion. The value of $D_s = 4 \times 10^{-5}$ cm$^2$sec$^{-1}$ was calculated. The same data for $V$ processed by the conventional dynamic method (using Eq. (4)) yielded values of $\Pi$ nearly 7 times higher than the theoretical ones. Similar results were obtained for water solutions of valeric ($C_5$) and caproic ($C_6$) acids in the concentration range where the equilibrium decrease of surface

Fig. 5. $V/V_{Re}$ vs. $h^{-1}$ for aniline films $+1.1 \times 10^{-2}$ M $C_{12}H_{25}OH$ (Ref. 30).



tension, $\Delta\sigma_0$, is still a linear function of $c_0$. According to Eq. (11) in this case $h_s = 6\mu D_s/\Delta\sigma_0$ must be a linear function of $\Delta\sigma_0^{-1}$ (Fig. 6). The results are not entirely consistent with the theory (for example, the lines on Fig. 6 do not pass through the zero), so that the values of $D_s$, which one can deduce from Fig. 6 must be considered only as an estimate: for both acids one gets $D_s$ of the order of $10^{-4}$ cm$^2$sec$^{-1}$, which correlates well with the values quoted in Ref. 12 and Ref. 32 for similar substances.

In order to prove that the dynamic method with correct treatment of the film thinning data (using Eq. (12)) may yield reliable information about the disjoining pressure and the surface mobility, we have studied the film thinning of nitrobenzene films with two surfactants of different kinds: silicon oil (Merck 350) and $C_{12}H_{25}OH$ (Ref. 33). The advantage of this
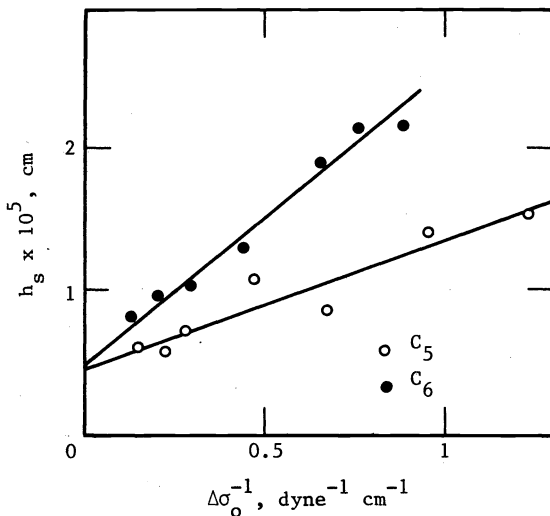
Fig. 6. Plot of $h_s$ vs. $\Delta\sigma_o^{-1}$ for aqueous solutions of valeric ($C_5$) and caproic ($C_6$) acids (Ref. 31).

system is that it is is possible to vary the surface mobility in a wide range. The comparison of Figs. 7a and 7b reveals an almost immobile surface with silicon oil and pronounced bulk and surface diffusion with dodecanol (intersection larger than one and finite slope in Fig. 7b; cf. Eq. (9)). All curves were calculated with the same theoretical disjoining pressure isotherm. The average values of the diffusivities of $C_{12}H_{25}OH$, calculated from Fig. 7b using surface tension data, are $D = 10^{-5}$ $cm^2sec^{-1}$ and $D_s = 7 \times 10^{-5}$ $cm^2sec^{-1}$.
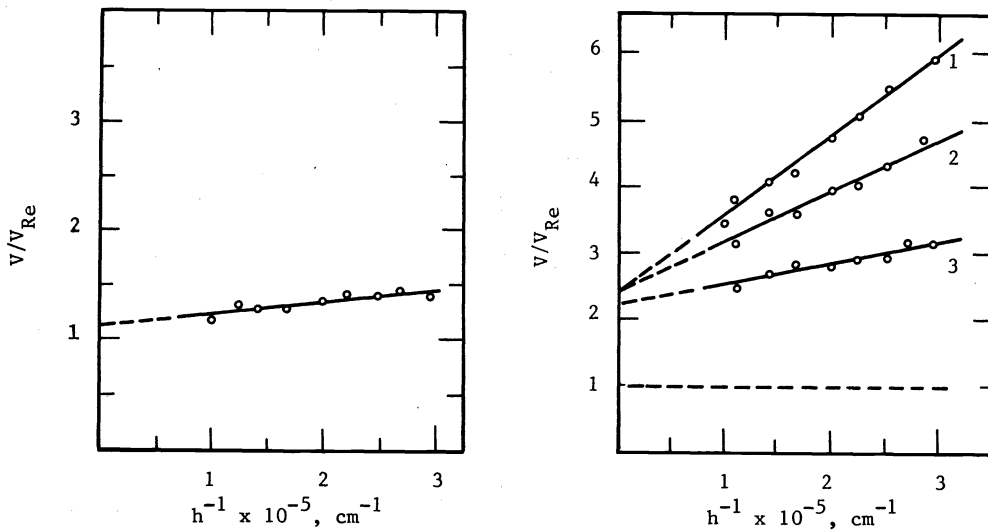


Fig. 7. $V/V_{Re}$ vs. $h^{-1}$ for nitrobenzene films: (a) surfactant silicon oil, $2.78 \times 10^{-5}$ M; (b) surfactant $C_{12}H_{25}OH$: (1) $1.1 \times 10^{-2}$ M; (2) $4.4 \times 10^{-2}$ M; (3) $17.8 \times 10^{-2}$ M (Ref. 33).

As $c_o \to 0$ both $b$ and $h_s$ go to infinity (see Eqs. (10) and (11)) so that $V$ should be apparently infinite also. It is not so, however, because in this case some of the assumptions used in deriving Eq. (9) fail. Most important is probably the failure of the lubrication approximation. Eq. (3a), for example, is based on the assumption that the radial velocity varies much faster normal to the film surface than in a radial direction. With $c_o \to 0$, however, the surface velocity increases so rapidly with $r$, that the above assumption does not hold any longer. This problem was considered in Ref. 34. By giving up the lubrication approximation in its conventional form, the following equation was derived:

$$V/V_{Re} = (1 + 1/\epsilon^f)/(1 + 4h^2/3R^2\epsilon^f). \qquad (13)$$

The merit of this equation is to give as limiting cases both Eq. (9) (when $4h^2/3R^2\epsilon^f \ll 1$) and the equation $V/V_{Re} = 3R^2/4h^2$ for the velocity of thinning of a plane-parallel foam

film without surfactant, i.e. with $\varepsilon^f \to 0$. Its shortcomings are numerous, the most import-
ant ones being, first, that the film may hardly be considered as being plane-parallel at
$c_0 \to 0$; second, the convective surfactant transfer in the film is perhaps not negligi-
ble; and third, the perturbation of the surfactant distribution, $(\Gamma_0-\Gamma)/\Gamma_0$, is certainly
not small as it was assumed when deriving (13). The second effect was estimated in Ref. 14.
Its contribution, which is of the order of $\mu V R^2/h\Gamma_0(\partial\sigma_0/\partial c_0)$, becomes sizable only at very
low concentrations, $c_0/a < 10^{-3}$, when the surfactant transfer is certainly dominated by the
surface diffusion. The estimate of the last approximation was given in Section 2, below
Eq. (7). The error introduced by it is $(\partial\Gamma_0/\partial c_0)/h \gg 1$ times larger than the one due to
the neglect of the convective diffusion.

