Hydrodynamics of Thin Liquid Films. On the Rate of Thinning of Microscopic Films with Deformable Interfaces

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Received April 21, 1976; accepted September 7, 1977

The process of thinning of a film formed between a deformable bubble and a solid substratum is considered. The solution is obtained by matching the asymptotic coordinate expansions, valid both in the vicinity of and at a distance from the axis of symmetry. It is demonstrated that when the interfaces are at a short distance from each other, the film can be considered as being practically plane-parallel. An expression is deduced for the rate of thinning of such a film, coincident in form with the well-known law of Reynolds. With the surfaces further apart from each other, equations are obtained for the deformation of the bubble and for the rate of its approach to the solid substratum.

1. INTRODUCTION

When interpreting the experimental data for the rate of thinning of microscopic foam and emulsion films, Reynolds' equation (Eq. [26] of this work) is currently used (see, e.g., (1–4)). However, it is well known that its applicability to foam and emulsion systems is questionable for two main reasons: (a) the film surfaces are not tangentially immobile, and (b) they are deformable and not plane-parallel. The first effect was taken into account by Radoev *et al.* (5, 6), and Ivanov and Dimitrov (7) for foam films, and by Murdoch and Leng (8), Reed *et al.* (9, 10), Ivanov and Traikov (11) and Traikov and Ivanov (12) for emulsion films. The second effect was considered theoretically by Princen (13), Lee and Hodgson (14), Hartland (15–17), Frankel and Mysels (18), and Radoev and Ivanov (19). In the main however, these studies deal either with the initial or middle stage of the film's evolution, when the deformation of the film surfaces and/or the deviation from Reynolds' equation are considerable. On the other hand, experimental investigations reveal that with sufficiently small thicknesses and bubble radii and high surfactant concentrations, the film surfaces are almost plane-parallel and the rate of thinning concurs reasonably well with Reynolds' equation (1–4).

True, the film's radius in these experiments is not too precisely set, but the film's thickness is measured directly. Therefore, though the applicability of Reynolds' law can be questioned with respect to the dependence of the rate of thinning on the film radius, with respect to the thickness, it is considered as being firmly established that with sufficiently thick films, where the disjoining pressure is so small as to be negligible, the rate of thinning is proportional to the third power of the thickness (1).

Hartland (15) has numerically calculated the alteration of the film's profile with time, making use, as initial condition, of the experimentally defined profile at a certain moment. It was found that the film's deformation at the center diminished as it thinned, but that a ring of lesser thickness remained along its perimeter. The theoretical analysis of the thinning of films

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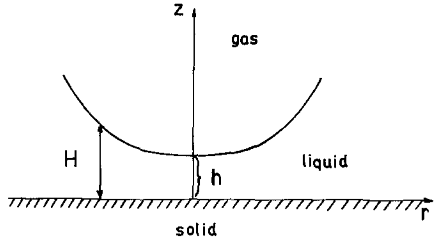

FIG. 1. Gas bubble moving along the axis z toward a solid plane.

at lesser thicknesses entails considerable mathematical difficulties, arising from the nonlinearity of the equations and from the numerous effects to be taken into account. Nevertheless, a number of theoretical treatments have recently appeared on this problem (20–24). In the main, these studies analyze the nature of the flow and the shape of the surface; they indicate that the profile of the surface may differ greatly, depending on the model used and on the thickness at the film's center. The various laws of thinning deduced greatly differ from Reynolds' law (20, 22).

This diversity of results is obviously associated with the complexity of the process itself, which may proceed in a different manner in each individual case. On the other hand, however, the above-cited experimental investigations indicate that conditions should exist at which Reynolds' law (in particular the proportionality of the rate of thinning to the third power of the thickness) is applicable. The present work is intended to demonstrate that it is possible for the film to be practically plane-parallel and to thin out in accordance with a law differing only in its numerical coefficient from Reynolds' law. Although only the case of a film formed by pressing a gas bubble against a solid substratum is considered, this conclusion is also valid for a film formed between two identical bubbles. The effect of the disjoining pressure will be taken into account in a subsequent paper. Since the presently used method of matched coordinate expansions is also applicable for a larger separation between bubble and substratum, in Section 5 we have again derived the results previously obtained in a different manner by Radoev and Ivanov (6, 19).

2. FORMULATION OF THE PROBLEM

The liquid flow is governed by the lubrication theory equations, which, for axial symmetry, have the form

$$\frac{\partial P}{\partial r} = \mu \frac{\partial^2 v_r}{\partial z^2}; \qquad [1a]$$

$$\frac{\partial P}{\partial z} = 0; \qquad [1b]$$

$$\nabla_r v_r + \frac{\partial v_z}{\partial z} = 0; \quad \nabla_r = \frac{1}{r}\frac{\partial}{\partial r} r. \qquad [1c]$$

Here μ is dynamic viscosity, P is pressure, and v_r and v_z are velocity components (see Fig. 1). Equations [1] are only valid if the interval H between the two film surfaces is much inferior to the bubble radius R_c (19, 25, 26). Assuming that outside of the film the bubble is spherical in shape, simple geometric reasoning indicates that $H/R_c \leqq 0.1$, with $r \lessapprox 0.4R_c$. As the film radius is usually inferior to 0.05 R_c (1) Eqs. [1] will also describe the flow in a fairly extensive region outside of the film, where there still is a noticeable dissipation of energy. Outside of this region, the flow has an insignificant effect on the balance of forces and can be disregarded, as the pressure gradient is proportional to H^{-3} (19). This, at high values of r ($r \to \infty$), makes it possible to disregard any surface deformation and to approximate the shape of the surface to a parabola (see [7]).

