THINNING OF FILMS WITH DEFORMABLE SURFACES: DIFFUSION-CONTROLLED SURFACTANT TRANSFER

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Abstract—General differential equations governing the shape of the film formed between two bubbles of different radii and surface properties are derived using the lubrication approximation. The role of a soluble surfactant with diffusion-controlled surfactant transfer onto the surface is analysed. Analytical solutions are obtained for the limiting cases of small and large deformations of the bubbles' caps. Results of previous investigators are also obtained under appropriate limiting conditions. The results are in qualitative agreement with the available experimental data.

1. INTRODUCTION

The process of attachment of a solid particle to a bubble is a very complicated one both from hydrodynamic and thermodynamic points of view. The particles are usually carried along the stream lines and can attach to the bubble only if the distance between the stream line and the bubble surface is small enough [1]. The attachment itself is, however, governed by the hydrodynamic processes taking place in the liquid film formed between the bubble and the particle: thinning, rupture and subsequent expansion of the perimeter of the three-phase contact line. Similar considerations hold for the coalescence of two bubbles or droplets. These processes are additionally influenced by the disjoining pressure (see e.g. [2–4]) in the thin film and the surfactant properties and repartition. The correct theoretical accounting of all these factors seems hardly possible for the time being, therefore some reasonably simplified models are needed. Such models can and have been used in two extreme cases. When the fluid particle (bubble or drop) is relatively far away from the other interface it is usually only slightly deformed and from the hydrodynamic point of view can be considered as being spherical. The problem for the movement of a non-deformed rigid sphere toward a plane surface was solved for the first time by Taylor [5]. In the opposite case, when the particle is close to the other interface, its cap is strongly deformed to the point of becoming flat (if the particle is small enough). A reasonable model for this situation is the plane-parallel film considered by Reynolds [6]. These models have been used by a number of investigators to account for the effect of the surface mobility on the film thinning (see e.g. [7, 8]). At the same time they suffer from a very important shortcoming, because of the assumed non-deformability of the interfaces, the normal stress boundary condition can be satisfied only integrally rather than locally. This, along with the experimental observation that in many systems the deformation can be so strong that the curvature at the cap of the particle can change sign and acquire a bell-type shape, called dimple, has led many investigators to use more refined treatments [9–17].

Most of the above treatments deal with systems with specific geometry (e.g. bubble approaching a plane solid surface) and pay little or no attention to the surface mobility of the interfaces. On the other hand, the only consistent way to check the ability of the Taylor and Reynolds' models to account for the effects of the surface mobility is to solve the more general case—a system with deformable and tangentially mobile surfaces and to compare the results which the simplified models lead to under the same circumstances.

Our aim will be now to formulate an approach as general as possible. We shall do that for the system shown in Fig. 1: two bubbles of different radii and interfacial properties moving toward each other along their axis of symmetry. This will allow us to obtain from the general equations the results derived previously for some particular systems: symmetrical film [11, 17] (between identical bubbles) or film between a bubble or solid sphere and an infinite interface: solid/liquid or fluid [10, 17–20].
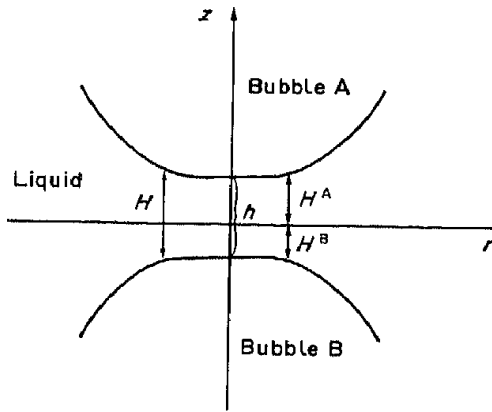
Fig. 1. Mutual approach, along the axis z, of two different bubbles A and B of radii R_c^A and R_c^B, and surface tensions σ^A and σ^B.

A more general treatment and a review of thin film dynamics in membrane systems is given elsewhere [20].

The basic hydrodynamic equations and boundary conditions will be formulated in lubrication approximation. We realize that in a limited number of circumstances, this approximation may not be valid [7, 21]. However, our analysis is restricted to small slowly moving bubbles where problems with the validity of the lubrication approximation should not arise.

In the present paper we will be concerned mostly with diffusion limited surfactant transfer, which is more frequently encountered with thin films [7]. In a subsequent paper [22] a more general mechanism of surfactant transfer will be considered but the treatment will be restricted to plane-parallel films. In the next section the basic equations and boundary conditions are formulated. In Section 3, the diffusion and Laplace's equations are used to derive a general equation allowing the calculation of the film shape and the drag force, F. This equation should be able to describe all stages of the film evolution. Similar, though less general, equations have been used by other authors for this purpose. However, we have some doubts concerning the correctness of such an approach. In fact, the experimental observations show [16, 23, 24] that at least with small bubbles (radii below 1 mm) the dimple persists up to a certain thickness and then is pushed out of the film and virtually a plane-parallel film forms. One gets the impression that at this moment an instability appears. No theoretical treatment based on the lubrication approximation has ever predicted such an instability. Therefore, we intend to apply our equations only to two limiting cases: (i) large separations between the two interfaces, when the deformations are small (Section 4) and (ii) small separations, when the dimple presumably has been already pushed out (Section 5). In this way we will obtain asymptotic results which allow in the former case to predict the initial deformation and in the latter case lead to the conclusion that the film is nearly plane-parallel. The results are discussed in Section 6.

The results should apply with good accuracy to emulsion films (drops rather than bubbles) with surfactant soluble in the continuous phase because for this system the liquid flow in the drops has virtually no influence [25-27]. The behaviour of the film depends on so many interacting effects that it is necessary to make, at certain stages of the derivation, some additional simplifications. Note that the range of validity of the approximations used depends strongly on the film thickness and the surfactant properties and both can vary widely.

2. BASIC EQUATIONS AND BOUNDARY CONDITIONS

When the bubbles are close enough and the surfactant concentration is not very low, the liquid flow is governed by the lubrication theory equations. Assuming that the flow is axisymmetric, we can write these equations in the form:

$$\frac{\partial p}{\partial r} = \mu \frac{\partial^2 V_r}{\partial z^2}, \tag{1a}$$

$$\frac{\partial p}{\partial z} = 0, \tag{1b}$$

$$\nabla_r V_r + \frac{\partial V_z}{\partial z} = 0; \quad \nabla_r = \frac{1}{r}\frac{\partial}{\partial r}r. \tag{1c}$$

Here μ is dynamic viscosity, p is pressure, V_r and V_z are velocity components (see Fig. 1). Equation (1) can be integrated by using the boundary conditions

$$V_r = U^{A,B} \quad \text{at } z = H^{A,B}, \tag{2a}$$

$$V_z = \pm\frac{\partial H^{A,B}}{\partial t} \pm U^{A,B} \partial H^{A,B} \quad \text{at } z = H^{A,B}, \tag{2b}$$

where t denotes time and the superscript A, B means that the respective equation is to be applied both to the upper film surface, $x = H^A(r)$, and the lower surface, $z = -H^B(r)$ (for the sake of brevity the notation $z = H^{A,B}$ will be used hereafter). From (1) and (2) we get

$$V_r = \frac{z^2}{2\mu}\frac{\partial p}{\partial r} + Az + B, \tag{3a}$$

$$A = \frac{U^A - U^B}{H} - \frac{H^A - H^B}{2\mu}\frac{\partial p}{\partial r}, \tag{3b}$$

$$B = \frac{U H^A - U^B H^B}{H} - \frac{H^A H^B}{2\mu}\frac{\partial p}{\partial r}, \tag{3c}$$

$$-\frac{\partial H}{\partial t} = \nabla_r\left[\frac{H}{2}(u^A + u^B) - \frac{H^3}{12\mu}\frac{\partial p}{\partial r}\right], \tag{3d}$$

where $H(r) = H^A + H^B$ is the local film thickness. Equation (3d) is the general integral form of eq. (1). The conditions under which it applies were discussed in [17]. The surface velocity U^A and U^B in (3d) can be expressed through the flow parameters by using the condition for continuity of the tangential component of the stress tensor. A general form of this condition was derived by Scriven [28]. For slow motion, axial

symmetry and with lubrication approximation it reads:

$$\pm \mu \frac{\partial V_r}{\partial z} = \frac{\partial \sigma^{A,B}}{\partial r} + \mu_s^{A,B} \frac{\partial}{\partial r} (\nabla_r U^{A,B}) \quad \text{at } z = H^{A,B},$$
(4)

where σ is surface tension and μ_s, denoting the sum of the surface dilational and shear viscosities, will be called for hereafter brevity surface viscosity. Other forms of the tangential boundary condition were derived and used in [29, 30].