In the case of wetting films one can assume that the radial velocity is zero at the solid/
liquid interface. The resulting equation for the velocity of thinning is (Refs. 14, 27 &
34)

$$V/V_{Re} = 4 \frac{3/4 + b + h_s/2h}{3 + b + h_s/2h} \tag{14}$$

At relatively large concentrations, where both $b$ and $h_s/h$ are much smaller than unity,
Eq. (14) reduces to the Reynolds equation. In the opposite case, $c_0 \to 0$ (pure liquid),
when $b$ and $h_s$ tend to infinity, Eq. (14), unlike Eq. (9), leads to finite velocity of
thinning, $V = 4V_{Re}$. The reason for that is, of course, the tangential immobility of the
solid interface, which prevents the surface velocity of the liquid/gas surface from reaching
large values and thus keeps the velocity of thinning finite at all surfactant concentrations.

### 4. EMULSION FILMS

The thinning of plane-parallel emulsion films was considered theoretically in Refs. 20, 26, 35,
36. In Ref. 35 more attention was paid to the flow inside the film, whereas the flow inside
the drops was accounted for merely by replacing the shear stress on the drop side, $\mu^d(\partial v_r^d/\partial z)$
in Eq. (8), by $\mu^d v_r^d/\delta$, where $v_r^d$ and the boundary layer thickness, $\delta$, remained as unspeci-
fied parameters of the theory. Ref. 26 and Ref. 36 both attempted detailed treatments of
the flow in the droplets, but have different ranges of validity. The authors of Ref. 36
neglected in Navier-Stokes equations the convective terms but kept the transient terms. If
it were possible to assume that the film had existed at rest at some initial thickness and
suddenly had started to thin, this approximation would have been valid at the beginning of
the thinning process: then the velocity is zero, but the acceleration is finite. As the
film thins the convective terms gradually increase and become comparable in magnitude with
the transient terms. Since the film undergoes a long evolution before becoming plane-
parallel (see Section 1), we believed it necessary to keep both the convective and the
transient terms, i.e. not to use ad hoc simplifications of Navier-Stokes equations in the
drop. Two different methods of solution were used in Ref. 26, leading to almost identical
results. The expression for the velocity of thinning obtained for a symmetric film (two
identical drops) is

$$V/V_{Re} = 1 + 1/\varepsilon^e \; ; \qquad \varepsilon^e = (a_1^2\rho^d\mu^d\Delta P h^4/108R^2\mu^3)^{1/3} \tag{15}$$

where $a_1 \stackrel{\sim}{\sim} -1$ is a weak function of $h$ tabulated in the first Ref. 26. By introducing
the "emulsion thickness"

$$h_e = (108R^2\mu^3/a_1^2\rho^d\mu^d\Delta P)^{1/4} \tag{16}$$

one has $\varepsilon^e = (h/h_e)^{4/3}$. With $\mu = \mu^d = 10^{-2}$ g cm$^{-1}$sec$^{-1}$, $h_e \stackrel{\sim}{\sim} 5 \times 10^{-3}$ cm. Therefore,
for all practical purposes

$$V/V_{Re} = 1/\varepsilon^e = (h_e/h)^{4/3}. \tag{17}$$

Combining this with Reynolds equation (4), one gets

$$V = (32\Delta P^2/a_1^2\rho^d\mu^d R^4)^{1/3} h^{5/3} \tag{18}$$

For $\Pi = 0$ this equation may be written in an alternative form. Since $R$ and $\Delta P$ are
both determined by the driving force, $F$, from Eqs. (2) and (5) one obtains:

$$\Delta P/R^2 = 4\pi\sigma_0^2/FR_c = 3\sigma_0^2/R_c^5 g\Delta\rho \tag{19}$$

and

$$V = (96\sigma_0^2/a_1^2 g\mu^d\rho^d\Delta\rho R_c^5)^{1/3} h^{5/3} \tag{20}$$

Similar to what was observed with foam films, in the case of emulsion films also the sur-
face mobility not only increases the velocity of thinning, V, as compared with Reynolds

velocity, but also changes its functional dependence on h: V decreases as $h^{5/3}$ rather than $h^3$. The difference with foam films is that now even the dependence of V on $\Delta P$ and R (alternatively, on $\sigma_0$ and $R_c$, cf. Eq. (20)) is different. Most interestingly, however, V does not depend on the viscosity of the film, $\mu$. The reason for that is the high surface velocity which brings the liquid in the drops into intensive circulation, so that the major dissipation of energy takes place inside the drops. This conclusion is corroborated by the results of Beshkov et al. (Ref. 5) for the velocity of mutual approach of two non-deformed very viscous drops ($\mu^d \gg \mu$) at small separations ($h \ll R_c$):

$$V = F/(3\pi^3/8)\mu^d R_c \sqrt{R_c/2h} \ . \tag{21}$$

In this case too, V does not depend on $\mu$.

Quite the opposite is true when one of the surfaces is solid/liquid. Then (Ref. 26):

$$V/V_{Re} = 4(1 + \varepsilon_1^e)/(1 + 4\varepsilon_1^e) \tag{22}$$

where $\varepsilon_1^e$ has the same meaning but differs by a numerical coefficient from $\varepsilon^e$ (cf. Eq. (15)). Since $\varepsilon_1^e$ is very small, $V \approx 4V_{Re}$. Therefore, because of the low surface velocity in this system (see the discussion of Eq. (14)), the circulation in the drop is small and almost all the energy is dissipated inside the film. In the general case of two different droplets A and B, suspended in a third liquid, one has (Ref. 38)

$$V/V_{Re} = 1 + 3 \frac{1 + \varepsilon_A^e + \varepsilon_B^e}{\varepsilon_A^e + \varepsilon_B^e + 4\varepsilon_A^e\varepsilon_B^e} \tag{23}$$

which for $\varepsilon_A^e, \varepsilon_B^e \ll 1$ gives

$$V = \left\{ \frac{128 \, \Delta P^2 \, h^5}{a_1^2 R^4 [(\rho_A\mu_A)^{1/2} + (\rho_B\mu_B)^{1/2}]^2} \right\}^{1/3} . \tag{24}$$

One must bear in mind that in this case the film is not flat so that special care must be taken to define properly $\Delta P$ and R (Ref. 16).