We shall formulate the boundary conditions in a more general form, as it will allow us to derive a differential equation applicable in other cases as well. Let us suppose we have not just one, but two bubbles A and B approaching each other along their line of centers (Fig. 2). The equations of the generatrices of their surfaces are $H^A = H^A(r)$ and $H^B = H^B(r)$ and the thickness of the liquid core is $H = H^A + H^B$. In the region where the energy is mainly dissipated (see above), we assume $\partial H^A/\partial r \ll 1$ and $\partial H^B/\partial r \ll 1$. Then the appropriate boundary conditions will be

$$\left.\begin{aligned} v_r &= U^A, \\ v_z &= \frac{dH^A}{dt} = \frac{\partial H^A}{\partial t} + U^A \frac{\partial H^A}{\partial r}, \end{aligned}\right\} \quad \text{at} \quad z = H^A, \qquad \begin{matrix}[2a]\\ [2b]\end{matrix}$$

$$\left.\begin{aligned} v_r &= U^B, \\ v_z &= -\frac{dH^B}{dt} = -\frac{\partial H^B}{\partial t} - U^B \frac{\partial H^B}{\partial r}, \end{aligned}\right\} \quad \text{at} \quad z = -H^B, \qquad \begin{matrix}[2c]\\ [2d]\end{matrix}$$

$$P_g{}^A - P = \sigma^A \Delta_r H^A, \qquad [2e]$$

$$P_g{}^B - P = \sigma^B \Delta_r H^B, \qquad [2f]$$

$$P = P_m = P_g{}^A - \frac{2\sigma^A}{R_c{}^A} = P_g{}^B - \frac{2\sigma^B}{R_c{}^B} \quad \text{at} \quad r \to \infty, \qquad [2g]$$

$$H = h \quad \text{and} \quad \partial H/\partial r = 0 \quad \text{at} \quad r = 0, \qquad [2h]$$

where $\Delta_r = (1/r)(\partial/\partial r)r(\partial/\partial r)$, P_g being the gas pressure in the bubble, P_m the pressure in the liquid at $r \to \infty$, σ the surface tension, and R_c the bubble radius. Equations [2e] and [2f] follow from [1b] and from Laplace's equation for the capillary pressure, and Eq. [2g] allows for the vanishing at $r \to \infty$ of the pressure disturbance caused by the flow.

By integrating [1a] with [2a] and [2c], we have:

$$v_r = \frac{z^2}{2\mu}\frac{\partial P}{\partial r} + \left[U^A - U^B - \frac{H^A - H^B}{2\mu} H \frac{\partial P}{\partial r}\right] \times \frac{z}{H} + U^B - \frac{(H^B)^2}{2\mu}\frac{\partial P}{\partial r} + \left[U^A - U^B - \frac{1}{2\mu}\frac{\partial P}{\partial r} \times (H^A - H^B)H\right]\frac{H^B}{H}.$$

Inserting this in [1c] and integrating over z from $-H^B$ to H^A, by means of [2b] and [2d] we obtain

$$-\frac{\partial H}{\partial t} = \nabla_r\left[\frac{H}{2}(U^A + U^B) - \frac{H^3}{12\mu}\frac{\partial P}{\partial r}\right]. \qquad [3]$$

In the general case, the film profile H is dependent on the time t, explicitly and through $h = H(0)$, i.e., $H = H[r,t,h(t)]$. To simplify the solution, we shall proceed to a quasi-steady assumption; we assume that H, and hence all other values are dependent on t solely through h (5–7, 11, 19). This enables us to substitute in the left-hand side of [3]

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial h}\frac{dh}{dt} = -V_0 \frac{\partial H}{\partial h}, \qquad [4]$$

where $V_0 = -dh/dt$, rate of thinning at the film center. It was shown by Riolo *et al.* (31) that the quasi-steady assumption is fully justifiable for thin films with non-deformable interfaces (e.g., a thin film formed between two plane-parallel surfaces or two solid spheres (5–7, 11, 19)) as, at small values of Reynolds' number, the

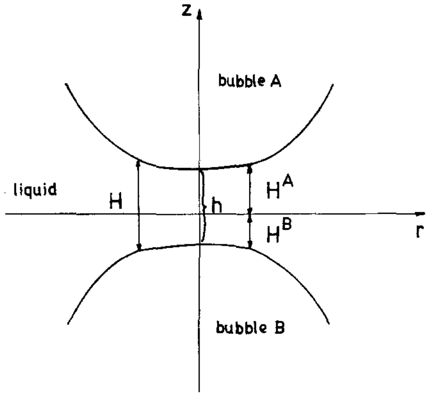

FIG. 2. Mutual approaching along the axis z of two different bubbles A and B of radii R_c^A and R_c^B and surface tensions σ^A and σ^B.

velocity field can be dependent on the time only through the boundary conditions (28).