In order to determine the dependence of σ on r the surfactant repartition has to be considered. We shall follow basically Levich's phenomenological procedure [31] which was recently given statistical–mechanical background by Brenner and Leal [32–35]. Following Levich we shall concern ourselves with the case of small deviations of the surface tension σ, the surfactant adsorption, Γ, and the bulk concentration, c, from the respective equilibrium values of σ_0, Γ_0 and c_0. Then the condition for surfactant conservation at the interfaces will read:

$$\Gamma_0^{A,B} \nabla_r U^{A,B} - D_s^{A,B} \Delta_r \Gamma^{A,B} = j_n^{A,B}$$

$$\text{at } z = H^{A,B}, \quad (5)$$

where

$$\Delta_r = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) = \nabla_r \frac{\partial}{\partial r},$$

D_s is the surface diffusion coefficient and j_n is the bulk surfactant flux along the normals $n^{A,B}$ to the film surfaces.

When writing down eq. (5), two terms were neglected: $\partial \Gamma / \partial t$ and $U \nabla_r \Gamma$. We shall be considering in this paper mostly the cases of regular drainage when all points of the two surfaces are steadily moving toward each other, although because of the deformation of the surfaces, with different speeds. If such is the case all quantities can be assumed to depend on time only implicitly, via the thickness along the axis of symmetry, $h = H(t, r = 0)$. We call this a quasi-steady state assumption. Then

$$\frac{\partial \Gamma}{\partial t} = - V \frac{\partial \Gamma}{\partial h} \sim \frac{V}{h} (\Gamma_0 - \Gamma),$$
(6)

where

$$V(0) \equiv V = - \frac{dh}{dt}.$$
(7)

The order of magnitude of the second term is $U \nabla_r \Gamma \sim U (\Gamma_0 - \Gamma) / R_f$, where R_f is the radial length scale, e.g. the film radius R_e (see Section 5). From the continuity equation (1c) $U \sim V R_f / h$ and the two terms turn out to be of the same order of magnitude. It was shown (see e.g. [7,20,36]) that usually the leading term in eq. (5) is

$$D_s \Delta_r \Gamma \sim D_s (\Gamma_0 - \Gamma) / R^2.$$
(8)

Then from (6) and (8) one gets

$$\frac{\partial \Gamma}{\partial t} / D_s \Delta_r \Gamma \sim Pe \frac{D}{D_s} \frac{R_f^2}{h^2},$$
(9)

where $Pe = Vh/D$ is Peclet number and D is bulk diffusivity. The ratio $D/D_s \sim 0.1$ [36] and R_f^2/h^2 must be at least 10^2 in order to use the lubrication theory. Therefore, Peclet number must be smaller than 10^{-3} in order to neglect the terms $\partial \Gamma / \partial t$ and $U \nabla_r \Gamma$. Although Pe is usually even smaller, it is clear that under certain circumstances, e.g. very low surfactant concentrations, the present theory will fail. More detailed estimates of the above and other approximations, for the case of a plane-parallel film are quoted in [7].

The explicit expression for j_n depends on the mechanism with which the surfactant is transported onto the surface. Since our present aim is to treat in more detail the deformation of the film surfaces, we must restrict ourselves with a single mechanism, the diffusion-limited surfactant transfer (i.e. slow diffusion).

In this approximation it is assumed that there is no hindrance to the adsorption of the surfactant molecules once they have reached the subsurface. If in addition the reorientation of the adsorbed molecules is very fast, both σ and Γ will depend only on the subsurface concentration [37, 38] $c_s = c(r, z = H^{A,B})$ and their relationship with c_s will be the same as in equilibrium. Then we can use

$$\frac{\partial \sigma^{A,B}}{\partial r} = \frac{\partial \sigma_0^{A,B}}{\partial c_0} \frac{\partial c}{\partial r}, \quad \text{at } z = H^{A,B}$$
(10)

$$\Delta_r \Gamma^{A,B} = \frac{\partial \Gamma_0^{A,B}}{\partial c_0} \Delta_r c \quad \text{at } z = H^{A,B}.$$
(11)

With small Peclet number the surfactant distribution in the bulk $c(r, z)$ is governed by the second Fick's law:

$$\Delta_r c + \frac{\partial^2 c}{\partial z^2} = 0.$$
(12)

In this way the bulk diffusion flux

$$j_n^{A,B} = - D \frac{\partial c}{\partial n^{A,B}} \quad \text{at } z = H^{A,B}$$
(13)

and the other quantities in eqs (4) and (5), dependent upon c and Γ, can be calculated.

Another boundary condition which has to be used is the condition for continuity of the normal component of the stress tensor at the interfaces. Although this condition is well known (see e.g. [28, 31, 39, 40]), its application to thin films requires some additional comments. In systems with curved interfaces the lubrication theory of eqs (1a)–(1c) are only valid in the region where the local thickness $H(r, t)$ is much smaller than the bubble radius R_c (the bubble's radii R_C^A and R_C^B) [41, 42]. Assuming that the bubble shape is spherical, simple geometric considerations indicate that $H/R_C < 0.1$ with $r < 0.4 R_C$. The radii of the dimple or the plane-parallel film are usually less than $0.05 R_C$ [23]. Therefore eq. (1) will govern the liquid flow in a fairly extensive region outside the film. The main purpose of our calculations will usually be the drag force which depends on the pressure gradient. Since $\partial p / \partial r$ is proportional to H^{-3}, only the region in close proximity to the axis of symmetry gives noticeable

contribution to the drag force. The above reasoning allows the assumption that eq. (1) is still valid relatively far away from the axis of symmetry, i.e. in regions where the flow does not influence the force balance and the liquid could be considered as being quiescent. Thus at large values of $r (r \to \infty)$ we can disregard any deviation from the equilibrium. Moreover, we can approximate the generatrix of the unperturbed interface in this region with a parabola. Under these conditions $\partial H^{A,B}/\partial r \ll 1$ and the normal component of the stress tensor reduces to the pressure p. The latter should obey the following equations:

$$p_g^{A,B} - p = \sigma_0^{A,B} \Delta_r H^{A,B}, \qquad (14)$$

$$p = p_1 = p_g^{A,B} - \frac{2\sigma_0^{A,B}}{R_C^{A,B}} \quad \text{at } r \to \infty \qquad (15)$$

where p_1 and $p_g^{A,B}$ are the pressures in the bulk liquid and the bubbles. The latter equation could be written also as

$$\Delta_r H^{A,B} = 2/R_C^{A,B} \quad \text{at } r \to \infty. \qquad (16)$$

To simplify the treatment, we have neglected in (14) the contribution of the disjoining pressure. It becomes sizable only with very thin films (< 500 Å) [43]. In this thickness range the film is either plane-parallel or ruptures [23, 44]. In (14) σ_0 stands for σ, because we have assumed that $(\sigma_0 - \sigma)/\sigma_0 \ll 1$.

The force balance, leading to the drag force, F, reads:

$$F \approx 2\pi \int_0^{R_C^{A,B}} (p - p_1) r \, dr \approx 2\pi \int_0^\infty (p - p_1) r \, dr$$

$$= 2\pi \sigma_0^{A,B} \left[r \frac{\partial (H_\infty^{A,B} - H^{A,B})}{\partial r} \right]\Big|_0^\infty \qquad (17)$$

where $H^{A,B}$ is the equation of the unperturbed surface at $r \to \infty$. Equation (17) can be applied only in two particular cases: (i) each of the bubbles experiences the same force F pushing them against each other and (ii) one of them is immobile while the other is pushed by a force F.

3. DIFFUSION-LIMITED SURFACTANT FLUX IN LUBRICATION APPROXIMATION

All the equations in Section 2 except eqs (12) and (13) were formulated in lubrication approximation. The use of eq. (12) in the form it stands is possible but inconvenient. First of all, this would lead to complicated calculations. Second, this procedure is obviously not self-consistent since it involves additional use of the lubrication approximation in the final results. For example, in the case of a foam, plane-parallel film of thickness h and radius R, expansion in series over $h/R \ll 1$ is needed [44]. These complications could be avoided by an appropriate formulation of the lubrication approximation for the surfactant bulk diffusion flux. For a plane-parallel film between two identical bubbles (or drops) this was done in [26] by representing $c(r, z)$ as a series $c(r, z) = c_0 + c^{(1)}(r) + c^{(2)}(r) z^2/2$. It was also shown there that whenever $c(r, z)$ is not differentiated with respect to z, the term with z^2 should be disregarded. The same

reasoning will obviously apply to a film with deformable interfaces between two different bubbles (or drops) but in this case a term linear with respect to z must be added. Therefore, we can assume the solution of (12) to be of the form

$$c(r, z) = c_0 + c^{(0)}(r) + c^{(1)}(r) z + c^{(2)}(r) \frac{z^2}{2}. \qquad (18)$$

From (12) and (18) we get:

$$\Delta_r c = -c^{(2)}.$$

Then, at $z = H^{A,B}$

$$\frac{\partial c}{\partial z} = c^{(1)} \pm H^{A,B} c^{(2)} = c^{(1)} \mp H^{A,B} \Delta_r c. \qquad (19)$$

We now need to represent $\partial c/\partial n$ in terms of the concentration gradients $\partial c/\partial z$ and $\partial c/\partial r$. Since in the lubrication approximation $\partial H/\partial r \ll 1$, from simple geometric considerations we obtain

$$\frac{\partial c}{\partial n^{A,B}} = \pm \left(\frac{\partial c}{\partial z} \right)_{z = H^{A,B}} - \frac{\partial c}{\partial r} \frac{\partial H^{A,B}}{\partial r}. \qquad (20)$$

From the identity

$$\nabla_r \left(H^{A,B} \frac{\partial c}{\partial r} \right) = H^{A,B} \Delta_r c + \frac{\partial c}{\partial r} \frac{\partial H^{A,B}}{\partial r} \qquad (21)$$

and (19) and (20) we finally get

$$\frac{\partial c}{\partial n^{A,B}} = \pm c^{(1)} - H^{A,B} \Delta_r c - \frac{\partial c}{\partial r} \frac{\partial H^{A,B}}{\partial r}$$

$$= \pm c^{(1)} - \nabla_r \left(H^{A,B} \frac{\partial c}{\partial r} \right), \qquad (22)$$

which has to be used in (13).