The only available experimental data suitable to check the above theory are those of Sheele and Leng (Ref. 37). In Ref. 26 they were used to calculate the critical thickness of rupture from the measured life-times. The result, $h_{cr} = 6.3 \times 10^{-6}$ cm, seems quite reasonable.

Very interesting results were obtained for surfactant containing systems (Ref. 20). Two special cases were considered: surfactant soluble either in the continuous phase or in the drops (system I and II in Fig. 8). The velocity of thinning, V', for system I was found to be:

$$V'/V_{Re} = 1 + 1/(\varepsilon^f + \varepsilon^e). \tag{25}$$

Since $\varepsilon^f \approx h/h_s$ (cf. Eq. (9)) and $\varepsilon^e = (h/h_e)^{4/3}$ at $h = 10^{-5}$ cm, $\varepsilon^e$ becomes comparable to $\varepsilon^f$ (with the assumed typical values of the system parameters) only at $c_0/a \lesssim 10^{-5}$. Therefore, almost always $\varepsilon^e$ can be neglected and (25) reduces to (9). In other words, even a small amount of surfactant soluble in the film is sufficient to suppress the dissipation of energy in the drop. Then $V'/V_{Re} \approx 1 + 1/\varepsilon^f$.

The solution for the surfactant distribution in system II showed that the concentration depends only on the normal coordinate, $c = c(z)$. The influence of the surfactant on the velocity of thinning is reflected by the term $\partial\sigma/\partial r$ in Eq. (8). In this case we have

$$\partial\sigma/\partial r = (\partial\sigma_0/\partial c_0)(\partial c/\partial r) = 0 \tag{26}$$

since $\partial c/\partial r = 0$. Therefore, the surfactant does not affect the velocity of thinning, V'', which for this system is the same as for a system without surfactant (cf. Eq. (15)):

$$V''/V_{Re} = 1 + 1/\varepsilon^e \approx 1/\varepsilon^e. \tag{27}$$

Therefore, the velocities of thinning for two systems differing only by the solubility (not concentration) of the surfactant may differ by orders of magnitude. For example, one can have a large surfactant concentration in the drop, $c_0 \gg a$, and still have, according to (27), $V'' \gg V_{Re}$. A surfactant, soluble in the continuous phase, with concentration $c_0 \gg a$, would have reduced V' to $V_{Re}$. Hence, in this case

$$V'/V'' = \varepsilon^e \ll 1. \tag{28}$$

SYSTEM I                                                SYSTEM II
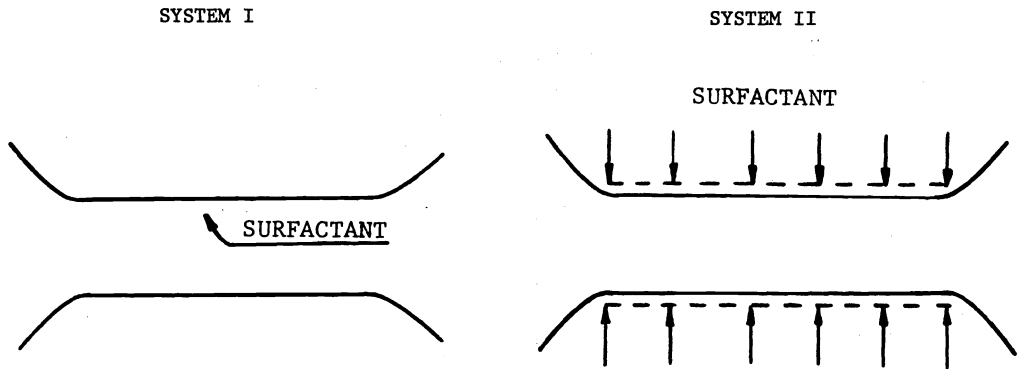
SURFACTANT



SURFACTANT

Fig. 8. Sketch of two emulsion systems containing surfactant. System I:
surfactant soluble in the continuous phase. System II: surfactant soluble
in the drops. The arrows indicate the surfactant path.

This dramatic difference between the two systems is due to the way the surfactant is trans-
ported. In system I it has to go a long way from the film perimeter. Since the driving
force of this process is the gradient of surface concentration along the surface, the diffu-
sion can never eliminate the surface tension gradient. In system II the surfactant has to
travel a much shorter distance: it is transported from the bulk of the drop onto the sur-
face across the diffusion boundary layer, whose thickness is much smaller than the film
radius. Besides, the surfactant flux is driven by the normal gradient of the concentration,
so that it can completely counterbalance the perturbation of $\Gamma$ caused by the surface con-
vective flux. The path of the surfactant is shown in Fig. 8 by arrows.

This effect is probably related to Bancroft's rule and its explanation, as given by Davies
(Ref. 39). Our results indicate that at least in the case of the droplets' coalescence
being preceded by the formation of a thin liquid film, the hydrodynamic factors for direct
and reverse emulsions in Davies' theory may differ substantially and cannot be equaled as
Davies did. This difference may perhaps be immaterial in the case of stable emulsions,
where the energetic barrier against coalescence is high, but for emulsions of low stability
the ratio of the hydrodynamic factors could play a decisive role. According to the results
of the present work, the hydrodynamic factor will be much greater for the droplets formed by
the liquid where the surfactant is soluble. This will lead to a faster coalescence of these
drops and will favor the formation of the emulsion in which the continuous phase is formed
by the liquid where the surfactant is soluble. This conclusion is in accordance with Ban-
croft's rule.

The theoretical conclusion about the independence of the velocity of thinning on the concen-
tration of the surfactant added to the drop seems to agree with the finding of Hodgson and
Lee (Ref. 40) that the addition of a water soluble surfactant makes little or no difference
to the behavior on coalescence of water droplets at an oil/water interface. More extensive
experimental study of this effect was carried out in Ref. 41 by measuring the velocity of
thinning and the life-times, $\tilde{t}$, of emulsion films. The qualitative agreement with the theory
was excellent although the measured life-times were larger than they should have been accord-
ing to the theory. A typical result from Ref. 41 is reproduced in Fig. 9, where $N = 150$
is the number of runs for the whole curve and $\Delta N$ is the number of films with life-times
within $\tilde{t} - \Delta\tilde{t}/2$, $\tilde{t} + \Delta t/2$, with $\Delta\tilde{t} = 0.2$ sec. As one can see the most probable life-
time is $0.3 \div 0.4$ sec for all surfactant concentrations up to the highest one, $2 \times 10^{-3}$ M.
The life-times with surfactant soluble in the continuous phase were much longer: 20 sec
for drops of pure water with continuous phase benzene + 0.1 M laurylic alcohol and 33 sec
for drops of pure benzene with continuous phase water + 0.3 M sodium chloride + $2 \times 10^{-3}$ M
sodium octylsulfonate.