It is shown in (19) that even with a deformable interface at the initial stages of the film formation, when the bubble slightly deviates from the spherical shape, the quasi-steady assumption yields the exact solution. It is also to be expected, in the case under consideration, with a slight deviation from the plane-parallel form of the film, that this assumption may be applicable. There seems to be supporting evidence of that in the experimental investigations (29), which indicate that the rate of thinning of such films is dependent on their thickness at a given moment but not on their prehistory.

It is difficult to say a priori whether the quasi-steady assumption can also be used in the intermediary stages of the film's evolution when the deformation of its surfaces is considerable. Frankel and Mysels (18) have investigated this case on the basis of an equation similar to [3], and have obtained analytical expressions for $h(t)$ and $H_d(t)$ (H_d is the barrier ring thickness, i.e., the minimum thickness of the film). However, the H_d/h ratio, which their theory leads to, is not explicitly dependent on t. This suggests that in this case the form of the surface does not explicitly depend on t, either, i.e., that the quasi-steady assumption [4] may be utilized. It will not be so, of course, if the deformation of the surface is due to some external factors, e.g., corrugations of the surface as a result of thermal fluctuations (27) or mechanical vibrations (30), or to some initial disturbances of the liquid within the drops, when the film is contiguous, at least on one of its surfaces, to a liquid phase (31). The quasi-steady assumption will not be applicable even when such external perturbations are absent, if h is a multiple-valued function of t.

Equation [3] is a concise formulation of Eqs. [1], [2a–d]. It is the governing equation for all cases of axisymmetric flow when the lubrication approximation is valid, i.e., when the distance $h = H(0)$ between the two surfaces is sufficiently small to assume the validity of [1] and of the approximations $\partial H^A/\partial r \ll 1$ and $\partial H^B/\partial r \ll 1$. It cannot be directly applied however to concrete systems because it relates four quantities: H, U^A, U^B, and P. Some of them can be expressed through the conditions for continuity of the components of the stress tensor at the film's surfaces and then Eq. [3] reduces to a differential equation either for P (nondeformable surfaces) or for H (deformable surfaces). Such equations were previously derived and used by many authors (6, 17–24).

For the system under consideration (see Fig. 1), $H^B = 0$, $U^B = 0$, and $R_c^B = \infty$. With respect to the bubble surface we consider only two limiting cases: (i) no slip ($U^A = 0$) and (ii) completely mobile surface ($\mu(\partial v_r/\partial z) = 0$ is substituted for [2a] in this case). Then Eq. [3] yields (we omit the superscript A):

$$3n\mu \frac{\partial H}{\partial t} = \nabla_r\left(H^3 \frac{\partial P}{\partial r}\right),$$

where $n = 4$ or 1 in case (i) or case (ii), respectively. The last equation was first derived by Hartland (see Eq. [8] in (17)). Making use of [2e] and [4], we obtain

$$\frac{3n\mu V_0}{\sigma}\frac{\partial H}{\partial h} = \nabla_r\left[H^3\frac{\partial}{\partial r}(\Delta_r H)\right]. \quad [5]$$

The relation between V_0 and the external driving force F impelling the bubble toward the substratum is given by the equation

$$F = 2\pi\sigma\left[r\frac{\partial(H^{(0)} - H)}{\partial r}\right]\Bigg|_0^\infty, \quad [6]$$

where

$$H^{(0)} = h + \frac{r^2}{2R_c} \quad [7]$$

is the approximated equation of the equilibrium (spherical) form of the bubble surface. Equation [6] follows from the balance of forces acting upon the bubble along the z-axis and from Eqs. [2e], [2g], and [7][2]:

$$F = 2\pi\int_0^{R_c}(P - P_m)rdr \approx 2\pi\sigma \times \int_0^\infty \Delta_r(H^{(0)} - H)rdr = 2\pi\sigma\left[r\frac{\partial(H^{(0)} - H)}{\partial r}\right]\Bigg|_0^\infty. \quad [8]$$

The bubble surface exhibits two distinct regions: In the first one (near the axis of symmetry where $H \approx h$) the deviation from the spherical form is considerable, and in the second (far from the axis of symmetry where $H \gg h$), the disturbance due to the flow is small. It is then convenient to introduce the dimensionless variable

$$y = 1 + \mathcal{H}r^2, \quad [9]$$

which in these regions is of the order $y \gtrapprox 1$ ($\mathcal{H}r^2 \ll 1$) and $y \gg 1$ ($\mathcal{H}r^2 \gg 1$), respectively. The parameter $\mathcal{H}$, which is approximately equal to the inverse square of the radius of the "boundary" between these regions (see Sect. 3), will obviously be dependent on h. Indeed, when the bubble moves away from the substratum, its deformation is very small, and only at $h = h_i = F/4\pi\sigma$ (6, 19) does its surface acquire the characteristic cupped form called "dimple." With $h \ll h_i$, the dimple turns into an almost plane-parallel film. Hence, with respect to h, we shall distinguish the cases of great thickness ($h \gg h_i$) and small thickness ($h \ll h_i$).

