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Thinning and Rupture of Ring-shaped Films

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The problem of the thinning and stability of a film with a dimple is treated by using a simplified model. The model is based on a premise that all the energy dissipation takes place in the " barrier " ring with thickness h. Analytical solutions are obtained for the velocity of thinning and critical thickness of rupture in terms of the radius of the bubble, radius of curvature of the dimple, inner and outer radii of the ring, surface tension and disjoining pressure. The results suggest that the presence of a dimple increases the velocity of thinning and decreases the critical thickness of rupture, in general, as compared with a film without a dimple.

Thinning and rupture of the intervening liquid film between a bubble and a solid surface can be the rate determining step in their attachment.[1] When a small drop or bubble approaches a solid or liquid surface this intervening film is usually plane parallel. However, when the bubble is large the film acquires a reverse curvature in its centre so that some fluid is entrapped by a thinner ring (fig. 1).[2-7] The central lens of liquid is normally referred to as " dimple " and the surrounding circular film as " barrier ring." Although considerable theoretical work has been done on the hydrodynamics of plane parallel films,[8-15] only a few papers have been devoted to hydrodynamic theory of the evolution of the dimple during the approach of two interfaces [see, *e.g.*, ref. (6), (8) and (14)]. While these theories serve as a valuable background for this work, they do not take into account the interaction forces (for example, the London–van der Waals dispersion forces which are important in the stability of these

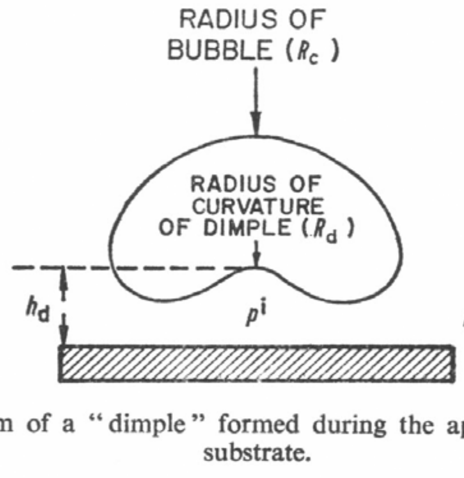

FIG. 1.—Schematic diagram of a " dimple " formed during the approach of a bubble to a solid substrate.

films) and the surface active agents which are usually present in such systems. In addition, these theories do not provide any information on the time constant and critical thickness of rupture. In the work reported here, a theoretical framework is presented that avoids approximations made by previous investigators [6] and leads to the results obtained previously for plane-parallel films as a special case.[14, 15]

GENERAL FORMULATION OF THE PROBLEM

For simplicity, we consider the system as shown in fig. 2: the liquid " barrier " ring of thickness h and external and internal radii R and R_i formed between a bubble and a solid substrate. The fluid outside the film is considered to be part of the bulk where the hydrodynamic effects can be neglected. The motion of liquid inside the ring is described by the linearized Navier–Stokes equations. The role of interaction forces present in the film is incorporated by adding the disjoining pressure, Π, in the normal stress balance. The treatment presented here considers surfactants soluble in the film. Furthermore, the analysis includes the Gibbs–Marangoni effect and both the surface constitutional dilational viscosity (μ_d) and the surface shear viscosity (μ_s). In the limit $R_i \rightarrow 0$, the results reduce to those obtained previously for plane parallel radially bounded films and in the limit $R_i \rightarrow 0$ and $R \rightarrow \infty$, the results for unbounded thin films can be obtained.

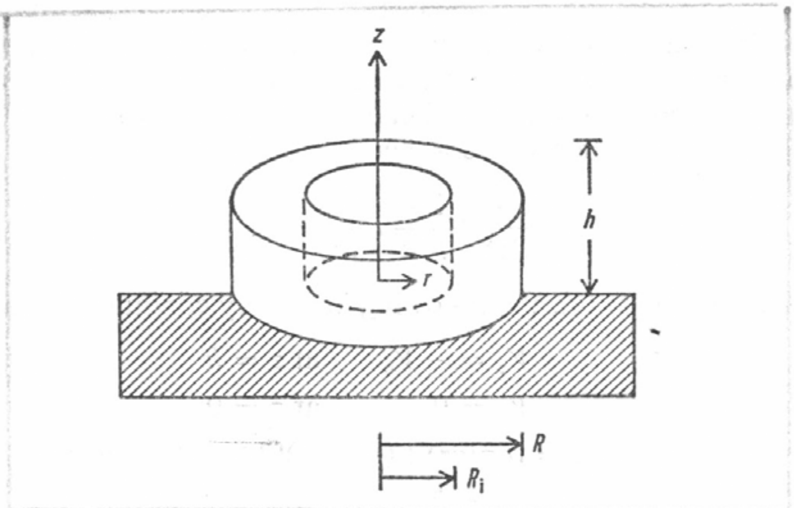

FIG. 2.—Model of the ring shaped film and the coordinate system.