When one of the interfaces is solid/liquid and the surfactant is soluble in the continuous
phase, the velocity of thinning is (Ref. 42)

$$V/V_{Re} = 4[1 + 3/(4b + 2h_s/h) + \varepsilon_1^e] / [1 + 3/(b + h_s/2h) + 4\varepsilon_1^e] . \qquad (29)$$

In the other case, surfactant soluble in the drop, as one should expect $c = c(z)$, i.e. V
does not depend on the surfactant concentration and V is again given by Eq. (22). Eq.
(29) yields as particular cases Eq. (14), for the velocity of thinning of a wetting film
with liquid/air interface, as well as Eq. (22). Again, very small amounts of surfactants

are sufficient to depress the circulation in the drop which is small anyway because of the presence of the solid surface.
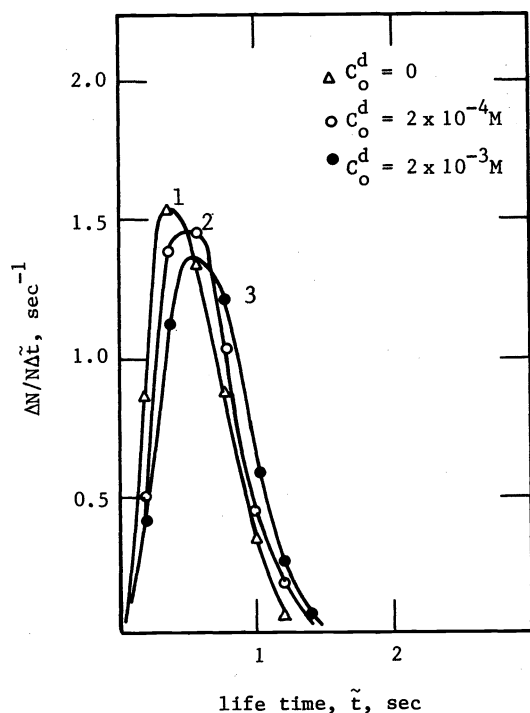


Fig. 9. Distribution curves for the lifetimes of symmetrical surfactant-free benzene films. Water drops + 0.3 M sodium chloride with different concentrations of surfactant sodium octylsulfonate: Curve 1, no surfactant added; Curve 2, $10^{-4}$ M; Curve 3, $2 \times 10^{-3}$ M.

## 5.  CRITICAL THICKNESS OF RUPTURE AND LIFE-TIME OF THIN FILMS

Numerous experiments have shown (Refs. 9 & 43) that even when they are plane-parallel, liquid films never thin to zero thickness but rupture or black (thinner) spots form, at a finite thickness, of the order of $5 \times 10^{-6}$ cm, called critical (Ref. 43). deVries (Ref. 44) was the first to point out that local fluctuations of the film thickness (which are always present either because of mechanical perturbations or thermal fluctuations) lead to two opposite effects:  positive contribution to the free energy due to the increase of the film area and negative contribution resulting from the increased negative van der Waals energy of interaction in the thinner part.  The latter effect increases as the average thickness decreases so that at a given thickness, $h_t$, which we will call "transitional" (it is called "critical" in Refs. 9 & 43) the two effects compensate each other.  Below $h_t$ the change of free energy is negative, the corrugations become unstable and will spontaneously increase their amplitude until the film surfaces touch each other.  When this happens the film will either rupture (at low surfactant concentrations) or a black spot will form, which is the nucleus of a thinner stable second black film.  We call "critical" the average film thickness at which either of these events occurs.  Later on Manev et al. (Ref. 45) were able to demonstrate experimentally the gradual transition from rupture to formation of black spots with increasing surfactant concentration. deVries derived an equation for the free energy change and found a very reasonable value of the transitional thickness, $h_t \approx 10^{-5}$ cm.

Scheludko (Ref. 43) did the next important step by relating the local fluctuations of the thickness to the surface thermal capillary waves (see Fig. 10) and by proposing a simpler method of calculation of the transitional thickness.  He derived a simple relation between $h_t$ and the wave length, $\lambda$:

$$h_t = (A\lambda^2/128\pi\sigma_o)^{1/4}. \tag{30}$$

More importantly, he showed that instability may occur at vanishing wave amplitudes, provided that the average film thickness, $h$, is small enough and thus opened the way to the linear stability analysis.

The latter was first applied to film rupture by Vrij and Vrij and Overbeeck (Ref. 46).  Vrij also realized that at the transitional thickness the rate of deepening of the corrugation is zero (see below) so that finite time is needed for the two surfaces to touch each other during which the average thickness of a thinning film will decrease.  Besides, there is not just one wave but an infinite set of them because the "roughness" of the film surfaces,
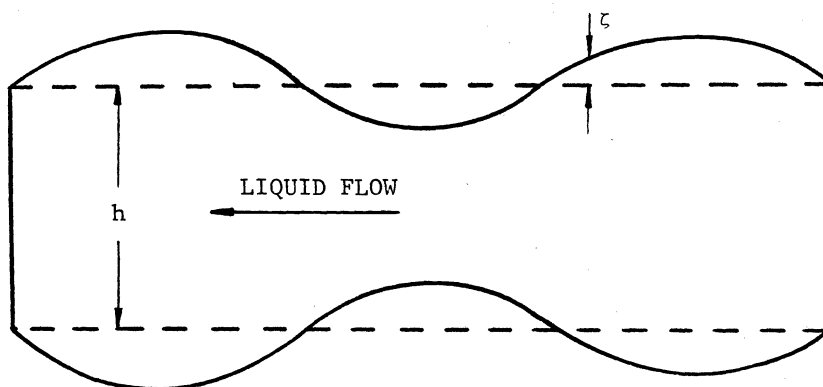
Fig. 10. Symmetric capillary waves in a thin film.