When substituting [9] into [5], the dependence of y on h (through $\mathcal{H}$) must be accounted for, i.e.,

$$\left(\frac{\partial H}{\partial h}\right)_r = \left(\frac{\partial H}{\partial y}\right)_h\left(\frac{\partial y}{\partial h}\right)_r + \left(\frac{\partial H}{\partial h}\right)_y = \mathcal{H}'r^2\frac{\partial H}{\partial y} + H',$$

where the primes indicate differentiation with respect to h. So we obtain:

$$\alpha\left[\mathcal{H}'(y-1)\frac{\partial H}{\partial y} + \mathcal{H}H'\right] = \frac{\partial}{\partial y}\left\{(y-1)H^3\frac{\partial^2}{\partial y^2} \times \left[(y-1)\frac{\partial H}{\partial y}\right]\right\} \quad [10]$$

where

$$\alpha = \frac{3n\mu V_0}{16\sigma\mathcal{H}^3}. \quad [11]$$

We shall, with respect to y, seek a solution to this equation by the method of matched coordinate expansions (32).

With $y \gg 1$, the expression for H can be found as follows. Because of [2h], the lower limit of [6] cannot give any contribution to F. Since $H^{(0)}$ is dependent on $r^2/2R_c$ (see [7]) for F to be finite, H must contain the same term. We must also include a term with $\ln y$ because this is the only function giving a finite contribution in [6]. With $y \gg 1$, the remaining part of $H(y)$ will be consistent with [2g] if it is represented as a series with respect to the negative powers of y. Taking the first two

[2] A similar force balance was used by Hartland (17). However, he has integrated over r only till the dimple radius. In this way a rather extensive region, where the energy dissipation is still noticeable, was disregarded.

terms of this series only, we can write (for $y \gg 1$):

$$H = \frac{y}{2\mathcal{H}R_c} - \frac{F}{4\pi\sigma}\ln y + a_0 + \frac{a_1}{y}, \quad [12]$$

where a_0 and a_1 are functions of h, and [6] has been used to determine the coefficient before ln y.

In order to find an equation for the coefficients a_0 and a_1, we shall substitute [12] into [10] and let $y \to \infty$. This means that in the final result, only the terms without y must be accounted for. The left-hand side (LHS) of [10] is transformed as follows:

$$\text{LHS} = \alpha\left[\mathcal{H}'(y-1) \times \left(\frac{1}{2\mathcal{H}R_c} - \frac{F}{4\pi\sigma y} - \frac{a_1}{y^2}\right) + \mathcal{H}\left(-\frac{y\mathcal{H}'}{2\mathcal{H}^2R_c} + a_0' + \frac{a_1'}{y}\right)\right]$$

$$= \frac{\alpha}{\mathcal{H}}\left(\mathcal{H}^2a_0' - \frac{\mathcal{H}'}{2R_c} - \frac{F\mathcal{H}\mathcal{H}'}{4\pi\sigma}\right) + O(y^{-1}).$$

Since in the right-hand side (RHS) of [10]

$$\frac{\partial^2}{\partial y^2}\left[(y-1)\frac{\partial H}{\partial y}\right] = \frac{2}{y^3}\left(\frac{F}{4\pi\sigma} - a_1\right) + \frac{6a_1}{y^4},$$

in the limit $y \to \infty$ it is sufficient to write

$$\text{RHS} = \frac{\partial}{\partial y}\left\{y\left(\frac{y}{2\mathcal{H}R_c}\right)^3\frac{2}{y^3} \times \left(\frac{F}{4\pi\sigma} - a_1\right)\right\} = \frac{F/4\pi\sigma - a_1}{4\mathcal{H}^3R_c^3}.$$

So we get:

$$4\alpha\mathcal{H}^2R_c^3\left(\mathcal{H}^2a_0' - \frac{\mathcal{H}'}{2R_c} - \frac{F}{4\pi\sigma}\mathcal{H}\mathcal{H}'\right) = \frac{F}{4\pi\sigma} - a_1. \quad [13]$$

In the region $\mathcal{H}r^2 \ll 1$ it is more convenient to use [5] instead of [10]. By means of the expansion $H = h + d_2r^2 + d_4r^4 + d_6r^6$ and [5], we have for this region

$$H = h + d_2r^2 + \frac{\alpha\mathcal{H}^3}{4h^3}r^4 + \frac{\alpha\mathcal{H}^3}{36h^4}(hd_2' - 6d_2)r^6. \quad [14]$$

The asymptotic solutions [12] and [14] are matched in the region $\mathcal{H}r^2 \ll 1$ by expanding ln y and y^{-1} in [12] in series with respect to $\mathcal{H}r^2$ and equating the coefficients in this series to those in [14]. We thus obtain

$$h = a_0 + a_1 + (2\mathcal{H}R_c)^{-1}, \quad [15]$$

$$\frac{\alpha\mathcal{H}}{4h^3} = a_1 + \frac{F}{8\pi\sigma}, \quad [16]$$

$$\frac{\alpha}{36h^4}\left[\frac{3}{R_c} - \frac{3F\mathcal{H}}{2\pi\sigma} - 6a_1\mathcal{H} + \frac{Fh\mathcal{H}'}{4\pi\sigma} + (a_1\mathcal{H})'h\right] = a_1 + \frac{F}{12\pi\sigma}. \quad [17]$$