Another approximation we shall use will be to neglect the term with μ_s in (4). With plane-parallel foam and emulsion films the contribution of this term to the velocity of thinning is of the order of $\mu_s h/\mu R^2$ [26, 44]. Since $R \sim 10^{-2}$ cm the surface viscosity contribution can be neglected with $\mu_s < 0.1$ s.p. This term is however very important in the theory of the capillary waves [44, 45] when the radial length scale (the wavelength) could be of the order of 10^{-4} cm. Therefore, the present treatment will be valid mainly with relatively thick films, when the wave motion is of less importance.

With (3a)–(3c) and (10), eq. (4) acquires the more appropriate form:

$$\frac{H}{2} \frac{\partial p}{\partial r} \pm \mu \frac{(U^A - U^B)}{H} = \frac{\partial \sigma_0^{A,B}}{\partial c_0} \frac{\partial c}{\partial r}. \qquad (23)$$

On the other hand, from (5), (11), (13) and (22) we have

$$\Gamma_0^{A,B} \nabla_r U^{A,B} - D_s^{A,B} \frac{\partial \Gamma_0^{A,B}}{\partial c_0} \Delta_r c$$

$$= -D \left[\pm c^{(1)} - \nabla_r \left(H^{A,B} \frac{\partial c}{\partial r} \right) \right]. \qquad (24)$$

By writing eq. (24) separately for the upper and the lower surfaces and summing up we can eliminate $c^{(1)}$.

The result can be cast in the form $\nabla_r\{\ \} = 0$ and integrated over r. Since from symmetry considerations at $r = 0$, $U^A = U^B = 0$ and $\partial c/\partial r = 0$, the integration constant has to be zero to avoid singularities at $r = 0$. The final result, thus, reads:

$$\Gamma_0^A U^A + \Gamma_0^B U^B - \left(D_s^A \frac{\partial \Gamma_0^A}{\partial c_0} + D_s^B \frac{\partial \Gamma_0^B}{\partial c_0} + DH\right)\frac{\partial c}{\partial r} = 0. \tag{25}$$

The concentration gradient $\partial c/\partial r$ can be eliminated from (23) and (25). Thus two linear algebraic equations for U^A and U^B are obtained, whose solution is:

$$U^{A,B} = \frac{2 \pm (K^A - K^B)\Gamma_0^{B,A}}{(K^A + K^B)(\Gamma_0^A + \Gamma_0^B)}\frac{H^2}{2\mu}\frac{\partial p}{\partial r} \tag{26}$$

with

$$K^{A,B} = \frac{\partial \sigma_0^{A,B}/\partial c_0}{D\mu}\left[1 + \left(D_s^A \frac{\partial \Gamma_0^A}{\partial c_0} + D_s^B \frac{\partial \Gamma_0^B}{\partial c_0}\right)/DH\right]^{-1} \tag{27}$$

From (26) and (3d) we get the desired general expression:

$$\frac{\partial H}{\partial t} = \nabla_r\left\{\left[1 - 3\frac{4 + (K^A - K^B)(\Gamma^B - \Gamma^A)}{(K^A - K^B)(\Gamma_0^A + \Gamma_0^B)}\right]\frac{H^3}{12\mu}\frac{\partial p}{\partial r}\right\}. \tag{28}$$

For convenience we will now introduce the quantities

$$b^{A,B} = -3\mu D/\Gamma_0^{A,B}(\partial\sigma_0^{A,B}/\partial c_0) \tag{29}$$

$$h_s^{A,B} = -6\mu D_s^{A,B}/\Gamma_0^{A,B}(\partial\sigma_0^{A,B}/\partial\Gamma_0^{A,B}), \tag{30}$$

accounting for the bulk and surface diffusion effects respectively. After some algebraic manipulations, eq. (28) can be then written in the following form:

$$\frac{\partial H}{\partial t} = \nabla_r\left[(1 + \bar{b} + \bar{h}_s/H)\frac{H^3}{12\mu}\frac{\partial p}{\partial r}\right], \tag{31}$$

where

$$\bar{b} = [4\Gamma_0^A\Gamma_0^B b^A b^B + 3(\Gamma_0^A - \Gamma_0^B)(\Gamma_0^B b^B - \Gamma_0^A b^A)]/$$
$$(\Gamma_0^A + \Gamma_0^B)(\Gamma_0^A b^A + \Gamma_0^B b^B), \tag{32}$$

$$\bar{h}_s = 2\Gamma_0^A\Gamma_0^B(h_s^A b^B + h_s^B b^A)/(\Gamma_0^A + \Gamma_0^B)$$
$$(\Gamma_0^A b^A + \Gamma_0^B b^B). \tag{33}$$

when $\bar{h}_s/H \ll 1 + b$, i.e. when the surface diffusion effects can be disregarded, eq. (31) reduces to:

$$\frac{\partial H}{\partial t} = \frac{1 + \bar{b}}{12\mu}\nabla_r\left(H^3\frac{\partial p}{\partial r}\right). \tag{34}$$

With two tangentially immobile surfaces one must set in (34) $\bar{b} = 0$. This result could have been derived from (3d) by setting there $U^A = U^B = 0$. This case was first considered by Reynolds. If the two surfaces have the same nature (e.g. if they were both liquid/air), eq. (31) is still valid with $\bar{b} = b$ and $\bar{h}_s = h_s$. (We have dropped the superscripts, which are the same for both surfaces.) Note, however, that the radii of the bubbles are not assumed to be equal in this case.

When one of the surfaces (e.g. the lower one) is solid/liquid, one usually assumes that it is tangentially

immobile and the surfactant flux to it is zero, i.e.

$$U^B = 0 \tag{35a}$$

$$\left(\frac{\partial c}{\partial n}\right)_{z = -H^B} = 0. \tag{35b}$$

From (22) we have for this case

$$c^{(1)} = -\nabla_r\left(H^B\frac{\partial c}{\partial r}\right). \tag{36}$$

Then the square brackets in the right-hand side of (24) (written for the upper surface, $z = H^A$) are transformed as follows:

$$-\nabla_r\left(H^B\frac{\partial c}{\partial r}\right) - \nabla_r\left(H^A\frac{\partial c}{\partial r}\right) = -\nabla_r\left(H\frac{\partial c}{\partial r}\right).$$

Instead of (24) we then obtain for the upper surface the following equation (dropping the superscript A):

$$\Gamma_0\nabla_r U - D_s\frac{\partial\Gamma_0}{\partial c_0}\Delta_r c = D\nabla_r\left(H\frac{\partial c}{\partial r}\right).$$

The final result of the derivation for wetting films reads:

$$\frac{\partial H}{\partial t} = \nabla_r\left[\left(1 - \frac{3}{K^w\Gamma_0 - 1}\right)\frac{H^3}{12\mu}\frac{\partial p}{\partial r}\right], \tag{37}$$

where [cf. (27)]:

$$K^w = \frac{\partial\sigma_0/\partial c_0}{D\mu}\left[1 + D_s\left(\frac{\partial\Gamma_0}{\partial c_0}\right)/DH\right]^{-1}$$

This result could have been obtained from (28) by assuming

$$\Gamma_0^B = 0 \quad \text{and} \quad K^B = K^A - 2/\Gamma_0^A \tag{38}$$

which would ensure $U^B = 0$. We were not able, however, to find any physical basis for this formal transition. That is why the case of wetting films will be treated hereafter separately. In terms of the notations defined by eqs (29) and (30), eq. (37) reads:

$$\frac{\partial H}{\partial t} = \nabla_r\left[\left(1 + \frac{b + h_s/2H}{1 + b/3 + h_s/6H}\right)\frac{H^3}{12\mu}\frac{\partial p}{\partial r}\right]. \tag{39}$$