caused by the thermal fluctuations, can be described properly only by the superposition of
an infinite number of waves with different wave lengths and amplitudes. The rate of local
deepening, $v_\zeta = \partial\zeta/\partial t$, (see Fig. 10 for notation) associated with each wave depends strongly
on its length and the film thickness (Eqs. (37) and (43)). That is why one can expect that
at the critical thickness, $h_{cr}$, one wave called critical will have the largest amplitude.
Its length can be determined by the condition (Ref. 47)

$$\partial\zeta/\partial\lambda = 0 \quad \text{at} \quad h = h_{cr}. \tag{31}$$

Using the above concepts Vrij (Ref. 46) developed a graphical procedure for calculating $h_{cr}$
of thinning films, which was later improved (Ref. 48). Another approach, leading to anal-
ytical expression for $h_{cr}$ and allowing also for the surface mobility, was developed in
Ref. 47. Both approaches differ numerically with less than 10%. The major shortcoming of
both approaches is that some of the equations they are based on are valid only for the
initial stage of instability, when $\zeta \ll h$, but are applied at the critical thickness when
$\zeta = h_{cr}/2$. It was suggested in Ref. 47 that this is probably immaterial because at the
critical thickness $v_\zeta \gg V$. This was confirmed numerically in Ref. 49, where it was shown
that as the film thins $\zeta$ increases very slowly and the ratio $\zeta/h$ for the critical wave
becomes equal to 0.1 only at thicknesses very close to $h_{cr}$. This is also confirmed by the
relatively good agreement between theory and experiment for aniline foam films at very high
dodecanol concentration, 0.11 M, when the surface is presumably nearly immobile (Fig. 11)
(Note b).

Another possible shortcoming of the theory is the use of the model of the plane-parallel
film. With small bubbles, however, the critical thickness is small enough for the film to
meet the requirement (1 ) and the film to be plane-parallel. This is also confirmed by the
Charles and Mason (Ref. 7) who took high-speed pictures of the process of rupture and found
that with surfactant present only rarely does the rupture take place off center. With large
bubbles with dimple, however, the rupture will most probably occur at the barrier ring (Ref.
51). A theory of the film rupture for such systems was developed in Ref. 49.

The role of the surface mobility on the wave motion in thin films was the subject of many
papers during the last decade (see Ref. 52 for foam and Ref. 53 for emulsion films). All of
them, but for the works of Jain and Ruckenstein for films with one interface solid/liquid,
treat insoluble surfactants (a more detailed review of these works is available elsewhere
(Ref. 54)). We preferred to restrict the validity of the solution with respect to the film
thickness and wave length only to the range relevant to the film rupture. This in return

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Note b. The large discrepancy between theory and experiment in Ref. 47 was mainly due to
the use of the experimentally determined values of the disjoining pressure, $\Pi(h)$. The
latter were calculated using Reynolds equation (4) and because of the neglect of the
surface diffusion, were too high (see Section 3). Curve 1 on Fig. 11 is calculated using
the theoretical values of $\Pi$, determined by the method of Ref. 29.

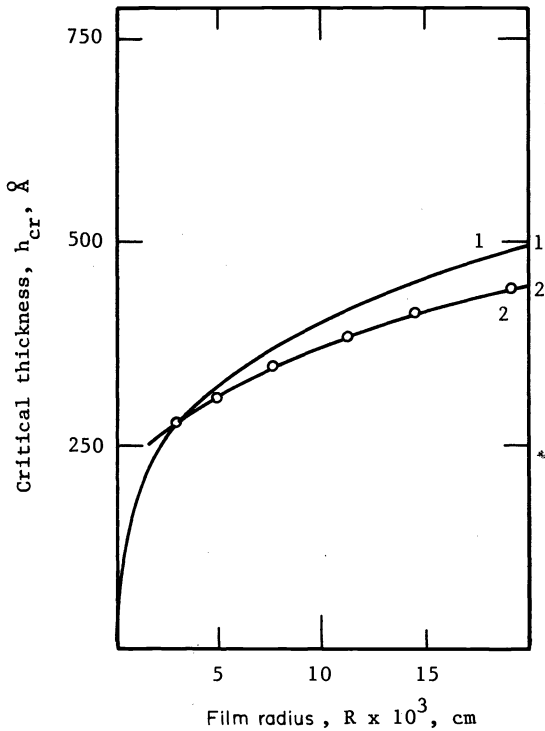allowed us to account in detail for the transfer of a soluble surfactant, as well as for the film thinning.



Fig. 11. Critical thickness of rupture, $h_{cr}$, vs. film radius, R, for foam aniline films. Curve 1 – theory; curve 2 – experiment with 0.11 M solution of dodecanol (Ref. 50).

Toward this aim, we confined ourselves with intermediate wave length,

$$h \ll \lambda \ll R. \tag{32}$$

The small wavelengths are inefficient in promoting instability, because they lead to high surface curvature, opposing the local thinning. The long waves are easily damped, because they involve liquid transport at large distances. These physical arguments, due to Scheludko (Ref. 43), are in agreement with the calculated length, from Eq. (31), of the critical wave, $\lambda_{cr} = (0.1 \div 0.01)R$. The values of the initial radii of the hole (Ref. 7) or the black spot (Ref. 45), which must be of the order of $\lambda_{cr}$, are similar. The first inequality (32), $h/\lambda \ll 1$, means that in this case too lubrication approximation can be used for the flow in the film.

The time dependence of the film shape is accounted as usual by assuming that all quantities are proportional to a time factor, $\exp(\omega t)$, where $\omega$ has the meaning of angular frequency. The transient term $\rho \partial v_r / \partial t$, that would appear in Eq. (3a), if it is to be applied to wave motion, will be $\omega h^2 / \nu$ ($\nu = \mu / \rho$ is kinematic viscosity) times smaller than the viscous terms. Because of the small thickness of the film this term also is usually very small, i.e. $\omega h^2 / \nu \ll 1$. The length scales of the flow in the drops in radial and normal directions are the same, $\lambda$, so that neither of these approximations can be used there.

The most important difference between the film thinning and the wave motion is that in the latter case the local curvature of the film may be high (see Fig. 10). The local capillary pressure tends to flatten the surface (Note c). On the other hand, in the thinner parts of the film the (negative) van der Waals disjoining pressure will be higher and will try to move the liquid toward the thicker parts. At the transitional thickness these effects cancel each other and there is no pressure variation along the film, $\partial p / \partial r = 0$; the wave is in a metastable equilibrium, so that

$$\omega = 0 \quad \text{at} \quad h = h_t. \tag{33}$$

At $h < h_t$, the thinner parts become thinner and thinner until rupture occurs.

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Note c. The capillary pressure is calculated from a modified Laplace equation (Ref. 14) in which the surface tension, $\sigma_o$, is replaced by the surface tension of the film, $\sigma^f$ (see also Ref. 28).