Equations [13], [15]–[17] allow the determination of the quantities a_0, a_1, $\mathcal{H}$, and α (i.e., V_0). The elimination of a_0 and α (by means of [15] and [16], respectively) yields

$$(1 + 2\tilde{a}_1)[3 + \tilde{\mathcal{H}}'\tilde{h} - 6\tilde{\mathcal{H}}(\tilde{a}_1 + 1) + \tilde{h}(\tilde{a}_1\tilde{\mathcal{H}})'] = 6\tilde{\mathcal{H}}\tilde{h}(1 + 3\tilde{a}_1), \quad [18]$$

$$8\tilde{\mathcal{H}}^2\tilde{h}^3(1 + 2\tilde{a}_1) \times (\tilde{\mathcal{H}} - \tilde{\mathcal{H}}\tilde{a}_1' - \tilde{\mathcal{H}}') = 1 - \tilde{a}_1, \quad [19]$$

where we have introduced the dimensionless quantities

$$\tilde{h} = \frac{4\pi\sigma h}{F}; \quad \tilde{\mathcal{H}} = \frac{FR_c\mathcal{H}}{4\pi\sigma};$$

$$\tilde{a}_1 = \frac{4\pi\sigma a_1}{F} \quad [20]$$

and the primes indicate differentiation with respect to $\tilde{h}$. Equations [18] and

[19] will be solved in Section 3 for the case of small thickness ($\tilde{h} = h/h_i \ll 1$) and in Section 5 for great thickness ($\tilde{h} \gg 1$).

3. LIQUID FILM OF SMALL THICKNESS ($\tilde{h} \ll 1$)

When F is the buoyancy force, $\tilde{h} = 3\sigma h/\rho g R_c^3$, where g denotes gravity and ρ, liquid density. Hence, with bubble radii $R_c = 10^{-1} \div 10^{-2}$ cm, the condition $\tilde{h} \leqq 0.1$ will be realized in the thickness range $0 \leqq h \leqq 10^{-3} \div 10^{-6}$ cm. As investigations of thin films are usually carried out in the range $3 \times 10^{-6} \leqq h \leqq 10^{-5}$ cm (1), this case is the most important one. Using the expansions

$$\tilde{a}_1 = A_0^{(0)} + A_1^{(0)}\tilde{h} + A_2^{(0)}\tilde{h}^2 + \ldots, \qquad [21]$$

$$\tilde{\mathscr{H}} = K_0^{(0)} + K_1^{(0)}\tilde{h} + K_2^{(0)}\tilde{h}^2 + \ldots, \qquad [22]$$

from [18] and [19] we find $A_0^{(0)} = 1$, $A_1^{(0)} = A_2^{(0)} = 0, \ldots$ and $K_0^{(0)} = 1/4$, $K_1^{(0)} = -1/5$, $K_2^{(0)} = 1/5, \ldots$. Thus, from [15], [16], and [12] (see also [19], [11], and [20]) we finally obtain

$$V_0 = \frac{8\pi\sigma^2 h^3}{n\mu F R_c^2} \times (1 - 1.6\tilde{h} + 2.24\tilde{h}^2 + \ldots), \qquad [23]$$

$$H = h + \frac{r^2}{2R_c} - \frac{F}{4\pi\sigma}\ln\left(1 + \frac{\pi\sigma r^2}{FR_c}\right) - \frac{r^2}{4R_c}\frac{1}{\left(1 + \frac{\pi\sigma r^2}{FR_c}\right)}. \qquad [24]$$

In setting down [24], all terms of the order of $\tilde{h}$ have been disregarded.

Equation [24] is a correct asymptotic expression with $\mathscr{H}r^2 \gg 1$ and $\mathscr{H}r^2 \ll 1$. In the transitional region between these two limiting cases it is however only a crude interpolation formula. According to [24], in the region near the axis of symmetry the film is almost plane-parallel. The function $H(r)$ in [24] exhibits only one extremum: a minimum at $r = 0$. However, this does not mean that the possibility for the film surface to be dimpled is ruled out altogether. Indeed, if a dimple does exist, its radius must be of the order of $1/\mathscr{H}^{1/2}$ (19), i.e., the dimple must be in the region in which Eq. [24] is only a rough approximation to the real film surface. As mentioned above, such a small dimple was found by Hartland (15).

An interesting feature of Eq. [24] is that it does not contain n and μ, i.e., the form of the surface is not dependent on the hydrodynamic behavior of the system. This conclusion, which was also reached intuitively by Princen (13), concurs with the results obtained for the initial deformations of the bubble at $\tilde{h} \gg 1$ (see Eq. [37]).