In reality the dimple edge is torus-shaped and not plane-parallel as shown in fig. 1. It is possible that the radius of curvature of such a toroidal surface may alter the behaviour in rupture. In addition, the pressure gradients outside the ring may not be zero as assumed here. While being aware of these short-comings of the model system considered here, we believe that they are outweighed by the advantages. The model not only makes it possible to obtain the exact solution to the problem, but also allows one to retain the essential features of the real system. The latter is satisfied because the pressures inside and outside the ring P_i and P_o are calculated by incorporating the geometry of the real system, *i.e.*, the radii of bubble (R_c) and dimple (R_d), respectively (fig. 1).

With the above assumptions the problem falls in the realm of hydrodynamic stability theory. The first step is to develop an expression for film thinning. This is followed by the linear stability analysis in which arbitrary perturbations are applied to the upper interface and conditions under which these perturbations grow to cause the film to rupture are calculated. The growth rate of perturbation gives the time constant of rupture. Finally, using the fact that the film will rupture when the amplitude of perturbation is equal to the thickness of film, an expression for the critical thickness of rupture is calculated.

RATE OF FILM THINNING

Since the film is thin [$h \ll (r-R_i)$] and the flow in it is slow, the use of the lubrication approximation is justified. In a cylindrical coordinate system, the equations of motion and continuity for axisymmetric flow are:

$$\frac{\partial^2 V_r}{\partial z^2} = \frac{1}{\mu}\frac{\partial P}{\partial r} \tag{1}$$

$$\frac{\partial P}{\partial z} = 0 \tag{2}$$

$$\frac{\partial V_z}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}(rV_r) = 0 \tag{3}$$

where V_r and V_z are the velocity components in the r and z directions, respectively, P is the pressure and μ is the fluid viscosity. It is assumed that the upper and lower interfaces of the ring are plane parallel. Because of the angular symmetry assumption, the angular component of velocity, V_θ, and the angular derivatives $\partial/\partial\theta$ are zero.

The concentration of soluble surfactant, C, in the film for small values of Peclet number is described by Fick's second law:

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial C}{\partial r} = 0. \tag{4}$$

In order to solve eqn (1)-(4), the following boundary conditions must be employed:

$$V_z = -V_o \qquad \text{at } z = h \tag{5}$$

$$V_z = 0 \qquad \text{at } z = 0 \tag{6}$$

$$\mu(\partial V_r/\partial z) = (\partial\sigma/\partial r) + (\mu_s + \mu_d)[\partial(\nabla_r V_r)/\partial r] \text{ at } z = h \tag{7}$$

$$V_r = 0 \qquad \text{at } z = 0 \tag{8}$$

$$P = P_i \qquad \text{at } r = R_i \tag{9}$$

$$P = P_o \qquad \text{at } r = R \tag{10}$$

$$\frac{\partial\Gamma}{\partial t} + \nabla_r(V_r\Gamma) - D_s\Delta_r\Gamma = -D\left(\frac{\partial C}{\partial z}\right) \quad \text{at} \quad z = h \tag{11}$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{12}$$

$$C = C_i \qquad \text{at } r = R_i \tag{13}$$

$$C = C_o \qquad \text{at } r = R. \tag{14}$$

Here $V_o = -\mathrm{d}h/\mathrm{d}t$ is the velocity of film thinning, t is time, D and D_s are the bulk and surface diffusivities, respectively, σ is the local value of surface tension, Γ is the surface concentration of surfactant, P_o and P_i are the equilibrium pressures, C_o and C_i are the equilibrium concentrations in the respective regions. Eqn (5) and (6) are based on the fact that the film thins at a rate V_o at $z = h$ and the plane $z = 0$ is fixed.

Eqn (7) represents the balance of tangential stresses at the upper interface;[16] eqn (8) is the no-slip boundary condition at the solid surface; eqn (11) is the mass balance at the upper interface;[17, 18] eqn (12) presumes zero flux at the solid interface and, finally, eqn (9), (10), (12) and (13) are the specified pressures and concentrations inside the dimple and outside in the bulk fluid, respectively.