With these modifications we can again use the procedure from Section 2 to describe the wave motion. We shall keep, however, the surface viscosity term in Eq. (8): since the radial length scale now is $\lambda \ll R$, it may be important even with small surface viscosities. Since,

$$\zeta \sim \exp(\omega t), \tag{34}$$

the evolution of the shape of a <u>non-thinning film</u> with time at a given thickness $h$ will be determined by $\omega$. An expression for $\omega$ of elmulsion films with arbitrary viscosity ratio, $\mu/\mu^d$, is available in Ref. 28. In the most interesting case of comparable viscosities, more precisely,

$$(kh)^{-1} \gg \mu/\mu^d \gg kh, \tag{35}$$

it reduces to

$$\frac{\omega}{\omega^{(0)}} = \frac{1 + k^2 h(\mu_s + M)/6\mu}{\varepsilon_k^e + k^2 h(\mu_s + M)/6\mu} \tag{36}$$

where $k \stackrel{\sim}{\scriptstyle\sim} 2\pi/\lambda$ is wave number,

$$\omega^{(0)} = (\sigma^f k^2 - 2\frac{d\Pi}{dh})k^2 h^3/24\mu \tag{37}$$

is the angular frequency for the same film with tangentially immobile surfaces and $\varepsilon_k^e = kh\mu^d/3\mu$ accounts for the circulation in the drops. The term $M$ accounts for the effect of Marangoni-Gibbs. When the surfactant is soluble in both liquids, either of the following equivalent expressions can be substituted for it:

$$M^d = -\frac{\Gamma_o(\partial\sigma_o/\partial c_o^d)}{Dk}\left(1 + \frac{kh}{2}\frac{D}{D^d}\frac{\partial\Gamma_o/\partial c_o^d}{\partial\Gamma_o/\partial c_o} + \frac{kD_s}{D^d}\frac{\partial\Gamma_o}{\partial c_o^d}\right)^{-1}, \tag{38}$$

$$M = -\frac{2\Gamma_o(\partial\sigma_o/\partial c_o)}{Dk^2 h}\left(1 + \frac{2}{kh}\frac{D^d}{D}\frac{\partial\Gamma_o/\partial c_o}{\partial\Gamma_o/\partial c_o^d} + \frac{2D_s}{Dh}\frac{\partial\Gamma_o}{\partial c_o}\right)^{-1}. \tag{39}$$

When the surfactant is soluble in only one of the phases the appropriate equation has to be used and the second term in parentheses has to be dropped. The quantity $M$ has the dimension of surface viscosity. Note, however, that it depends not only on the surfactant properties but also on $h$ and $k$. With surfactant soluble only in the film,

$$M = 6\mu\varepsilon^f/k^2 h. \tag{40}$$

Eq. (36) contains as particular cases our previous results for foam (Refs. 22 & 47) and emulsion films (Ref. 55). Other approximate expressions for $\omega$ can be found in Ref. 28. As already mentioned, the transitional thickness, $h_t$, is defined by $\omega = 0$, which yields (see Eq. (37)):

$$\sigma^f k^2 - 2(d\Pi/dh) = 0 \quad \text{at} \quad h = h_t. \tag{41}$$

The first term in Eq. (41) accounts for the capillary pressure whereas the second is due to the local variation of the disjoining pressure. If $\Pi$ obeys Hamaker's law, Eq. (41) differs only numerically from Scheludko's result, Eq. (30).

Eq. (36) was analyzed in Ref. 28. Its most important features are: (i) Very small amount of surfactant in either phase (note this important difference with film thinning; see Section 4) is sufficient to suppress the circulation in the drop, i.e. it enables one to neglect $\varepsilon_k^e$ in (36). (ii) With $\mu_s > 10^{-3}$ s.p., $k^2 h\mu_s/6\mu \gg 1$ and $\omega \stackrel{\sim}{\scriptstyle\sim} \omega^{(0)}$, i.e. with respect to the wave motion the surface behaves as tangentially immobile. (iii) When the surfactant is soluble in the film and $\mu_s = 0$,

$$\omega/\omega^{(0)} = 1 + 1/\varepsilon^f = 1 + b + h_s/h, \tag{42}$$

where Eqs. (9) and (40) were used.

Since the right-hand sides of Eqs. (42) and (9) are the same, everything said in Section 3 about the effect of the surfactant on the velocity of thinning will apply to the angular frequency, $\omega$, and hence to $\zeta$ and the velocity of deepening of the corrugation

$$v_\zeta = \partial\zeta/\partial t = \omega\zeta. \tag{43}$$

For example, the maximum damping of the wave will occur at the concentration $c_0^*$, at which $\varepsilon^f$ exhibits a maximum (see Section 3). At larger or smaller concentrations the damping is smaller, $v_\zeta$ is larger, and the rupture time of a non-thinning film will be accordingly shorter. (For more detailed analysis of the wave damping, see Refs. 52 & 53.) The damping coefficient of capillary waves at the liquid/air interface behaves similarly (Ref. 56) (d). This has lead some investigators to seek correlations between damping coefficients and elastic properties of the interface on the one hand and the experimentally observed decrease of foam stability (Ref. 57) and increased thickness of rupture with low surfactant concentrations on the other (see Fig. 12). We will show now that as far as rupture of thinning films is concerned, the situation is much more complicated and such a correlation, if there is any, may be fortuitous. This is one more example of how the "thinness" of the film makes its behavior much different from that of an interface.
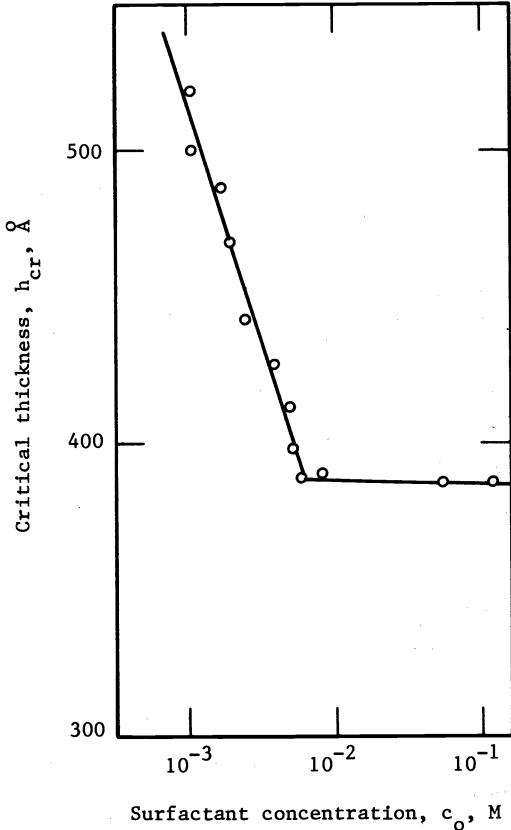


Fig. 12. Dependence of the critical thickness of rupture, $h_{cr}$, of aniline films on the concentration, $c_0$, of dodecanol (Ref. 50).