With $\tilde{h} \ll 1$ the series in parentheses in [23] is approximately equal to 1, and the velocity V_0, which in fact is the velocity of thinning of the whole central almost plane-parallel part of the film (that with $H \approx h$) will be given by the expression

$$V_0 = \frac{8\pi\sigma^2 h^3}{n\mu F R_c^2}. \qquad [25]$$

When the film is formed between two different bubbles, the theory is similar, but the calculations are more involved. These results are to be published subsequently. We merely mention now that if the bubbles are identical and their surfaces tangentially immobile, Eq. [25] with $n = 4$ will still be valid. This result is to be expected.

4. ON THE VALIDITY OF REYNOLDS' EQUATION

Equation [25] contains only measurable quantities and can, in principle, be tested experimentally, particularly in the case when the film is formed between a solid substratum and a bubble, pressed by the buoyancy force. Nevertheless, it is interesting to put it in the form of Reynolds' equation (33)

$$V_{Re} = (2h_V^3 F)/(3\pi\mu R_V^4) \qquad [26]$$

which gives the rate of thinning V_{Re} of a film of thickness h_V formed between two rigid circular plates of equal radii R_V.

When [26] is used for experimental purposes, the thickness h_V is usually measured by interferometry of 30 ÷ 50% of the film surface (34). As the film is practically plane-parallel the experimental value h_V can be considered as a virtual mean thickness and assumed equal to h in [25]. The film radius is determined visually, either as the radius of the plane-parallel part, or as the radius of the circumference comprised between the first and the second interference rings (35). The difference between the two definitions does not normally exceed 10%.

Since it is not possible to introduce the visual film radius in [25], we shall use the experimental observation that the latter does not differ appreciably from the radius R_e of the equilibrium film which eventually forms between the bubble and the substratum (36). The film radius R_e can be calculated from Derjaguin–Kussakov's formula (19, 37)

$$R_e^2 = FR_c/2\pi\sigma. \qquad [27]$$

By eliminating R_c from [25] and [27], we thus obtain (with $n = 4$):

$$V_0 = \frac{h^3F}{2\pi\mu R_e^4}. \qquad [28]$$

Except for the small difference in the numerical coefficients, this last equation is coincident with Reynolds' equation [26] if $h_V = h$ and $R_V = R_e$. In this case $V_0 = \frac{3}{4}V_{Re}$. Another way of comparing [26] and [28] is to choose the value of R_V in such a way that with $h_V = h$, both formulas give the same rate of thinning. In this case $R_V = 1.07R_e$. The difference between R_e and the value of R_V determined in this way is approximately equal to the uncertainty with which R_V is set at the experimental measurements (see above). The small difference between V_0 and V_{Re} (with $R_V = R_e$) or R_V and R_e (with $V_0 = V_{Re}$) proves that Reynolds' equation [26] gives the rate of thinning reasonably well. Analogous results are obtained when the bubble surface is tangentially mobile (put $n = 1$ in [25]), but in this case a factor 4 appears in the numerators of both [26] and [28].

We must emphasize that the relatively good numerical coincidence between [26] and [28] may to some extent be fortuitous. What is much more significant is that we find that the rate of thinning V_0 is proportional to the third power of the film thickness h, which concurs with the experimental results (29, 35).

When formulating the boundary conditions [2] and [6], we have assumed that the film is small, namely, that $R_e/R_c \ll 1$ (see the comment after Eqs. [1c]). If the bubble is moved by the buoyancy force $F = \frac{4}{3}\pi R_c^3\rho g$, from [27] we have

$$\frac{R_e}{R_c} = \left(\frac{F}{2\pi\sigma R_c}\right)^{1/2} = \left(\frac{2R_c^2\rho g}{3\sigma}\right)^{1/2}.$$

Since this ratio is decreasing with decreasing R_c, we see, therefore, that our theory will be valid only for sufficiently small bubbles. This is in agreement with the results of Buevich and Lipkina (23), whose computer solutions of Eqs. [1] have shown that with $R_e/R_c \ll 1$ the film could thin without dimpling. This conclusion depends however on the value of h and at greater thicknesses even small bubbles can have dimples (6, 19)). In this case however Eqs. [23], [24] are no longer valid and the film profile and the velocity of thinning are described by Eqs. [37], [38].

Cases in which the film is formed by blowing the bubble from a capillary tube to a plane substratum (36) (Fig. 3), or by sucking the liquid from a biconcave meniscus (1, 29, 35), are more complicated, as the driving force F for these systems cannot be directly measured. It can, however, be calculated as follows. Let the pressure in the equilibrium spherical bubble be P_g^0 and the pressure in the liquid be P_m (Fig. 3a). If the pressure in the bubble is suddenly increased to P_g, the bubble will be deformed and almost plane-parallel thinning film will be formed, which can eventually turn into an equilibrium film of radius R_e (Fig. 3b). The capillary pressures of the spherical bubble $P_c{}^0$ and of the meniscus in equilibrium with the film P_c will be (38, 39):

$$P_c{}^0 = P_g{}^0 - P_m = \frac{2\sigma}{R_c}\cos\varphi, \quad [29]$$

$$P_c = P_g - P_m = \frac{2\sigma(R_c\cos\varphi - R_e\sin\theta)}{R_c{}^2 - R_e{}^2}, \quad [30]$$

where R_c is the capillary radius and φ and θ are the contact angles between the meniscus and the capillary wall and the thin film, respectively. Since the driving pressure $\Delta P = P_g - P_g{}^0$ remains constant during the film thinning, it can be calculated through [29] and [30]:

$$\Delta P = P_c - P_c{}^0 \approx \frac{2\sigma R_e{}^2\cos\varphi}{R_c{}^3}, \quad [31]$$

where we have assumed $R_e \ll R_c$. Hence the driving force will be

$$F = \pi R_c{}^2\Delta P \approx \pi R_e{}^2\frac{2\sigma\cos\varphi}{R_c} = \pi R_e{}^2 P_c{}^0. \quad [32]$$