Integrating eqn (1)-(3) along with the boundary conditions (5), (6) and (8)-(10) leads to the following expressions for V_r, V_z and P in terms of the radial velocity of the upper interface, $V_r(z = h) = U(r)$:

$$V_r = \frac{1}{2\mu}\left(\frac{\partial P}{\partial r}\right)(z^2 - hz) + U\frac{z}{h} \tag{15}$$

$$V_z = -\frac{1}{r}\frac{\partial}{\partial r}\left[\left(\frac{r}{2\mu}\right)\left(\frac{\partial P}{\partial r}\right)\left(\frac{z^3}{3} - \frac{hz^2}{2}\right) + \frac{rUz^2}{2h}\right] \tag{16}$$

$$\frac{\partial P}{\partial r} = -\frac{12\mu}{h^3}\left(\frac{V_o r}{2} - \frac{hU}{2} + \frac{a_1}{r}\right) \tag{17}$$

$$P = -\frac{12\mu}{h^3}\left(\frac{V r_o{}^2}{4} + a_1 \ln r - \frac{h}{2}\int_{R_i}^{r} U\, dr\right) + a_2 \tag{18}$$

where

$$a_1 = \frac{-(P_o - P_i)(h^3/12\mu) - \frac{V_o}{4}(R^2 - R_i^2) + \frac{h}{2}\int_{R_i}^{R} U\, dr}{\ln (R/R_i)} \tag{19}$$

and

$$a_2 = P_i + \frac{12\mu}{h^3}\left(\frac{V_o R_i^2}{4} + a_1 \ln R_i\right). \tag{20}$$

In order to calculate the velocity of thinning from eqn (16) an explicit expression for the surface radial velocity, $U(r)$, must be obtained. This can be done by first solving eqn (4) for the concentration of surfactants. The surface concentration Γ can be represented as a sum of its equilibrium value Γ_0 and the perturbation Γ_p due to flow:

$$\Gamma = \Gamma_0 + \Gamma_p. \tag{21}$$

It has been shown previously [12] that in cases of practical interest, $\Gamma_p \ll \Gamma_0$, and therefore boundary condition (11) for the steady process can be rewritten:

$$\Gamma_0 \nabla_r U - D_s \Delta_r \Gamma = -D\left(\frac{\partial C}{\partial z}\right) \quad \text{at} \quad z = h. \tag{22}$$

Using the fact that $h/(R - R_i) \ll 1$ and the boundary conditions (12) and (22), the following expression is obtained by integrating eqn (4):

$$\left.\frac{\partial C}{\partial r}\right|_{z=h} = \frac{U}{\phi} + \frac{a_3}{r} \tag{23}$$

where

$$\phi = \left(D_s \frac{\partial \Gamma_0}{\partial C_o} + Dh\right)\Big/\Gamma_0. \tag{24}$$

The solution for $U(r)$ has the following form:

$$U = Ar+\frac{B}{r}. \tag{25}$$

Therefore, it is possible to integrate eqn (23) along with boundary conditions (13) and (14), to obtain the following expression for the concentration, C:

$$C = \frac{A}{2\phi}r^2+\left(\frac{B}{\phi}+a_3\right)\ln r+a_4. \tag{26}$$

Here the integration constants a_3 and a_4 are given by:

$$a_3 = \frac{C_o-C_i}{\ln(R/R_i)}-\frac{A}{2\phi}\frac{(R^2-R_i^2)}{\ln(R/R_i)}-\frac{B}{\phi} \tag{27}$$

$$a_4 = C_o-\frac{A}{2\phi}R^2-\left(\frac{B}{\phi}+a_3\right)\ln R. \tag{28}$$

In order to obtain explicit expressions for A and B in terms of the system parameters, one needs eqn (7). It has been shown previously [12, 13] that the influence of surface viscosities (μ_s and μ_d) on the velocity of thinning is negligible, therefore eqn (7) can be simplified:

$$\mu\left(\frac{\partial V_r}{\partial z}\right) = \left(\frac{\partial\sigma_0}{\partial C_o}\right)\left(\frac{\partial C}{\partial r}\right) \quad \text{at} \quad z = h$$

$$= \left(\frac{\partial\sigma_0}{\partial C_o}\right)\left(\frac{U}{\phi}+\frac{a_3}{r}\right). \tag{29}$$

Once the expression for V_r from eqn (15) is substituted into eqn (29) and coefficients of r and $1/r$ are collected, the following relations for A and B are obtained:

$$A = \frac{3V_o\alpha_1}{h(1+4\alpha_1)} \tag{30}$$

$$B = \left(\frac{\partial\sigma_0}{\partial C_o}\right)\left(\frac{h}{\mu}\right)\frac{(C_o-C_i)}{\ln(R/R_i)}-\frac{h^2}{2\mu}\frac{(P_o-P_i)}{\ln(R/R_i)}+\left[1.5A-1.5\frac{V_o}{h}-\left(\frac{\partial\sigma_0}{\partial C_o}\right)\left(\frac{hA}{2\mu\phi}\right)\right]\frac{(R^2-R_i^2)}{\ln(R/R_i)} \tag{31}$$

where

$$\alpha_1 = \frac{\mu D}{[-\Gamma_0(\partial\sigma_0/\partial C_o)]}\left[1+\frac{D_s(\partial\Gamma_0/\partial C_o)}{Dh}\right]. \tag{32}$$