Thus far we have been concerned only with the surface mobility terms in eq. (3d). As already pointed out, beause of (1b), the pressure gradient $\partial p/\partial r$ can be expressed by eq. (14). At this point, a new variable, H^A or H^B, will appear in eq. (31) and/or (39). This variable can be eliminated via the relationship

$$\sigma_0^B\Delta_r H^B = \frac{2\sigma_0^B}{R_c^B} - \frac{2\sigma_0^A}{R_c^A} + \sigma_0^A\Delta_r H^A \tag{40}$$

using eqs (14) and (15). Equation (40) is easily integrated over r and the result can be put in the form

$$H^A = H - H^B$$

$$= \frac{\bar{\sigma}_0}{\sigma_0^A}H - \bar{\sigma}_0\left(\frac{1}{\sigma_0^A R_c^B} - \frac{1}{\sigma_0^B R_c^A}\right)\frac{r^2}{2}$$

$$+ \frac{\bar{\sigma}_0}{\sigma_0^B}h^A - \frac{\bar{\sigma}_0}{\sigma_0^A}h^B, \tag{41}$$

where

$$\bar\sigma_0 = \sigma_0^A \sigma_0^B / (\sigma_0^A + \sigma_0^B). \tag{42}$$

Equation (41) along with eq. (14) (written for the upper surface $z = H^A$) and (31) leads finally to:

$$\frac{12\mu}{\bar\sigma_0}\frac{\partial H}{\partial t} = \nabla_r\left\{\left[\left(1+\bar b+\frac{\bar h_s}{H}\right)H^3\right]\frac{\partial}{\partial r}\Delta_r H\right\}. \tag{43}$$

For wetting films one of the surface tensions, e.g. σ_0^B can be assumed infinitely large, so that $\sigma_0 = \sigma_0^A \equiv \sigma_0$. Then eqs (41) and (39) yield:

$$\frac{12\mu}{\sigma_0}\frac{\partial H}{\partial t} = \nabla_r\left\{\left[\left(1+\frac{b+h_s/2H}{1+b/3+h_s/6H}\right)H^3\right]\right.$$
$$\left.\times\frac{\partial}{\partial r}\Delta_r H\right\}. \tag{44}$$

The rest of the present paper is devoted to the solution of eqs (43) and (44).

The boundary conditions (16) and the force balance (17) are transformed in a similar way. Let us write the equation of the unperturbed local thickness H_∞ as

$$H_\infty = H_\infty^A + H_\infty^B = h_\infty + r^2/2\bar R_c, \tag{45}$$

where

$$\bar R_c = R_c^A R_c^B / (R_c^A + R_c^B) \tag{46}$$

and $h_\infty = H_\infty$ ($r = 0$) is the distance that would exist between the caps of the two bubbles if they were immobile. A more convenient form of (16) will then be

$$\Delta_r H = 2/\bar R_c \quad \text{at } r \to \infty \tag{47}$$

and the force balance becomes

$$F/2\pi\bar\sigma_0 = \left[r\frac{\partial(H_\infty - H)}{\partial r}\right]\Big|_0^\infty. \tag{48}$$

4. ONSET OF DEFORMATION AND VELOCITY OF MUTUAL APPROACH OF TWO DIFFERENT BUBBLES

At large separations the hydrodynamic interaction between the two surfaces is weak and the deviation from the spherical shape is small. As a result, in the framework of the lubrication approximation the solution can be written as $H = H_\infty + H_1$, where H_1 is the shape perturbation caused by the flow.

It is convenient at this stage to integrate eq. (43) over r and to write it in the form

$$x\frac{\partial H_1}{\partial x} = -\frac{3\mu\bar R_c^2}{\bar\sigma_0}\int_0^x \mathrm{d}x\int_\infty^x \frac{\mathrm{d}x}{(1+\bar b+\bar h_s/H)}\int_0^x \frac{\partial H}{\partial t}\mathrm{d}x, \tag{49}$$

where we have used the boundary condition (47) and have introduced the variable

$$x = r^2/2\bar R_c. \tag{50}$$

Note that the left-hand side of (49) includes only the perturbation H_1 and the right-hand side includes the total (local) thickness $H \gg H_1$. Therefore, eq. (49) can be solved by an iteration procedure, which consists of replacing in the right-hand side H by H_∞ from eq. (45).

One thus obtains:

$$x\frac{\partial H_1}{\partial x} = \frac{3\mu V_\infty \bar R_c^2}{\bar\sigma_0 \bar h_s \bar d}\left[\left(1+\frac{x}{h_\infty}+\bar d\right)\right.$$
$$\left.\times \ln\left(1+\frac{\bar d h_\infty}{h_\infty + x}\right) - (1+\bar d)\ln(1+\bar d)\right], \tag{51}$$

where the quantity

$$\bar d = \bar h_s/h_\infty(1+\bar b) \tag{52}$$

accounts for the diffusion effects. Here $V_\infty = -\mathrm{d}h_\infty/\mathrm{d}t$ is the velocity of thinning of the undeformed parts of the film. Equation (51) along with the force balance (48) leads to the final expression for the velocity of thinning, V_∞:

$$V_\infty = \frac{F\bar h_s}{12\pi\mu\bar R_c^2}\left[-1+\left(1+\frac{1}{\bar d}\right)\ln(1+\bar d)\right]^{-1}. \tag{53}$$

This equation has two limiting forms: (1) strong effect of the surface diffusion, i.e. $\bar d \gg 1$ or alternatively $\bar h_s/(1+b) \ll h$. Then (53) reduces to:

$$V_\infty = F\bar h_s/12\pi\mu\bar R_c^2(\ln\bar d - 1) \tag{54}$$

and (2) in the opposite case, $\bar d \ll 1$, i.e. weak effect of the surface diffusion, one obtains:

$$V_\infty = \frac{F h_\infty}{6\pi\mu\bar R_c^2}(1+\bar b+\bar h_s/3h_\infty). \tag{55}$$

Equation (51) could in principle be integrated one more time over x to give the film shape H. This would lead however to untractable results which would be, moreover, of little interest. Indeed, at large separations the effect of the surface diffusion can be hardly very strong, so that only the case $\bar d \ll 1$ is of real importance. In the latter case, (51) simplifies to [see also (55)]:

$$\frac{\partial H_1}{\partial x} = -\frac{F}{4\pi\bar\sigma_0}\frac{1}{(h_\infty+x)}\left[1-\frac{\bar d}{3}\frac{h_\infty}{(h_\infty+x)}\right], \tag{56}$$

which upon integration, leads to

$$H = h + x - \frac{F}{4\pi\bar\sigma_0}\left[\ln\left(1+\frac{x}{h_\infty}\right)+\frac{\bar d h_\infty}{3(h_\infty+x)}\right]. \tag{57}$$

Here we have used the boundary condition $H = h$ at $x = 0$ and have neglected the term with $\bar d^2$. (Note that $h \gtrsim h_\infty$).

Analogous treatment of eq. (44) leads to the following results:

$$x\frac{\partial H_1}{\partial x} = \frac{3\mu V_\infty \bar R_c^2}{16\bar\sigma_0(3+4b)h_\infty d_1^2}\left[\frac{9x}{h_\infty}\ln\frac{h_\infty+x+d h_\infty}{h_\infty+x}\right.$$
$$+9(1+d_i)\ln\frac{h_\infty+x+d_1 h_\infty}{(h_\infty+x)(1+d)}$$
$$\left.+\frac{d_1^2(3+4b)x h_\infty}{2(h_\infty+x)}\right], \tag{58}$$

$$V_\infty = \frac{2F h_\infty}{3\pi\mu\bar R_c^2}\left\{1+\frac{9h_\infty}{h_s}\left[\left(1+\frac{1}{d_1}\right)\right.\right.$$
$$\left.\left.\times\ln(1+d_1)-1\right]\right\}^{-1}, \tag{59}$$

where

$$d_1 = \frac{2h_s}{(3+4b)h_\infty}.$$ (60)

In the limit $d_1 \gg 1$, one has:

$$V_\infty = \frac{2Fh_\infty}{3\pi\mu R_c^2}\left(1 - \frac{9h_\infty}{h_s}\ln d_1\right).$$ (61)

In the other limiting case, $d_1 \ll 1$, eqs (58) and (59) lead to:

$$\frac{\partial H_1}{\partial x} = -\frac{F}{4\pi\sigma_0}\frac{1}{(h_\infty+x)}\left[1 - \frac{3d_1 h_\infty}{4(3+b)(h_\infty+x)}\right]$$ (62)

$$V_\infty = \frac{Fh_\infty}{6\pi\mu\bar{R}_c^2}\frac{(3+4b)}{(3+b)}\left[1 + \frac{3d_1}{4(3+b)}\right]$$ (63)

$$H = h + x - \frac{F}{4\pi\sigma_0}\left[\ln\left(1+\frac{x}{h_\infty}\right) + \frac{3d_1 h_\infty}{4(3+b)(h_\infty+x)}\right].$$ (64)

5. HIGHLY DEFORMED BUBBLES AT SMALL THICKNESSES

The method used in the previous section obviously cannot be applied when the two bubbles are close to each other and their caps are strongly deformed. In this case the behaviour of the system can be rather complicated. As it was already pointed out, in many cases dimples form (very often of irregular shape) and persist until the film ruptures or thinning stops. However, if the bubbles are small and the surface tension not very low, at thicknesses of the order of 1000 Å, the dimple (if there was any) disappears and the central part of the film has an (almost) uniform thickness. Our purpose will be now to investigate this particular case. It was treated in [17] for films with tangentially immobile surfaces. Although the calculations for the system under considerations in the present paper are much more complicated, the method used is essentially the same as the one used in [17]. Therefore, only outlines of the method and some important equations will be given in the present section.

