Hydrodynamics of Thin Liquid Films. Rate of Expansion of the Perimeter of the Three-Phase Contact

One of the important stages in the process of attachment of a particle to a froth bubble and in the coalescence of two bubbles is the expansion of the three-phase contact line. For the sake of brevity further on we shall discuss mainly the former process on the basis of the modeling experiments of Scheludko *et al.* (1) where a bubble, blown out of a capillary of radius R_c, was attached to a solid substratum. The process occurs in the following way. In the thicker film formed initially, one or more black spots (nuclei of a thinner second film) appear. They expand (or coalesce) and eventually occupy the whole surface of the film thus turning the latter into a second black film. Up to this moment the film radius R_1 is constant and the meniscus (bubble) surface is immobile. Once formed the second black film begins to increase its radius until the final equilibrium radius R_2 is reached.

The approximate theory of the film expansion presented in this paper in some aspects resembles the theory of dynamic contact angles (2). The basic assumptions we use are the following: (a) the second film contains a liquid core of constant thickness $h_{0'}$. (b) During the expansion, the contact angle at the film perimeter is constant and equal to the final equilibrium angle θ_2. (c) The radial component of the velocity goes to zero at the film perimeter. (d) The motion of the meniscus is caused by the excess pressure due to the change of the contact angle θ from its initial value θ_1 to its final value θ_2. Indeed, if with $\theta = \theta_1$ and $R = R_1$ the meniscus has been immobile, the pressure difference between the gas phase and the meniscus $P_g - P_m$ must have been equal to the initial capillary pressure P_c'. It can be calculated by setting $\theta = \theta_1$ and $R = R_1$ in the equation (3)

$$P_c(R,\theta) = \frac{2\sigma(R_c - R \sin \theta)}{R_c^2 - R^2}, \qquad [1]$$

where σ denotes the surface tension of the liquid in the meniscus; the contact angle between the meniscus and the capillary wall is assumed zero. When the black spots have covered the initial film, the contact angle sharply increases to θ_2. Since this occurs at $R = R_1$ the capillary pressure drops to $P_c(R_1,\theta_2) < P_g - P_m$ and the meniscus cannot longer be in equilibrium at the same pressure difference $P_g - P_m$. The excess pressure ΔP thus arising, causes the film expansion to the final radius R_2 at which the capillary pressure $P_c''(R_2,\theta_2)$ again becomes equal to $P_g - P_m$. Since $P_c' = P_c''$, the excess pressure ΔP for any radius R of the expanding film can be expressed either through P_c' or P_c'', i.e.,

$$\Delta P = P_c' - P_c(R,\theta_2) = P_c'' - P_c(R,\theta_2).$$

In Fig. 1 the schematic profile of the meniscus in the vicinity of the perimeter of an expanding film is shown. Since for a steady process the thickness H depends on time t only through the instant value $R(t)$ of the film radius, the velocity component v_z at $z = H$ is given by (4)

$$v_z = \frac{\partial H}{\partial t} + v_r \frac{\partial H}{\partial r} = U \frac{\partial H}{\partial R} + v_r \frac{\partial H}{\partial r}, \qquad [2]$$

where $U = dR/dt$. Then the governing equation of the process will be [for details of the derivation see (4)]:

$$\frac{\epsilon}{rH^3} \int_R^r \frac{\partial H}{\partial R} r dr = \frac{\partial}{\partial r}(\Delta_r H): \quad \epsilon = \frac{3n\mu U}{\sigma}, \qquad [3]$$

where μ is dynamic viscosity,

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

$n = 4$ for expansion of a film with tangentially immobile meniscus surface on a substratum and $n = 1$ for expansion of a foam film or of a film on substratum in the absence of surfactant.

Since $U \approx 10^{-2}$ cm/sec (1) the parameter ϵ does not usually exceed 10^{-4}. This allows Equation [3] to be solved by means of an iteration procedure. The zero approximation $H^{(0)}$ (at $\epsilon = 0$) gives the equilibrium shape of the meniscus in the vicinity of the film perimeter. Putting $r - R = \delta$ and using the approximations $R/R_c \ll 1$, and $\delta/R \ll 1$ we obtain (note that $H = h_0$ and $\partial H/\partial r = tg\theta_2$ at $r = R$):

$$H^{(0)} = h_0 + \theta_2\delta + \left(\frac{1}{R_c} - \frac{\theta_2}{2R}\right)\delta^2 - \frac{\delta^3}{3R_cR}. \qquad [4]$$

When deriving Eq. [4] we have assumed $tg\theta_2 \approx \theta_2$ and have only kept the terms of the order of $(\delta/R)^2$. Substituting Eq. [4] in the left side of Eq. [3] after long but trivial calculations we obtain for the first approximation