Since the upper interface of the film is assumed to be parallel to the solid substrate, the condition for continuity of the normal component of the stress tensor has to be replaced by the approximate integral condition for equality of the normal forces acting at the upper surface:

$$F_{\psi} = 2\pi\int_0^{R_1}(P_i-P_o)r\,dr+2\pi\int_{R_1}^{R}(P-P_o)r\,dr$$

$$= \pi\Pi(R^2-R_i^2)-\tfrac{1}{2}\pi(P_o-P_i)(R^2-R_i^2)/\ln(R/R_i)+\frac{3\pi\mu V_o(R^2-R_i^2)R_{\text{eff}}^2}{2h^3}\left(\frac{1+\alpha_1}{1+4\alpha_1}\right) \tag{33}$$

where

$$R_{\text{eff}}^2 = (R^2+R_i^2)-(R^2-R_i^2)/\ln(R/R_i) \tag{34}$$

and F_b is the external driving (*e.g.*, buoyancy) force. After a slight re-arrangement, eqn (33) leads to the following explicit expression for the velocity of thinning, V_o:

$$V_o = \frac{2h^3\Delta P}{3\mu R_{\text{eff}}^2}\left(\frac{1+4\alpha_1}{1+\alpha_1}\right) \tag{35}$$

where

$$\Delta P = \frac{F_b}{\pi(R^2-R_i^2)}-\Pi+\frac{(P_o-P_i)}{2\ln(R/R_i)}. \tag{36}$$

When the surfactants are present in large quantities, α_1 would tend to zero and when the system has no surface active agent, α_1 would tend to infinity. Taking these two limits, one obtains from eqn (35) that addition of surfactants to the film may reduce its drainage velocity by a factor of four $[V_o(\alpha_1 \to \infty) = 4V_o(\alpha_1 = 0)]$. In the limit when $R_i = 0$ and $\alpha_1 = 0$, the velocity V_o reduces to Reynolds' velocity V_{Re} with which a film of radius R_o between two solid planes, under the same pressure difference, ΔP, would thin:

$$V_{\text{Re}} = \frac{2h^3\Delta P}{3\mu R^2}. \tag{37}$$

The fluid enters the ring from the dimple at the following rate:

$$Q_i = 2\pi R_i\int_0^h v_r(R_i)\,\mathrm{d}h = \pi R_i^2 V_o\left[1+\frac{hU(R_i)}{R_i V_o}\right]+2\pi a_1 \tag{38}$$

and fluid leaves the ring at the following rate:

$$Q_o = \pi R^2 V_o\left[1+\frac{hU(R)}{RV_o}\right]+2\pi a_1. \tag{39}$$

Therefore, the net rate at which fluid is drained out of the ring is:

$$Q_{\text{net}} = Q_o-Q_i = \pi(R^2-R_i^2)(V_o+hA). \tag{40}$$

LINEAR STABILITY ANALYSIS

The equations that describe the motion due to any arbitrary, small disturbance, ε at the upper interface of the film are (in the following equation small letters, v_r, v_z, c and γ, denote the perturbed velocities, bulk and surface concentrations, respectively):

$$\frac{\partial^2 v_r}{\partial z^2} = \frac{1}{\mu}\frac{\partial p}{\partial r} \tag{41}$$

$$\frac{\partial^2 v_\theta}{\partial z^2} = \frac{1}{\mu}\frac{1}{r}\frac{\partial p}{\partial \theta} \tag{42}$$

$$0 = \frac{\partial p}{\partial z} \tag{43}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(rv_r)+\frac{1}{r}\frac{\partial v_\theta}{\partial \theta}+\frac{\partial v_z}{\partial z} = 0. \tag{44}$$