Naturally, the same result is obtained for a film formed in a biconcave meniscus. Substituting this value for F in [28], we obtain

$$V_0 = \frac{h^3 P_c{}^0}{2\mu R_e{}^2}, \quad [33]$$

which is analogous to Reynolds' equation in the form used by Scheludko for the system under consideration in the absence of disjoining pressure (1, 29):

$$V_{Re} = \frac{2h_V{}^3 P_c{}^0}{3\mu R_V{}^2}. \quad [34]$$

Equation [32] in the form $F = \pi R_V{}^2 P_c{}^0$ was derived by Scheludko (40) by assuming that the film thins under the action of the driving pressure $\Delta P = P_c{}^0$ applied on the film area $\pi R_V{}^2$. Although our derivation leads to the same result [32], it is noteworthy that our driving pressure is given by [31] and is much smaller than $P_c{}^0$. Indeed, with $R_c = 10^{-1}$ cm, $R_e = 10^{-2}$ cm, $\sigma = 50$ dyn cm^{-1} and $\varphi = 0$, we obtain $\Delta P = 10$ dyn cm^{-2}, whereas $P_c{}^0 = 10^3$ dyn cm^{-2}. The very small value of the driving pressure explains the extreme sensitivity of these systems to external perturbations affecting the pressure (1).

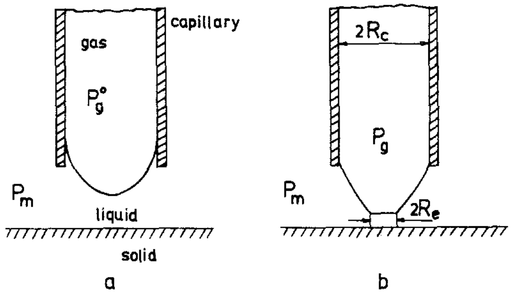

FIG. 3. Schematic representation of the formation of a thin liquid film of equilibrium radius R_e by blowing out a bubble from a capillary of a radius R_c: (a) spherical bubble in equilibrium with gas and liquid phases of pressures $P_g{}^0$ and P_m, respectively; (b) after increasing the gas pressure to P_g the bubble is deformed and an equilibrium film forms.

5. WIDELY SEPARATED BUBBLE AND SUBSTRATUM ($\tilde{h} \gg 1$)

When the distance between the cap of the bubble and the substratum is very great ($\tilde{h} \gg 1$), the bubble is only slightly deformed. In this case asymptotic expressions for the coefficients $\tilde{a}_1$ and $\tilde{\mathscr{H}}$ in [18] and [19] can be obtained by using the expansions

$$\tilde{a}_1 = A_0{}^{(\infty)} + A_1{}^{(\infty)}\tilde{h}^{-1} + \ldots, \quad [35]$$

$$\tilde{\mathscr{H}} = K_0{}^{(\infty)} + K_1{}^{(\infty)}\tilde{h}^{-1} + \ldots. \quad [36]$$

Substituting these series into [18] and [19], we find $A_0{}^{(\infty)} = 0$, $A_1{}^{(\infty)} = 9/24, \ldots$, $K_0{}^{(\infty)} = 0$, $K_1{}^{(\infty)} = 1/2, \ldots$ Thus from [11], [12], and [9], also taking into account [7], [2], and [16], we obtain the following expressions for the equation of the bubble surface $H(r)$ and the velocity V_0:

$$H = h + r^2/2R_c - (F/4\pi\sigma)\ln(1 + r^2/2R_c h), \quad [37]$$

$$V_0 = 2hF/3n\pi\mu R_c^2. \quad [38]$$

Equations [37] and [38] (with $n = 4$) coincide, respectively, with the first approximation for the bubble surface and the zero approximation for the velocity V_0 obtained by Radoev and Ivanov (19), using the method of the parametric expansion with respect to the small parameter $\epsilon = F/4\pi\sigma R_c \ll 1$. When F is the buoyancy force, $\epsilon = R_c^2\rho g/3\sigma$ and we reach again the conclusion that the present solution (and that in (19) as well) is valid for small bubbles. Since Eqs. [37] and [38] are analyzed in (19), we shall merely note at present that, with $n = 1$, Eq. [38] gives the rate of approach of a slightly deformed bubble with a wholly mobile tangential surface toward a solid substratum.

ACKNOWLEDGMENT

We are indebted to one of the referees, whose valuable remarks have contributed to the improvement of the manuscript.