In this case the shape of the bubbles exhibits two distinct regions: near the axis of symmetry, the caps are flat, whereas far away, the bubbles are practically spherical. We will try now to construct an interpolation formula, which has correct asymptotic behaviour at small and large values. (In the lubrication approximation the latter case corresponds to $r \to \infty$.) Let the dimensionless variable y be related to r by the following expression:

$$y = 1 + \kappa r^2.$$ (65)

To simplify the treatment we also use the quasi-steady assumption (see Section 1) which allows us to write:

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial h}\frac{dh}{dt} = -V\frac{\partial H}{\partial h}.$$ (66)

The boundary conditions at $r = 0$ in the present

sections are:

$$H = h$$ (67a)

$$\partial H/\partial r = 0$$ (67b)

$$\frac{\partial}{\partial r}(\Delta_r H) = 0.$$ (67c)

Equation (47) applies at $r \to \infty$ and the force balance in the form of eq. (48) can be used.

With eqs (65) and (66), eq. (43) takes the form

$$\alpha\left[\kappa'(y-1)\frac{\partial H}{\partial y} + \kappa H'\right]$$
$$= \frac{\partial}{\partial y}\left\{(y-1)[(1+\bar{b})H^3 + \bar{h}_s H^2]\frac{\partial^2}{\partial y^2}\right.$$
$$\left.\times\left[(y-1)\frac{\partial H}{\partial y}\right]\right\},$$ (68)

where

$$\alpha = 3\mu V/4\bar{\sigma}_0\kappa^3$$ (69)

and the primes indicate differentiation with respect to h. At large values of r, i.e. $y \to \infty$, we seek a solution of (68) in the form

$$H = y/2\kappa\bar{R}_c - (F/4\pi\bar{\sigma}_0)\ln y + a_0 + a_1 y^{-1}.$$ (70)

The coefficient before $\ln y$ in the last equation is chosen so that the force balance (48) is automatically satisfied. The undetermined coefficients a_0 and a_1 are functions of h. A relationship between a_0 and a_1 is obtained by substituting (70) in (68) and letting $y \to \infty$. The result is:

$$4\kappa^2\bar{R}_c^3\alpha\left[\kappa^2 a_0' - \kappa'/2\bar{R}_c - L\kappa\kappa'\right] = (1+\bar{b})(L-a_1),$$ (71)

where

$$L = F/4\pi\bar{\sigma}_0.$$ (72)

In the region $\kappa r^2 \ll 1$, it is more convenient to use directly eq. (43) in which eq. (66) has to be substituted for $\partial H/\partial t$. The thickness H can then be written as a power series of r, which satisfies the boundary conditions (67):

$$H = h + d_2 r^2 + d_4 r^4 + d_6 r^6.$$ (73)

The substitution of (73) in (43), after equating the coefficients before the equal powers of r, yields

$$\alpha^2\kappa^3 = 4d_4[(1+\bar{b})h^3 + \bar{h}_s h^2],$$
$$\alpha\kappa^3 d_2' = 8[3(1+\bar{b})h^2 + 2\bar{h}_s h]d_2 d_4$$
$$+ 36d_6[(1+\bar{b})h^3 + \bar{h}_s h^2].$$ (74)

Equation (70) can be written in the form of (73) by expanding $\ln y$ and y^{-1} in power series of κr^2. By equating this expansion to (73) we get four relationships between the coefficients in (70) and (73). Those are:

$$h = (2\kappa\bar{R}_c)^{-1} + a_0 + a_1$$
$$d_2 = (2\bar{R}_c)^{-1} - \kappa(a_1 + L)$$
$$d_4 = (a_1 + L/2)\kappa^2$$
$$d_6 = -(a_1 + L/3)\kappa^3.$$ (75)

After some algebraic manipulations, the set of equations (71), (74) and (75) reduces to:

$$\kappa\alpha = 2\left[(1+\bar{b})h^3 + \bar{h}_s h\right](2a_1 + L), \qquad (76)$$

$$8\kappa^2 h^2 \bar{R}_c^2 (L+2a_1)\left[(1+\bar{b})h + \bar{h}_s\right]\left[\kappa - \kappa a_1' - L\kappa'\right]$$
$$= (1+\bar{b})(L-a_1), \qquad (77)$$

$$2(L+2a_1)\left[3(1+\bar{b})h + 2\bar{h}_s\right]\left[\frac{1}{2\bar{R}_c} - \kappa(L+a_1)\right]$$

$$+ 2h(L+2a_1)\left[(1+b)h + \bar{h}_s\right]\left[L\kappa' + a_1\kappa' + a_1'\kappa\right]$$

$$= 6\kappa h\left[(1+b)h + \bar{h}_s\right]\left[L+3a_1\right]. \qquad (78)$$

The group $F/4\pi\bar{\sigma}_0 = L$ in (70) has dimension of length and is, therefore, the natural length scale for the process under consideration. For a particle moved by buoyancy force it becomes $L = R_c^3\Delta\rho g/3\bar{\sigma}_0$ where g is the gravitational acceleration and $\Delta\rho$ is the density difference between the particle and the continuous phase. For a bubble of radius 0.1 cm and a surface tension 30 dyne cm^{-1}, L is of the order of 10^{-2} cm, i.e. it is much larger than any thickness in the system considered here. Therefore, we can introduce the dimensionless quantities:

$$\tilde{h} = h/L; \quad \tilde{a}_1 = a_1/L; \quad \tilde{\kappa} = \kappa L\bar{R}_c \qquad (79)$$

and seek a solution of eqs (77) and (78) by expanding $\tilde{a}_1$ and $\tilde{\kappa}$ in power series of $\tilde{h}$:

$$\tilde{a}_1 = A_0 + A_1\tilde{h} + \ldots,$$
$$\tilde{\kappa} = \kappa_0 + \kappa_1\tilde{h} + \ldots. \qquad (80)$$

The result for the coefficients in (80) is $A_0 = 1, A_1 = 0$, $\kappa_0 = 1/2, \kappa_1 = 1/4$, etc.

By substituting (80) in (70) and (76), one gets the final results for $H(r, h)$ and V [see also (69)]. If one neglects all terms of the order of $\tilde{h}$, they read:

$$H = h + x - L\ln\left(1 + \frac{x}{2L}\right) - \frac{x}{2\left(1 + \frac{x}{2L}\right)} \qquad (81)$$

$$V = \frac{h^3\bar{\sigma}_0}{2\mu\bar{R}_c^2 L}(1 + \bar{b} + \bar{h}_s/h). \qquad (82)$$

Similar calculations for wetting films, based on eq. (44) lead to:

$$H = h + x - L\ln\left(1 + \frac{x}{2L}\right) - \frac{x}{2\left(1 + \frac{x}{2L}\right)} \qquad (83)$$

$$V = \frac{\sigma_0 h^3}{2\mu\bar{R}_c^2 L}\frac{3+4b+2h_s}{3+b+h_s/2h}. \qquad (84)$$

6. DISCUSSION

One of the purposes of the present paper was to derive differential equations governing the shape of the film formed between two bubbles with allowance made for the role of a soluble surfactant with diffusion controlled surfactant transfer onto the surface. The equations so obtained are (43) and (44). The former equation refers to the case of two fluid interfaces.

Neither the bubbles' radii nor the nature of the two interfaces are assumed to be the same. Indeed, the effective surface tension $\bar{\sigma}_0$ [eq. (42)], bubble radius $\bar{R}_c$ [eq. (46)], the bulk and surface diffusion factors $\bar{b}$ [eq. (32)] and $\bar{h}_s$ [eq. (33)] are represented through the respective quantities for each surface. By using suitable values, one can obtain various limiting cases of interest, e.g. mutual approach of two identical bubbles A and B ($R_c^A = R_c^B$, $\sigma_0^A = \sigma_0^B$, etc.), a bubble A approaching a flat fluid interface ($R_c^B = \infty$), etc., eq. (44) refers to the case of a fluid interface approaching a solid/liquid interface, the so-called wetting film. In this case the two particles A and B can have different radii of curvature, R_c^A and R_c^B, but the surface quantities σ_0, b and h_s refer only to the fluid surface.