Since at $h < h_t$ the wave becomes aperiodic (steady deepening of the corrugation) and $\omega h^2/\nu \ll 1$, the effect of the thinning on the wave shape can be accounted for by realizing that $\zeta$ will depend on time only via $h(t)$. Then the following quasi-steady approximation can be used (Ref. 47):

$$v_\zeta = \frac{\partial \zeta}{\partial t} = \frac{\partial \zeta}{\partial h}\frac{dh}{dt} = -V\frac{\partial \zeta}{\partial h} . \tag{44}$$

This, along with Eq. (43), leads upon integration from $h_{cr}$ to $h_t$ to:

$$h_{cr}/2 = \overline{\zeta}(h_{cr}) = \overline{\zeta}(h_t)\exp[-\int_{h_t}^{h_{cr}} (\omega/V)dh], \tag{45}$$

where $\overline{\zeta}(h_t)$ denotes average value over the film area. The set of Eqs. (31), (41) and (45), along with the appropriate expressions of $\omega$ and $V$ (they depend on the surface mobility), allows the calculation of the critical thickness (for details see Refs. 22 & 47).

Eq. (45) suggests that each factor affecting to the same extent both $\omega$ and $V$ should have no influence on the critical thickness (Refs. 14 & 47). For example, the critical thickness of foam films should not depend on the film viscosity, $\mu$, (note that $D\mu$ and $D_s\mu$ in Eq. (39) do not depend on $\mu$), which was experimentally confirmed in Ref. 58. Indeed, the decrease

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Note d. The concentration at which maximum damping of capillary waves occurs is smaller than the respective concentration for $\varepsilon^f$ because of the enhanced role of surface diffusion in thin films (cf. Section 3).

of viscosity eases the wave motion and the wave will reach the same amplitude, $\zeta = h_{cr}/2$ which corresponds to rupture at larger values of $\mu$, for a shorter time. Simultaneously, the thinning is also faster so that for this shorter time the film is able to thin to the same thickness, at which the rupture will again occur.

Eqs. (9) and (42) suggest that the same should be true for the role of the surfactant concentration, $c_o$: since both $\omega$ and $V$ increase by the same factor as $c_o$ decreases, the critical thickness should remain the same, which contradicts experimental results (Fig. 12).

A plausible explanation of the variation of the critical thickness with the surfactant concentration was put forth in Ref. 22. It is based on the different dependence of $V$ and $\omega$ on the surface viscosity, $\mu_s$, discussed above and in Section 2. If at large concentrations $\mu_s$ is within the range of $10^{-3}$ s.p. $< \mu_s < 0.1$ s.p., it would reduce $\omega$ to $\omega^{(0)}$ without affecting $V$. Then the integrand in Eq. (45) for this case, $\omega^{(0)}/V$, would be smaller (by absolute value) than the integrand, $\omega/V$, for $\mu_s = 0$. Hence, according to (45), the critical thickness would also be smaller. Since $\mu_s$ is usually zero when the surface coverage is not complete (Refs. 59 & 60), below a certain concentration $\mu_s$ is expected to drop sharply and $h_{cr}$, accordingly, to rise.

Although this mechanism may be operational for some surfactants, it can be hardly considered as being general nor can it explain the variation of critical thickness for surfactants with $\mu_s = 0$, such as fatty acids (Ref. 61). Some recent results suggest (Ref. 16) that the most probable mechanism is the hydrodynamic coupling between the wave motion and the film thinning. Indeed, the corrugation of the surface will obviously affect the outflow of the liquid and vice versa. The role of this effect was pointed out for films with tangentially immobile surfaces by Gumerman and Homsy (Ref. 62), but these authors overestimated it. Its relative contribution in this case is of the order of $\lambda^2/R^2$ (Ref. 14) and in view of the estimate $\lambda_{cr} = (0.1 \div 0.01)R$, quoted above, is negligible. The numerical solution leads to the same conclusion (Ref. 49). Gumerman and Homsy assumed $\lambda_{cr} \sim R$ and reached accordingly a different conclusion.

The hydrodynamic coupling is also negligible when the surface mobility is controlled by bulk diffusion, whose contribution to the mobility ratio does not depend on the thickness (see Eq. (10)). The situation is quite different, however, when surface diffusion is effective. Since it affects more strongly the thinner parts of the film, it will enhance the local deepening more than the thinning, i.e. the decrease of the average thickness. The net outcome of this is a larger increase of the ratio $\omega/\omega^{(0)}$ than predicted by Eq. (42). Our results show (Ref. 16) that this may well be the reason for the variation of the critical thickness with surfactant concentration.

The analysis of the ratio $\omega/V$, and hence the critical thickness, of emulsion films is much more complicated, first because of the numerous parameters involved, and second because under certain circumstances some of the approximations used may be false. Perhaps the two most interesting conclusions reached in Refs. 14 & 28 are: (i) The critical thickness depends on the viscosity ratio, $\mu/\mu^d$, and decreases as $\mu^d$ increases. (ii) Since the presence of a surfactant in the drop does not affect the velocity of thinning but does reduce $\omega$, it will reduce the critical thickness more when added to the drop rather than to the continuous phase. The latter appears to be in agreement with some experimental observations in Ref. 41.

The studies of the stability of thin films are interesting and important per se, because they improve our understanding of the mechanism of rupture and provide theoretical estimates of the order of magnitude of the critical thickness. The variations of the critical thickness from system to system, however, makes little or no difference on the life-time of drops and bubbles which is determined (in the absence of long-range repulsive forces) mostly by the large variations of the velocity of thinning. To demonstrate this let us confine ourselves to the comparison of the life-times for tangentially immobile surfaces, $\tilde{t}^{(0)}$, and highly mobile surfaces, $\tilde{t}$. In the latter case, Eqs. (9) and (15) have both the form $V/V_{Re} = (h_n/h)^n$ with $n = 1$ or $4/3$, respectively; $h_n$ stands for $h_s$ and $h_e$. By substituting the appropriate expression for $V$ in

$$\tilde{t} = \int_{h_{cr}}^{\infty} \frac{dh}{V} \tag{46}$$

one gets

$$\frac{\tilde{t}^{(0)}}{\tilde{t}^{(n)}} = (1 - \frac{n}{2}) \left[ 1 + \frac{h_{cr}^{(0)} - h_{cr}^{(n)}}{h_{cr}^{(0)}} \right]^{2-n} \left( \frac{V}{V_{Re}} \right) \Bigg|_{h_{cr}^{(0)}} \tag{47}$$

where $V/V_{Re} \gg 1$ is evaluated at $h_{cr}^{(0)}$. The reported values of $h_{cr}$ vary between $3 \times 10^{-6}$ and $6 \times 10^{-6}$ cm so that the second factor in (47) can hardly exceed two. There-

fore, the reported variations of $\tilde{t}$ from fractions of a second to tens and even hundreds of seconds can be explained (in the cases when the above model applies) only in terms of variations of the velocity of film thinning.