REFERENCES

1. Scheludko, A., *Advan. Colloid Interface Sci.* **1,** 391 (1967).
2. MacKay, G. D. M., and Mason, S. G., *Canad. J. Chem. Eng.* **41,** 203 (1963).
3. Allen, R. S., Charles, G. E., and Mason, S. G., *J. Colloid Sci.* **16,** 150 (1961).
4. Sonntag, H., and Strenge, K., "Koagulation und Stabilität Disperser Systeme." VEB Deut. Verlag Wiss., Berlin, 1970.
5. Radoev, B., Manev, E., and Ivanov, I., *Kolloid Z. Z. Polym.* **234,** 1037 (1969); Radoev, B. P., Dimitrov, D. S., and Ivanov, I. B., *Colloid Polym. Sci.* **252,** 50 (1974).
6. Radoev, B. P., and Ivanov, I. B., *God. Sofii. Univ. Khim. Fak.*, **66,** 631 (1971/1972).
7. Ivanov, I. B., and Dimitrov, D. S., *Colloid Polym. Sci.* **252,** 982 (1974).
8. Murdoch, P., and Leng, D., *Chem. Eng. Sci.* **26,** 1881 (1971).
9. Reed, X., Riolo, E., and Hartland, S., *Int. J. Multiphase Flow* **1,** 411 (1974).
10. Reed, X., Riolo, E., and Hartland, S., *Int. J. Multiphase Flow* **1,** 437 (1974).
11. Ivanov, I. B., and Traikov, T. T., *Int. J. Multiphase Flow* **2,** 397 (1976); Ivanov, I. B., and Traikov, T. T., *God. Sofii. Univ., Khim. Fak.*, **66,** 641 (1971/1972).
12. Traikov, T. T., and Ivanov, I. B., *Int. J. Multiphase Flow*, **3,** 471 (1977).
13. Princen, H. M., *J. Colloid Sci.* **18,** 178 (1963).
14. Lee, J., and Hodgson, T., *Chem. Eng. Sci.* **23,** 1375 (1968).
15. Hartland, S., *Chem. Eng. Sci.* **24,** 987 (1969).
16. Hartland, S., *J. Colloid Interface Sci.* **26,** 383 (1968); Hartland, S., *J. Colloid Interface Sci.* **35,** 227 (1971).
17. Hartland, S., *Chem. Eng. Progr. Symp. Ser.* **65,** 82 (1969).
18. Frankel, K. J., and Mysels, S. P., *J. Phys. Chem.* **66,** 190 (1962).
19. Radoev, B. P., and Ivanov, I. B., to appear.
20. Voinov, O. V., *Dokl. Akad. Nauk SSSR* **216,** 285 (1974).
21. Voinov, O. V., *Zh. Prikl. Mekh. Tekhn. Fys.* No 3, 67 (1974).
22. Buevich, Yu. A., and Lipkina, E. H., *Izv. Akad. Nauk SSSR, Mech. Jidk. Gasa* No 2, 39 (1973).
23. Buevich, Yu. A., and Lipkina, E. H., *J. Prikl. Mech. Techn. Phys.* No 2, 80 (1975).
24. Starov, V. M., and Churaev, N. V., *Kolloid Zh.* **37,** 711 (1975); **38,** 100 (1976).
25. Radoev, B. P., *God. Sofii. Univ., Khim. Fak.* **66,** 625 (1971/72).
26. Lamb, H., "Hydrodynamics." University Press, Cambridge, 1963.
27. Ivanov, I., Radoev, B., Manev, E., and Scheludko, A., *Trans. Faraday Soc.* **66,** 1212 (1970).
28. Berker, R., *in* "Encyclopedia of Physics" (S. Flügge, Ed.), Vol. VIII/2 (C. Truesdell, Co-ed.), p. 1, Springer–Verlag, Berlin, 1963.
29. Scheludko, A., *Proc. Kon. Ned. Akad. Wetensch. Ser. B* **65,** 76 (1962).
30. Gillespie, T., and Rideal, E. K., *Trans. Faraday Soc.* **52,** 173 (1956).
31. Riolo, E., Reed, X. B., and Hartland, S., *Chem. Eng. J.* **6,** 121 (1973).
32. van Dyke, M., "Perturbation Methods in Fluid Mechanics." Academic Press, New York/London, 1964.
33. Reynolds, O., *Phil. Trans. Roy. Soc. London* **177,** 157 (1886).
34. Platikanov, D., and Manev, E., *Izv. Inst. Fizikokhim. Bulg. Akad. Nauk.* **4,** 185 (1964).
35. Scheludko, A., Platikanov, D., and Manev, E., *Discuss. Faraday Soc.* **40,** 253 (1965).
36. Platikanov, D., *J. Phys. Chem.* **68,** 3619 (1964).
37. Derjaguin, B. V., and Kussakov, M. M., *Acta Physicochim. USSR* **10,** 25 (1939).
38. Toshev, B. V., and Ivanov, I. B., *God. Sofii. Univ., Khim. Fak.* **65,** 329 (1970/1971).
39. Toshev, B. V., and Ivanov, I. B., *Colloid Pol. Sci.* **253,** 558 (1975).
40. Scheludko, A., *Kolloid Zh.* **155,** 39 (1957).