The validity of eqs (43) and (44) is restricted by several approximations formulated during their derivation. The most important is the lubrication approximation. It restricts the solution to the case of small bubbles so that inertial effects can be neglected (see Section 1). The case of films with two fluid interfaces requires the presence of small amounts of surfactants to decrease the surface mobility. (The mutual approach of two bubbles in pure liquids was considered in [46–48].) If these two conditions are met, eqs (43) and (44) can be used as a basis for numerical investigation of the process.

We, however, attempted analytical solutions for the limiting cases of small and large deformation of the bubbles' caps, which allowed us to derive relatively simple expressions. In spite of some additional limitation, they lead to some interesting results, which we will discuss in the rest of this section. Most of the discussion will be centred around films with two fluid interfaces. The same effects are observed with wetting films, but due to the rigidity of the solid surface, which prevents the fluid from reaching high velocities, the effects are less pronounced. The reader interested in wetting films should refer to the respective equations derived in Sections 4 and 5.

The range of validity of the iteration procedure we used in Section 4 to solve eq. (49) will obviously depend both on the separation between the two bubbles and the distance from the axis of symmetry. Since we assumed that the perturbation $H_1(= H - H_\infty)$ of the local distance between the two surfaces is small, the larger the distance, h, between the caps of the bubbles, the smaller is their deformation and the better is the validity of our results. Similarly, the larger is r, the better eq. (51) describes the film shape. Since the general equations with the diffusion terms, d, are not amenable to simple interpretation, we will illustrate this point for the case of a film with tangentially immobile surfaces. The respective equations are obtained by setting $d = 0$. As already pointed out many experimental observations reveal that when the two bubbles are close enough the curvature at their caps, i.e. the derivative $\partial^2 H^{A,B}/\partial r^2$ can change sign and a dimple forms. The situation is more complicated when the two bubbles have different radii. Since experimentally usually the thickness of the film is recorded, then

the dimple formation can be assumed to occur when $\partial^2 H/\partial r^2 = 0$ at $r = 0$, though the surface of one of the bubbles may be convex. The radius of the dimple, i.e. the distance r_d, at which the thickness H has a minimum, is determined by the condition $\partial H/\partial r = 0$. In this way from (57), with $\bar{d} = 0$, one obtains

$$\bar{h}_i = F/4\pi\bar{\sigma}_0 \equiv L \tag{85}$$

$$r_d^2 = \frac{F\bar{R}_c}{2\pi\bar{\sigma}_0}\left(1 - \frac{h_\infty}{L}\right), \tag{86}$$

where $\bar{h}_i$ is the value of h_∞ at which the dimple appears. With $h_\infty \ll \bar{h}_i$ eq. (86) leads to the final value, R_c, of the dimple radius (see Appendix I). According to (85)

$$R_c^2 = \frac{F\bar{R}_c}{2\pi\bar{\sigma}_0}. \tag{87}$$

The latter equation, first published in [49], is the general expression for the radius of contact between two bubbles. The following particular case are of importance (Fig. 2): (1) $\bar{R}_c/\bar{\sigma}_0 = R_c/\sigma_0$, i.e. $R_c^2 = FR_c/2\pi\sigma_0$. This case is realized in Systems 1a (bubble—non-deformable plane surface), 1b (solid sphere with radius R_c plane deformable surface liquid/gas with surface tension σ_0) and 1c (two identical bubbles), (2) $\bar{R}_c/\bar{\sigma}_0 = 2R_c/\sigma_0$, i.e. $R_c^2 = FR_c/\pi\sigma_0$ (bubble—plane deformable surfaces liquid/gas both with surface tension σ_0) and (3) $\bar{R}_c/\bar{\sigma}_0 = R_c/2\sigma_0$, i.e. $R_c^2 = FR_c/4\pi\sigma_0$ (solid sphere—bubble with surface tension σ_0 both with equal radii). The equations for R_c for System 1a has been previously derived by Derjaguin and Kussakov [2]; for System 1b by Allan et al. [24]; for 1c, by Princen [50] and Lee and Hodgson [51] and System 2, by Chappelear [52]. The expression for R_c for System 3 has not been derived previously to our knowledge.

The only reported experiments more or less suitable for verification of eqs (85) and (86) are those of MacKay and Mason [53]. These authors have carried out measurements with very small bubbles and have recorded approximately the thickness $\bar{h}_i$ of dimple formation and the radius r_d. They have shown that r_d is close to but smaller than the equilibrium radius of contact R_c and that it enlarges with the thinning of the film. These observations agree with our formula (86). The only parameter MacKay and Mason have
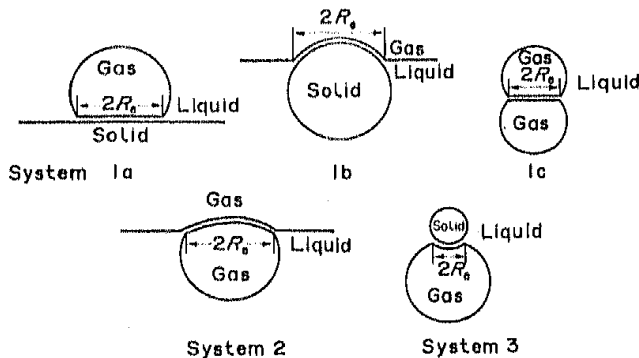
varied (in very narrow limits) is the bubble radius, R_c. In Fig. 3 their experimental data for the thickness of dimple formation, $\bar{h}_i$, are plotted vs R_c. The slope, $d\ln h_i/d\ln R_c$, is very close to its theoretical value 3 [see eq. (85), where $F \sim R_c^3$]. Despite this qualitative correct behaviour of our result, one must note that the quantitative agreement between theory and experiment is very poor—the theoretical values are several times higher than the experimental ones. One possible reason for this discrepancy could be due to the high velocity of motion of the bubble at these thicknesses. The latter could have resulted in a delay in the onset of the dimple formation. A much more probable explanation, however, is the fact that the theory can not be applied at thicknesses where the dimple forms. This conclusion corroborates the discussion in the beginning of the present section on the range of validity of our results. From the same viewpoint it is clear why the results for the dimple radius should be in much better agreement with the experiment. Indeed, the dimple radius lies in the region where the bubble deformation is very slight. That is why it should not be surprising that the obviously incorrect limiting conditions $h_\infty \to 0$ in (86) leads to the correct expression (87) for R_c.

It is possible to derive from (57) relatively simple analogs of eqs (85) and (86) for the case $\bar{d} \ll 1$. The results read:

$$\bar{h}_i = L\left(1 - \frac{\bar{d}}{3}\right), \tag{88a}$$

$$r_d^2 = \frac{F\bar{R}_c}{2\pi\bar{\sigma}_0}\left[1 - \frac{2\bar{d}h_\infty}{3L} - \frac{h_\infty}{L}\right]. \tag{88b}$$

It is not possible in (88b) to take the limit $h_\infty \to 0$, since at that limit $\bar{d} \to \infty$, which contradicts the assumption made in deriving (57). The second term in the square brackets in (88a) will decrease the values of the thickness of dimple formation, $\bar{h}_i$, as compared with those calculated from (85) and will bring the theory in somewhat closer agreement with the results of MacKay and Mason. However, at thicknesses of the
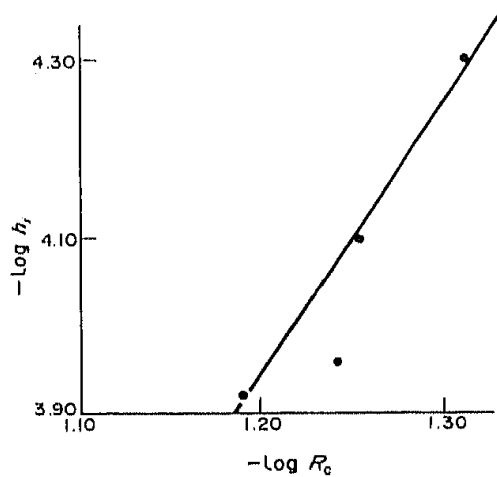

Fig. 3. Comparison between experimental data (●) and analysis of the film thickness at the onset of dimple formation, h_i versus bubble radius, R_c. Data were obtained from Ref. [54].

Fig. 2. Equilibrium contact between particles with gas/liquid or solid/liquid interfaces.

order of 10^{-4} cm the diffusion term can be hardly big enough to account for the whole discrepancy between theory and experiment.

Another indirect experimental check of the present theory is the fact that it leads (see Appendix II) to the experimentally observed [54] dependence of the dimple radius, r_d, on the time, t, elapsed since the moment of dimple formation:

$$r_d = \beta t^{1/2}. \tag{89}$$

For the case of a rising bubble

$$\beta = \frac{F}{2\pi \sqrt{3\mu\bar{\sigma}_0 R_c}}.$$

Unfortunately, no quantitative comparison with the experimental results of Sagert and Quinn [54] is possible because their experiments were not done with rising bubbles. If, however, the driving force in their experiments had been kept constant (which is probable) there is no reason to doubt that the same functionality of r_d with t, i.e. eq. (89), will be observed in experiments with rising bubbles. We are not aware of similar experimental data.