Here, angular dependence of the disturbances is incorporated in the analysis to study the role of Rayleigh–Taylor instabilities, such as found in liquid cylinders. The linearized boundary conditions [16, 17] for the system are:

$$v_r = 0; \quad v_\theta = 0; \quad v_z = 0 \quad \text{at} \quad z = 0 \tag{45}$$

$$\mu \frac{\partial v_r}{\partial z} = \left(\frac{\partial \sigma_0}{\partial C_o}\right)\left(\frac{\partial c}{\partial r}\right) + \mu_d\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rv_r) + \frac{1}{r}\frac{\partial v_\theta}{\partial \theta}\right)\right] + \mu_s\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rv_r)\right) + \frac{1}{r^2}\left(\frac{\partial^2 v_\theta}{\partial \theta^2} - 2\frac{\partial v_\theta}{\partial \theta}\right)\right] \quad \text{at} \quad z = h \tag{46}$$

$$\mu \frac{\partial v_\theta}{\partial z} = \left(\frac{\partial \sigma_0}{\partial C_o}\right)\frac{1}{r}\left(\frac{\partial c}{\partial \theta}\right) + \mu_d\left[\frac{1}{r}\frac{\partial}{\partial \theta}\left(\frac{1}{r}\frac{\partial}{\partial r}(rv_r) + \frac{1}{r}\frac{\partial v_\theta}{\partial \theta}\right)\right] + \mu_s\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)\right) + \frac{1}{r^2}\left(\frac{\partial^2 v_r}{\partial \theta^2} + 2\frac{\partial v_r}{\partial \theta}\right)\right] \quad \text{at} \quad z = h \tag{47}$$

$$p = \sigma^f \Delta_H \varepsilon - \varepsilon \frac{d\Pi}{dh} \tag{48}$$

where σ^f is the film surface tension at the upper surface. For most cases of interest σ^f is approximately equal to σ_0, the interfacial tension.[14] The surfactant concentration is given by:

$$\frac{\partial^2 c}{\partial z^2} + \Delta_H c = 0 \tag{49}$$

with the boundary conditions:

$$\frac{\partial c}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{50}$$

$$\frac{\partial \gamma}{\partial t} + \Gamma_0 \nabla_H v_r + \gamma \nabla_H U - D_s \Delta_H \gamma = -D(\partial c/\partial z) \quad \text{at} \quad z = h. \tag{51}$$

Here ∇_H and Δ_H are the surface divergence and Laplacian. In addition, the following kinematic condition describes the motion at the upper interface:

$$v_z \cong \frac{\partial \varepsilon}{\partial t} + U \frac{\partial \varepsilon}{\partial r}. \tag{52}$$

The presence of terms which contain the radial velocity V_r leads to a dispersion equation with variable coefficients and, therefore, an exact solution cannot be obtained analytically. However, these terms become negligible when the surfactant concentration is large and the film is very thin (Appendix 1). Therefore, in order to obtain an analytical solution to the problem, these terms in eqn (51) and (52) are disregarded. Note that the base flow is time-dependent, but it enters the stability analysis only through the thickness $h(t)$. Since the rate of thinning at thickness close to the critical thickness of rupture is usually smaller than the rate of growth of perturbations, the stability analysis can be carried out assuming a quasi-steady-state. Bessel functions of the first and second kind (J_n and Y_n) being the solutions of the Helmholtz equation.

the following form is assumed for the perturbations:

$$\begin{bmatrix} \varepsilon \\ v_z \\ p \\ c \end{bmatrix} = \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \begin{bmatrix} \hat{\varepsilon}_{n,m} \\ \hat{v}_{z,n,m}(z) \\ \hat{p}_{n,m}(z) \\ \hat{c}_{n,m}(z) \end{bmatrix} [J_n(k_m r)+E_{n,m}Y_n(k_m r)] \exp(in\theta)\exp(\beta_{n,m}t). \quad (53)$$

The constant $E_{m,n}$ and wavenumber k_m are determined using the assumption that the disturbances vanish at $r = R_i$ and $r = R$. Therefore,

$$E_{n,m} = -\frac{J_n(k_m R_i)}{Y_n(k_m R_i)} \quad (54)$$

and k_m is given by:

$$J_n(k_m R)Y_n(k_m R_i) = J_n(k_m R_i)Y_n(k_m R). \quad (55)$$

In the limit $R_i \to 0$, $E_{n,m}$ becomes zero. When $k_m R \to \infty$ and $k_m R_i \to \infty$, one obtains

$$k_m \cong \left(\frac{m\pi}{R-R_i}\right). \quad (56)$$

In addition, when the angular dependence is neglected ($v_\theta = 0$ and $\partial/\partial\theta = 0$), one has $n = 0$.