## 6. THIN FILMS WITH DEFORMABLE SURFACES

Since the model of the plane-parallel film is of crucial importance for the validity of the results presented so far, it seems pertinent at this point to give a brief account of some results for films with deformable surfaces, which bear out the applicability of the model and establish its limitations as well.

The lubrication theory approximation applies not only to the thinnest part of the film ($r < R$ in Fig. 1) but also to a region extending beyond $R$ (Ref. 8). That is why the method described in Section 2 can be applied also to films with deformable interfaces. Eqs. (3) can be integrated in general form for two different bubbles, A and B, to give (Ref. 16),

$$\frac{\partial H}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} r \left\{ \left[ 1 - 3 \frac{4 - (\kappa^A - \kappa^B)(\Gamma_o^A - \Gamma_o^B)}{(\kappa^A + \kappa^B)(\Gamma_o^A + \Gamma_o^B)} \right] \frac{H^3}{12\mu} \frac{\partial p}{\partial r} \right\} \tag{48}$$

where $H(r)$ is the local distance between the two surfaces and

$$\kappa^{A,B} = \frac{\partial \sigma_o^{A,B}/\partial c_o}{D\mu} \left[ 1 + \left( D_s^A \frac{\partial \Gamma_o^A}{\partial c_o} + D_s^B \frac{\partial \Gamma_o^B}{\partial c_o} \right) / DH \right]^{-1}. \tag{49}$$

For two identical bubbles, (48) reduces to (see Eq. (10))

$$12\mu \frac{\partial H}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r(1 + b + \frac{h_s}{H})H^3 \frac{\partial p}{\partial r} \right]. \tag{50}$$

If one uses Laplace's equation

$$p = p_{gas} - \frac{\sigma_o}{2} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial H}{\partial r} \right) \tag{51}$$

to eliminate the pressure, one obtains a differential equation for the film shape $H(r,t)$. The respective equation for tangentially immobile surfaces is obtained by setting $b = h_s = 0$.

Reasonably simple solution of this equation is possible only for small bubbles ($\varepsilon \ll 1$) in two thickness ranges: $h \ll F/2\pi\sigma_o$ and $h \gg F/2\pi\sigma_o$. The most interesting results, derived in Ref. 16 by using the method of Ref. 8, can be summarized as follows:

1) Small gap width ($h \ll F/2\pi\sigma_o$).

a)  As already discussed in Section 2, virtually plane-parallel film of thickness $h$ forms.

b)  Its velocity of thinning, $V = -dh/dt$, is

$$V/V_{immob} = 1 + b + h_s/h \tag{52}$$

where $V_{immob}$, the velocity of thinning of a deformable film with tangentially immobile surfaces (Ref. 8),

$$V_{immob} = 2\pi\sigma_o^2 h^3/\mu F R_c^2 = h^3 F/2\pi\mu R^4 \tag{53}$$

differs slightly from Reynolds' velocity. The velocity ratio in (52) is the same as for a plane-parallel film (cf. Eq. (9)).

c)  When the film is formed between two different bubbles  A  and  B  the radius of the line of contact is (see also Ref. 63)

$$R^2 = F\bar{R}_c/2\pi\bar{\sigma}_o \tag{54}$$

where effective bubble radius, $\bar{R}_c$, and surface tension, $\bar{\sigma}_o$, have been introduced:

$$\bar{R}_c = \frac{R_c^A R_c^B}{R_c^A + R_c^B} ; \quad \bar{\sigma}_o = \frac{\sigma_o^A \sigma_o^B}{\sigma_o^A + \sigma_o^B}. \tag{55}$$

Eq. (54) is true only when the contact angle between the film and the bubbles is zero.
The limiting cases of flat or solid surface are derived by making in (55) one of the radii
or surface tensions infinite, e.g. $R_c^B \to \infty$ or $\sigma_o^B \to \infty$. Eq. (55) comprises as particular
cases the various formulae so far derived (Deryaguin and Kussakov (Ref. 11), Allan et al.
(Ref. 10), Princen (Ref. 64) and Chappelear (Ref. 65)) as well as some other special cases,
e.g. contact between a solid particle and a bubble.

2) Large gap width ($h \gg F/2\pi\sigma_o$).

a) With negligible surface diffusion, $D_s = 0$, the shape of the slightly deformed bubbles
does not depend on the surface mobility, and the velocity of mutual approach, $V = -dh/dt$, of
two different bubbles A and B is

$$V/V_{immob} = 1 - 3\frac{4 - (K_b^A - K_b^B)(\Gamma_o^A - \Gamma_o^B)}{(K_b^A + K_b^B)(\Gamma_o^A + \Gamma_o^B)} \tag{56}$$

with

$$V_{immob} = Fh/6\pi\mu\overline{R}_c^2, \tag{57}$$

$K_b^{A,B} = (\partial\sigma_o^{A,B}/\partial c_o)/D\mu$ (cf. Eq. (49)); $h$ denotes the minimum gap width and $\overline{R}_c$ is defined
by Eq. (55). With $R_c^B \gg R_c^A = R_c$, Eq. (57) reduces to Taylor's formula (see for example
Brenner in Ref. 5) for the drag force on a solid sphere close to an infinite solid plane
If either of the surfaces is solid/liquid,

$$V/V_{immob} = (3 + 4b)/(3 + b), \tag{58}$$

and if they are both identical (two identical bubbles)

$$V/V_{immob} = 1 + b. \tag{59}$$

The velocity ratios (58) and (59) coincide with the respective expressions (9) and (14) for
plane-parallel films. With $c_o \to 0$, i.e. $b \gg 1$ and $R_c^B \gg R_c^A = R_c$, Eq. (58) yields
the small gap width's limit of Brenner's expression for the drag force on a solid sphere
approaching a flat surfactant-free gas/liquid interface (see also Ref. 1).

b) The surface diffusion affects the shape of the bubbles and leads to a mobility ratio
which is slightly different from (52):

$$V/V_{immob} = 1 + b + h_s/3h. \tag{60}$$

Since the effect of the surface diffusion decreases as the gap width, H, increases, its con-
tribution to the mobility ratio is smaller than for a plane-parallel film with thickness h.

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