Equation (53), as well as its simplified forms (54) and (55), are generalizations of the familiar Taylor's formula for the velocity, V_T, at which a solid sphere of radius R_c, is approaching a rigid flat surface:

$$V_T = F h_\infty / 6\pi\mu R_c^2. \tag{90}$$

The latter equation follows from (53) or (55) by setting $\bar{h}_s = \bar{b} = 0$ and $R_c^B \to \infty$. Equations (53)–(55) however account not only for the different curvatures of the two surfaces and for their surface mobilities (through $\bar{b}$ and $\bar{h}_s$), but are also valid for slightly deformed spheres. The latter is obvious from the way they were derived in Section 4.

The general effect of the diffusion terms, which account for the surface mobility, is to increase the velocity of thinning V_∞ and the deformability of the surfaces. The latter is accounted for by the perturbation terms. Due to the increasing distance between the two surfaces with r, the effect of the surface diffusion on the velocity of thinning, however, is less pronounced than for two bubbles with strongly deformed caps (*cf.* e.g. eq. (55) with eq. (91) below].

A peculiarity of the equations, describing the film profile, that is worth noting, is the fact that the bulk and surface diffusion terms are coupled—they enter as a group $\bar{d} = \bar{h}_s / h_\infty (1 + \bar{b})$. Only at very large thicknesses, when $\bar{d} \to 0$, the surface diffusivity can be disregarded. In this case $\bar{h}_s$ in (55) can be put equal to zero. From the respective eq. (57) or H it follows that the film profile will not depend then on the bulk diffusion, i.e. it will be the same as for a film with tangentially immobile surfaces. The latter conclusion was already reached in [11] for the case of two identical bubbles with bulk diffusion-controlled surfactant transfer. The equations for V_∞, H, $\bar{h}_i$ and r_d, derived in [11] can be obtained from the respective equations of the present paper by setting $\bar{h}_s = 0$,

$R_c^A = R_c^B$ and $b^A = b^B$. The case of a bubble with tangentially immobile surface ($U^A = 0$) approaching a solid plane, considered in [10] corresponds to a wetting film from the present paper with $R_c^B \to \infty$ and $h_s = b = 0$. Since the derivation in [10] and [11] was carried out by the method of expansion in terms of the small parameter $F/2\pi\sigma_0 R_c$ the coincidence of the results is an additional argument in favour of the correctness of the used perturbation procedures.

A procedure similar to the one used in the present paper was employed by Dukhin *et al.* [18] for the particular case of a solid sphere approaching a flat liquid surface with surfactant obeying Henry's adsorption isotherm, i.e. Γ_0/c_0 = constant. Their result for V_∞ coincides with our eq. (59) for small concentrations, i.e. when $\partial r_0/\partial c_0$ can be approximated by Γ_0/c_0. We found however a difference in the numerical coefficient before the term with h_s/h_∞. We obtain its value equal as 9, and they obtain 9/2.

In the case of strongly deformed bubbles (Section 5), the results deserving most attention are eq. (82), giving the velocity of thinning of a film with fluid interfaces and eq. (84) for the velocity of thinning of wetting films. With $\bar{b} = \bar{h}_s = 0$ and $R_c^B \to \infty$ (i.e. $\bar{R}_c = R_c^A$) it coincides with the equation previously derived in [17] for a deformable bubble approaching a solid plane surface. We will only briefly summarize the most important conclusions already reached to in Ref. [17]. The analysis of eq. (81) reveals that the function $H(r)$ exhibits only one extremum—a minimum at $r = 0$. At the same time in a rather extensive region, whose radius is of the order of $\kappa^{-1/2}$, the film is almost plane-parallel. This means that this whole central part thins with the same velocity, V, given by eq. (82). A rather unusual result, already pointed out by Hartland [12] is that V is inversely proportional to the driving force, F, through L. This apparent contradiction is due to the fact that the film radius, R_c, according to (87) also depends on F. If one eliminates $\bar{R}_c$ between (82) and (87), one obtains:

$$V = V_0(1 + \bar{b} + \bar{h}_s/h) \tag{91}$$

where

$$V_0 = \frac{F h^3}{2\pi\mu R_c^4} \tag{92}$$

is the velocity of thinning of a deformable film with tangentially immobile surfaces. Equation (92) is a generalization of eq. (28) from [17] for the case of different bubbles. As already discussed in [17], this equation differs only with a numerical coefficient from the well known formula of Reynolds for the velocity of thinning, V_{Re}, of a film between two circular rigid discs of radius R_c. More specifically, $V_0 = \frac{3}{4} V_{Re}$. Since experimentally the film radius is determined with a precision not better than 10% [23], one is unable to conclude that V_0 coincides practically with V_{Re}. Another important feature of eq. (92) is the fact that V_0 is proportional to h^3 which is in agreement with the experimental findings of many authors (see e.g. [23]). One must point out that theories, predicting thin films with dimples, lead to different functionality of V_0 on h

(see e.g. [9, 11]). All the above arguments strongly bear out the applicability of the model of the plane-parallel film. This conclusion, which was already reached in [17], is also corroborated by the results of Buevich and Lipkina [13], Jones and Wilson [15] and Barber and Hartland [8]. At the same time one must keep in mind that our theory and, therefore, the validity of the above conclusion is restricted to small bubbles, namely for bubbles radii satisfying the condition [17]:

$$\frac{R_c}{\bar{R}_c} = \left(\frac{F}{2\pi\bar{\sigma}_0 \bar{R}_c}\right)^{1/2} \ll 1. \tag{93}$$

When the system consists of two bubbles of different radii, e.g. bubble approaching a flat fluid interface, the two film surfaces will still be parallel but no longer plane. Since our theory is valid only when $\partial H^{A,B}/\partial r \ll 1$, the results can be used only for small film curvature; when the curvature is high the approach developed by Hartland [12] for a spherical film is more appropriate. The above results can be used also for films formed in small capillary tubes but then the driving force has to be expressed through the capillary pressure of the miniscus (see [17]).

In a series of previous works (see e.g. [7] and refs therein), it was shown that the velocity of thinning, V, of a foam (symmetric) plane-parallel film with diffusion controlled surfactant transfer is:

$$V = V_{Rc}(1 + b + h_s/h). \tag{94}$$

The latter equation is in fact identical with eq. (91) and describes the same dependence of the velocity of thinning of a film with deformable surfaces on the surfactant properties and concentration.

Similar results hold for a wetting film. By eliminating R_c between (84) and (87), one obtains

$$V = V_0 \frac{3 + 4b + 2h_s}{3 + b + h_s/2h}, \tag{95}$$

where V_0 is given again by (92). For a plane-parallel wetting film the respective equation reads [7]:

$$V = V_{Re} \frac{3 + 4b + 2h_s}{3 + b + h_s/2h} \tag{96}$$

which is practically the same as eq. (95). The reader is referred to [7] for detailed discussion of the role of the bulk and surface diffusion on the thinning of foam and wetting films.

Equations (81) and (83) reveal that the film shape at small thicknesses does not depend on kinetic parameters such as liquid viscosity. The same is true at large separations when the effect of the surface diffusion can be neglected (see above). Princen [50] reached intuitively the same conclusion. It is no longer true, however, at large separations and significant surface diffusion $(\bar{d} \gtrsim 1)$ when the film surfaces have larger surface mobility and can undergo fast deformations. Then the film shape depends, through $\bar{d}$, on the viscosity and the Marangoni–Gibbs effect. Yet, the effect of the liquid viscosity will probably still be very small if one can assume that the product μD_s, similar to μD, does not depend on μ.

NOTATION

a_0, a_1	coefficients in the expansion at $y \to \infty$, eq. (70)
$\tilde{a}_0 = \dfrac{a_1}{L}$	non-dimensional coefficient, eq. (79)
A, A	integration constant, eq. (3b); superscript for the surface of bubble A
$A_0, A_1, \ldots$	coefficients in the expansion of $\tilde{a}_1$ at small thicknesses, eq. (80)
$b^{A,B}$	$-3\mu D/\Gamma_0^{A,B}(\partial\sigma_0^{A,B}/\partial c_0^{A,B})$, bulk diffusion exchange coefficient, eq. (29)
$\bar{b}$	average bulk diffusion exchange coefficient, defined by eq. (32)
B, B	integration constant, eq. (3c); superscript for the surface of bubble B
c	bulk surfactant concentration
c_0	equilibrium bulk surfactant concentration
$c^{(0)}, c^{(1)}, c^{(2)}$	coefficients in the expansion of $c(r, z)$, eq. (18)
c_s	subsurface concentration
$\bar{d}$	$\bar{h}_s/h_\infty (1 + \bar{b})$, eq. (52)
d_1	$2h_s/h(3 + 4b)$, eq. (60)
d_2, d_4, d_6	coefficients in the expansion of H at small r, eq. (73)
D	bulk diffusion coefficient
$D_s^{A,B}$	surface diffusion coefficients for bubbles A and B
F	driving force
h	$H(r = 0)$, for deformed bubbles or thickness of plane-parallel film
h_∞	the distance at $r = 0$ between the two undeformed bubbles
$\tilde{h}$	h/L
h_i	thickness at which the curvature changes its sign, eq. (85)
$h_s^{A,B}$	$-6\mu D_s^{A,B}/\Gamma_0^{A,B}(\partial\sigma_0^{A,B}/\partial\Gamma_0^{A,B})$, eq. (30)
$\bar{h}_s$	quantity defined by eq. (33)
H	$H^A + H^b$, local film thickness
H_∞	$h_\infty + r^2/2\bar{R}_c$, parabola, describing the local distance between the nondeformed bubble surfaces
j_n	bulk surfactant flux to the film surface, eq. (5)
$K^{A,B}$	defined by eq. (27)
K^w	defined by eq. (37)