In order to obtain the growth coefficient, $\beta_{m,n}$, eqn (49) is solved along with the boundary conditions (54) and (55) to obtain an expression for $\hat{c}_{n,m}(z)$. This is followed by the integration of eqn (41)-(43) along with the boundary conditions (45)-(47) to obtain an expression for v_r and v_θ in terms of the system parameters. Integration of eqn (43) along with the boundary condition (49) leads to the following expression for the pressure:

$$\hat{p}_{m,n} = \left(\sigma_0 k_m^2 - \frac{d\Pi}{dh}\right)\hat{\varepsilon}_{m,n}. \quad (57)$$

Finally, eqn (44) is integrated along with the boundary condition (45) to derive an expression for v_z. Using the kinematic condition (52), the following expression for $\beta_{m,n}$ is obtained:

$$\beta_{m,n} = \frac{\hat{v}_{z,m,n}}{\hat{\varepsilon}_{m,n}} \qquad z = h$$

$$= -\frac{\sigma_{\text{eff}} h^3 k_m^4}{12\mu}\left(\frac{1+4\alpha_1+\alpha_2}{1+\alpha_1+\alpha_2}\right) \quad (58)$$

where

$$\alpha_2 = \frac{(\mu_d+\mu_s)k_m^2 h}{\mu}\alpha_1 \quad (59)$$

and

$$\sigma_{\text{eff}} = \left[\sigma_0 - \frac{1}{k_m^2}\left(\frac{d\Pi}{dh}\right)\right]. \quad (60)$$

Since in problems of practical interst both α_1 and α_2 are positive, the sign of $\beta_{m,n}$ will depend upon the sign of σ_{eff}. When $\sigma_{\text{eff}} < 0$, the film is unstable at a given thickness h and when $\sigma_{\text{eff}} > 0$, the film is stable. The critical wavenumber, k_c which corresponds to $\beta_{m,n} = 0$, is given by:

$$k_c = \left[\frac{1}{\sigma_0}\left(\frac{d\Pi}{dh}\right)\right]^{\frac{1}{2}}. \tag{61}$$

Therefore, the film will be unstable to perturbations with wavenumbers $k < k_c$. When the film is unstable, the growth coefficient exhibits a maximum at the dominant wavenumber k_d, which can be obtained by setting $\partial\beta_{m,n}/\partial k_m = 0$. In the limit of interest $k_c h \ll 1$,

$$k_d \cong k_c/\sqrt{2} = \left[\frac{1}{2\sigma_0}\left(\frac{d\Pi}{dh}\right)\right]^{\frac{1}{2}} \tag{62}$$

and the corresponding growth coefficient is:

$$\beta_d \cong \frac{h^3}{48\mu\sigma_0}\left(\frac{d\Pi}{dh}\right)^2\left(\frac{1+4\alpha_1+\alpha_2}{1+\alpha_1+\alpha_2}\right). \tag{63}$$

When only dispersion forces are important and Hamaker's law can be used

$$\Pi = -\frac{\tilde{A}}{6\pi h^3}. \tag{64}$$

Here, $\tilde{A}$ is the Hamaker constant for the system. In this case, the time constant for rupture, evaluated as β^{-1}, is given by:

$$\tau \cong 192\pi^2\mu\sigma_0 h^5 \tilde{A}^{-2}\left(\frac{1+\alpha_1+\alpha_2}{1+4\alpha_1+\alpha_2}\right). \tag{65}$$

When surfactants are present in large quantities, both α_1 and α_2 could be equal to zero and therefore:

$$\tau \cong 192\pi^2\mu\sigma_0 h^5\tilde{A}^{-2}. \tag{66}$$

On the other hand, when the system has no surface active agent, α_1 may tend to infinity and

$$\tau \cong 48\pi^2\mu\sigma_0 h^5\tilde{A}^{-2}. \tag{67}$$

This limit, however, may violate the assumption that terms containing "U" can be neglected in eqn (51) and (52).

The growth coefficient, critical and dominant wave numbers and time constant of rupture for the present geometry have the same expressions as obtained previously by Jain and Ruckenstein [15] using the body force approach for a radially unbounded film on a solid substrate.

CRITICAL THICKNESS OF FILM RUPTURE

The mean thickness of film at which rupture occurs, referred to as the critical thickness, h_{cr}, depends on both the motions due to thinning and the present perturbations. These two motions can be combined by realizing that

$$v_\varepsilon = \frac{\partial\varepsilon_{m,n}}{\partial t} = \beta_{m,n}\varepsilon_{m,n} = \left(\frac{\partial\varepsilon_{m,n}}{\partial h}\right)\frac{dh}{dt} = -\left(\frac{\partial\varepsilon_{m,n}}{dh}\right)V_o. \tag{68}$$

This assumption is consistent with the assumption that the flow is quasi-steady. Therefore, all time-dependent quantities depend on t only *via* h.