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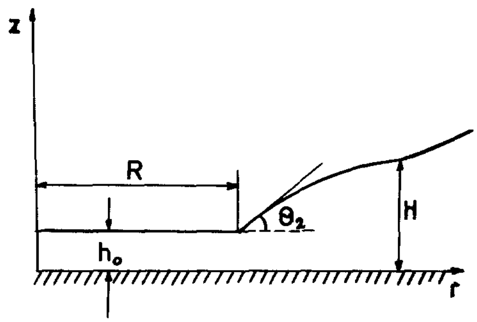

FIG. 1. Sketch of the film and the meniscus in the vicinity of the perimeter of the film.

$$H = \left(\theta_2 - \epsilon \ln \frac{\theta_2 \delta}{h_0}\right)\delta. \quad [5]$$

At different stages of the derivation we have used the approximations $\theta_2^2 \gg 4h_0/R_c$ and $\delta\theta_2 \gg h_0$. The latter approximation is valid for the region where interference fringes can be observed ($\delta = 10^{-3}$ cm). Equation [5] relates the shape of the surface to the rate of expansion and allows the experimental verification of the theory. However, in some cases it might be necessary to calculate the velocity U from other properties of the system. The expression for the drag force F reads [see Eq. [8] in (4)]

$$\frac{F}{2\pi\sigma} = \int_R^{R_c} \Delta_r(H^{(0)} - H)rdr$$

$$\approx \int_0^\infty \delta \frac{\partial}{\partial r}(\Delta_r H)d\delta, \quad [6]$$

where the approximations $R/R_c \ll 1$ and $\delta/R \ll 1$ were used. The substitution of the derivative $\partial(\Delta_r H)/\partial r$ in Eq. [6] by the left side of Eq. [3] (where H is expressed through [4]), with the aid of the approximation $\theta_2^2 \gg 4h_o/R_c$, leads to a relation between F and U:

$$U = \frac{\theta_2^2 F}{6\pi\mu n R \ln(R_c\theta_2^2/12{,}2h_0)}. \quad [7]$$

On the other hand, when the bubble is blown out of a capillary, we have also

$$F = \pi(R_c^2 - R^2)\Delta P. \quad [8]$$

Analogous expressions for a bubble, moved by the buoyancy force F_b, can be derived from the balances of forces during the film expansion:

$$F = F_b + 2\pi\sigma R \sin\theta_2 - \pi(P_g - P_m)R^2, \quad [9]$$

and before (a) and/or after (b) expansion:

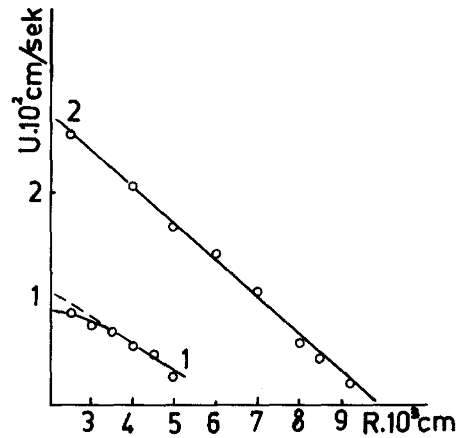

FIG. 2. Dependence of the rate of expansion U on the film radius R for aqueous solutions of dodecylamine at pH = 4.5 (curve 1) and pH = 5.1 (curve 2).

$$\text{a.} \quad F_b + 2\pi\sigma R_1 \sin\theta_1 = \pi(P_g - P_m)R_1^2;$$
$$\text{b.} \quad F_b + 2\pi\sigma R_2 \sin\theta_2 = \pi(P_g - P_m)R_2^2. \quad [10]$$

For example, Eqs. [9] and [10b] yield:

$$F = [F_b(R_2 + R) + 2\pi\sigma R R_2 \sin\theta_2] \times (R_2 - R)/R_2^2. \quad [11]$$

Equation [7], combined with Eqs. [8] or [11], leads to the sought expressions of U through the properties of the system. Depending on the character of the systems under investigation the expressions for the driving force F can acquire a simpler form. For the expansion of the perimeter of a film on a solid substratum, for example, the initial radius R_1 can be assumed zero (1). Thus according to Eqs. [1], [7], and [8] we can write (put $R_1 = 0$ and $\sin\theta_2 = R_2/R_c$ in $\Delta P = P_c' - P_c$):

$$U = \frac{\sigma\theta_2^2(R_c - R)}{3n\mu R_c \ln(R_c\theta_2^2/12{,}2h_0)}. \quad [12]$$

According to Eq. [12] the plot of U vs R must be linear. Figure 2 shows Tschalyovska's experimental results (unpublished data) for aqueous solutions of dodecylamine, 1.07 M, at pH 4.5 (curve 1) and 5.1 (curve 2) and contact angles, $\theta_2 = 3°$ and $5°$, respectively. The deviation from the linear dependence is only observed with small radii at pH 4.5.

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