L	$F/4\pi\bar{\sigma}_0$
$n^{A,B}$	normal to the bubble surfaces
P	hydrodynamic pressure
$P^{A,B}$	pressure in the bubbles A and B
P_1	equilibrium pressure in the bulk liquid
Pe	Vh/D, Peclet number
r	radial coordinate
r_d	dimple radius, eq. (86)
R_1, R_e	film radius, eq. (87)
$R_c^{A,B}$	bubble radii
$\bar{R}_c$	$R_c^A R_c^B/(R_c^A + R_c^B)$, eq. (46)
R_f	radial length scale
R^f	radius of curvature of the film, Figs A1 and A2
t	time
$U^{A,B}$	surface velocities
V	$-\partial H/\partial t$, local velocity of thinning
$V(0)$	$-dh/dt$, velocity of thinning at $r = 0$
V_∞	$-dh_\infty/dt$, rate of approach of the nondeformed surfaces
v_r, v_z	radial and axial velocity components
x	$r^2/2\bar{R}_{c_2}$
y	$1 + \kappa r^2$ dimensionless variable, eq. (65)
z	axial coordinate

Greek letters

α	$3\mu V/4\bar{\sigma}_0\kappa^3$, eq. (69)
β	$\dfrac{F}{2\tilde{n}\sqrt{3\mu\,\bar{\sigma}_0\bar{R}_c}}$
Γ	surface concentration
Γ_0	equilibrium surface concentration
κ	$(\kappa^{-1/2} \sim R_f)$, eq. (65)
$\tilde{\kappa}$	$\kappa L/\bar{R}_c$, eq. (79)
κ_0, κ_1	coefficients in the expansion of $\tilde{\kappa}$, eq. (79)
μ	bulk viscosity
μ_s	surface viscosity equal to the sum of the dilational and shear viscosities
σ	surface tension
$\sigma_0^{A,B}$	equilibrium surface tension of bubbles A and B, respectively
$\bar{\sigma}_0$	$\sigma_0^A\sigma_0^B/(\sigma_0^A + \sigma_0^B)$, eq. (42)
∇_r	$\dfrac{1}{r}\dfrac{\partial}{\partial r}r$
Δ_r	$\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial}{\partial r}\right) = \nabla_r\dfrac{\partial}{\partial r}$
$\Delta\rho$	density difference

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APPENDIX I
ON THE FORCE BALANCE OF SYSTEMS INVOLVING SMALL BUBBLES

Equation (87) for the "equilibrium" radius of the line of contact between the two bubbles was obtained as a limiting case of eq. (86) for $h_n \ll L$. We are presenting here a "quasistatic" derivation of eq. (87) which reveals better its main features and limitations.

Let us assume that the upper bubble "A" is immobile and the lower is pushed upward by the buoyancy force, F. We assume also that the film is thick enough so that the only role of the second (upper) surface is to change the pressure inside the film to a value, p^f, different from the bulk pressure, p^l. Note that the difference between p^f and p^l can be due both to static and hydrodynamic interactions between the two surfaces. In the latter case, the thinning process must be slow enough. Let the average pressure in the film be p^f. The force balance for the bubble "B" in vertical direction will then read

$$\pi R_c^2 (p^f - p^l) = F. \tag{A.1}$$

The static (thermodynamic) interactions, if there are any, are supposed to be so small that the two film surfaces (which are assumed also parallel) have the same surface tensions as the respective bubbles, σ_0^A and σ_0^B. Then from Laplace's equation applied to the film and bubble A surfaces, one obtains

$$p^f - p^l = 2\sigma_0^A \left(\frac{1}{R_0^A} - \frac{1}{R^f} \right), \tag{A.2}$$

where R^f is the radius of curvature of the film. Equation (A.2) will be true if the bubble is small enough to be spherical. On the other hand, the difference in gas pressure between the two bubbles can be written as

$$p_g^A - p_g^B = 2 \left(\frac{\sigma_0^A}{R_c^A} - \frac{\sigma_0^B}{R_c^B} \right) = \frac{\sigma_0^A + \sigma_0^B}{R^f} \tag{A.3}$$

which leads, after some algebra, to

$$\frac{1}{R_c^A} - \frac{1}{R^f} = \frac{\sigma_0^B}{\sigma_0^A + \sigma_0^B} \left(\frac{1}{R_c^A} + \frac{1}{R_c^B} \right). \tag{A.4}$$

Thus eqs (A.1), (A.2) and (A.4), along with (42) and (46) yield eq. (86), we seek:

$$R_c^2 = F \bar{R}_c / 2\pi \bar{\sigma}_0. \tag{A.5}$$

The situation is quite different when the film is so thin that there is a strong thermodynamic interaction between the two film surfaces. In this case the film can be considered as a membrane with film tension $\gamma \neq \sigma_0^A + \sigma_0^B$ (see Fig. A.2) and eq. (A.3) can be modified by substituting γ^f for $\sigma_0^A + \sigma_0^B$ in its right-hand side. Since the bubbles are again spherical, the following geometrical relations hold:

$$R_c = R^f \sin\theta = R_c^A \sin\theta^A = R_c^B \sin\theta^B. \tag{A.6}$$

Equations (A.6) and the modified eq. (A.3) then yield

$$\gamma^f \sin\theta = \sigma_0^A \sin\theta^A - \sigma_0^B \sin\theta^B \tag{A.7}$$

which is nothing but the familiar Newmann–Young equation taken in vertical direction. This is a rigorous result for the case of spherical bubbles. In other words, when the bubbles are assumed spherical, i.e. when eqs (A.6) and the modified eq. (A.3) are used, their equilibrium is determined solely by surface forces and *there can be no contribution of the buoyancy force to the force balance*. This system is similar to a floating lens, considered by Princen [55].

The above considerations should be true for any system containing small (spherical) bubbles. In the case of a bubble attached to a fluid flat surface (i.e. $R_c^B \to \infty$) one is bound to set in (A.7) $\theta^B = 0$ and the force balance becomes $\gamma^f = \sigma_0^A \sin\theta^A$. For example, Princen in his analysis of the equilibrium of very small bubbles and lenses [55] always assumed the planar surface undeformed.

Therefore, it does not seem correct to assume some elevation of the contact line above the level of the bulk liquid (as shown in Fig. A.3) and to include the buoyancy force in the force balance on the one hand and at the same time to consider the lower part of the bubble as part of a sphere. In other words, it is not correct to apply to it relationships of the kind given by eqs (A.2), (A.3) and (A.6).
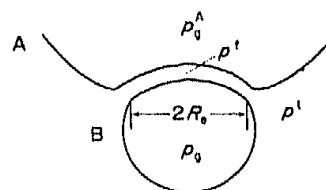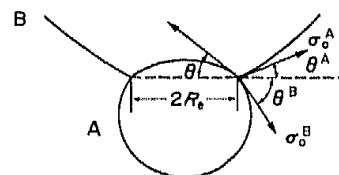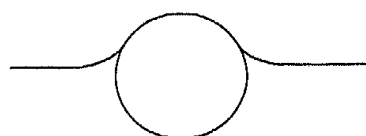

Fig. A.1.

Fig. A.2.

Fig. A.3.

APPENDIX II

ON THE RATE OF EXPANSION OF THE RADIUS OF THE DIMPLE

Equation (89) can be derived in several ways, but the simplest seems to be to use an iteration procedure similar to that already used throughout this paper. Since the dimple forms at a thickness $\bar{h}_i = L$ [eq. (85)] and increases its radius very fast one can assume that the latter process takes place in a thickness range $\Delta h \ll L$. By setting $h_\infty = L - \Delta h$, eq. (55)

(with $\bar{b} = \bar{h}_s = 0$) can be written as follows

$$V_\infty = -\frac{dh_\infty}{dt} = \frac{d\Delta h}{dt} \approx \frac{FL}{6\pi\mu \bar{R}_c^2},$$ (A.8)

Thus from (A.8) and eq. (86) upon integration (with $\Delta h = 0$ at $t = 0$), one obtains

$$r_d^2 = \frac{F^2}{12\pi^2\mu^2\bar{\sigma}_0\bar{R}_c}t$$ (A.9)

which is eq. (89).