Integration of eqn (68) leads to:

$$\varepsilon_{m,n}(h) = \varepsilon^{\circ}_{m,n}(h_0)\exp\left(-\int_{h_0}^{h}\frac{\beta_{m,n}}{V_o}\,dh\right). \tag{69}$$

The film will rupture when the amplitude of the wave with the largest value of ε is approximately equal to the thickness of the film at that time, *i.e.*, when $h_{cr} = \varepsilon_{cr}$ (Appendix 2). This condition would lead to an explicit expression for h_{cr} from eqn (69).[10] In order to simplify the analysis, α_2 is set equal to zero (but not α_1) in the expression for $\beta_{m,n}$ [eqn (58)]. In addition, n is set equal to zero. (This approximation is discussed later.) Consequently,

$$\varepsilon_m(h_{cr}) = \varepsilon_m^{\circ}(h_0) \exp\left[\frac{k_m^2 R_{eff}^2}{8} \int_{h_0}^{h_{cr}} \frac{(\sigma_0 k_m^2 - \Pi')}{\Delta P}\, dh\right] \tag{70}$$

where

$$\Pi' = d\Pi/dh.$$

Let us find the wavenumber that will lead to the maximum value of ε_m at $h = h_{cr}$ by setting $d\varepsilon_m/dk_m$ equal to zero. We will refer to this wave as the rupturing wave,* k_r, and the corresponding value of $h_0(k_r)$, saitsfying (61) as the transition thickness, h_t. Neglecting the dependence of ε_m° on k_m, one obtains the following expression for k_r:

$$k_r^2 = \frac{1}{2\sigma_0} \int_{h_t}^{h_{cr}} \frac{\Pi'}{\Delta P}\, dh \left(\int_{h_t}^{h_{cr}} \frac{dh}{\Delta P}\right)^{-1}. \tag{71}$$

Using the fact that $k_r^2 = \Pi'(h_t)/\sigma_0$ [see eqn (61)], it is possible to obtain the following relation between h_t and h_{cr} from eqn (71):

$$\int_{h_t}^{h_{cr}} \left[\frac{2\Pi'(h_t) - \Pi'(h)}{\Delta P}\right] dh = 0. \tag{72}$$

In reality, a disturbance is given by the superposition of an infinite number of waves [see eqn (53)], which is approximated here by an integral: [10, 19]

$$\varepsilon = \sum_{m=1}^{\infty} \varepsilon_m \approx (R_o - R_i) \int_0^{\infty} \varepsilon_m\, dk_m. \tag{73}$$

Since the function ε_m exhibits a sharp maximum around k_r, the integral in eqn (73) is evaluated by the method of steepest descent. The film will rupture when $h_{cr} = |\varepsilon|$.

Following Vrij [19] the root mean square $\sqrt{(\bar{\varepsilon}^2)}$ is used instead of $|\varepsilon|$ to calculate the critical thickness of rupture. The use of $\sqrt{(\bar{\varepsilon}^2)}$ also accounts, at least in part, for the neglected angular dependence of $\varepsilon(r, \theta)$.[10] In addition, the initial perturbation ε_m° is calculated using the Einstein's theorem [20] for thermal fluctuations:

$$k_B T = \pi \sigma_0 k_m^2 \int_{R_i}^{R_o} (\varepsilon_m^{\circ})^2\, r\, dr. \tag{74}$$

Using the above mentioned procedure, the following expression is obtained for the critical thickness of rupture:

$$h_{cr}^2 = \frac{2k_B T}{R_{eff}^2 \Pi'(k_t)} \left[\frac{(R_o - R_i)^2}{R_o^2 - R_i^2}\right] \left(\int_{h_{cr}}^{h_t} \frac{\Pi'}{\Delta P}\, dh\right)^{-1} \times \exp\left[\frac{R_{eff}^2 \Pi'(h_t)}{8\sigma_0} \int_{h_{cr}}^{h_t} \frac{\Pi'}{\Delta P}\, dh\right]. \tag{75}$$

Errors introduced in the calculation of h_{cr} due to the assumption of wave superposition and root mean square thickness are estimated in Appendices 3 and 4, respectively.

* This has been referred to as the critical wave in some previous works.[10, 14] Since, in the stability analysis, critical wavenumber corresponds to the marginal stability we have used this nomenclature.

ASYMPTOTIC FORMS AND NUMERICAL RESULTS

VELOCITY OF THINNING

Since the velocity of thinning plays a critical role in the behaviour of the wetting films, the role of the dimple on V_o is estimated here. The driving force F_b is set equal to the force exerted by a bubble or a capillary of radius R_c [see eqn (33)]. Therefore,

$$\Delta P = P_\lambda - \Pi = P_\sigma \left[\frac{1}{(1-\eta^2)} + \frac{(1+R_c/R_d)}{\ln(\eta)}\right] - \Pi \tag{76}$$

where $P_\sigma = 2\sigma_o/R_c$ and $\eta = R_i/R$. At η equal to zero, ΔP is simply $(P_\sigma - \Pi)$. As η increases, ΔP will vary depending on the value of (R_c/R_d), Π and P_σ. Typical values

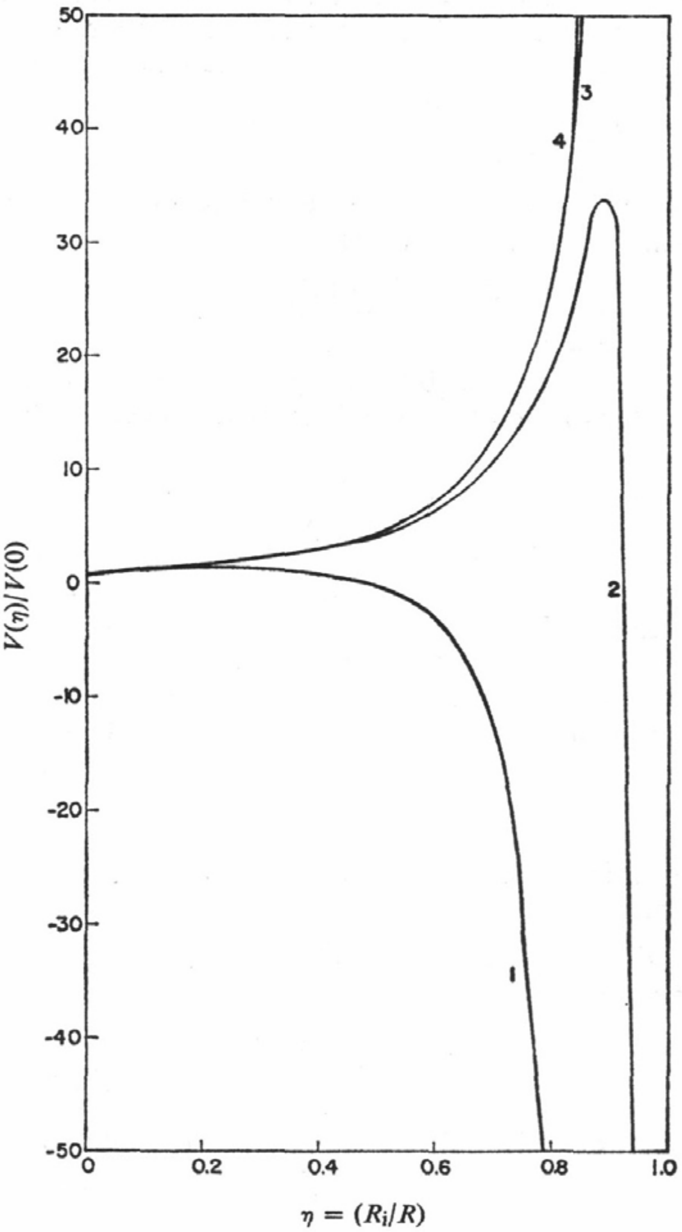

FIG. 3.—Effect of the ratio of the inside and outside radii of ring on the dimensionless velocity of thinning. The radius of dimple (R_d) varies from 0.1 to 100 cm. [$A = 10^{-12}$ erg; $\sigma_o = 50$ dyn cm^{-1}; $h = 50$ nm; $R_c = 0.2$ cm; $R_d = 0.1(1), 1(2), 10(3), 100(4)$ cm].

of the system parameters are taken as : $\sigma_o = 50$ dyn cm^{-1} ; $R = 10^{-2}$ cm ; $h = 5\times10^{-5}$ cm and $\tilde{A} = 10^{-12}$ erg. The value of R_d can be estimated by using the following relationship derived by Frankel and Mysels :[6]

$$h_d = R_r\sqrt{\frac{h}{3.05\,R_c}} \tag{77}$$

where h_d and h are the maximum and minimum thicknesses of the film and R_r is the mean radius of the barrier ring [$= (R+R_i)/2$] (fig. 1). Assuming that the dimple is the cap of a sphere of radius R_d, one can obtain the following relation between R_d and h_d :

$$R_d \approx \frac{2R_i^2}{(h_d-h)}. \tag{78}$$

Using the above values of parameters and $\eta = 0.9$, we obtain $R_d \approx 4$ cm for $h = 10^{-5}$ cm and $R_d \approx 6$ cm for $h = 0.4\times10^{-5}$ cm. Since the analysis in ref. (6) gives only an estimate of h_d,[7] we have chosen $R_d = 0.1$, 1, 10 and 100 cm. Shown in fig. 3 is the effect of a dimple on the velocity of thinning for a film with $h = 5\times10^{-6}$ cm. As R_d decreases, the velocity of thinning decreases and ultimately it becomes negative (*i.e.*, the film starts thickening). As the magnitude of disjoining pressure increases (due to an increase in $\tilde{A}$ and/or decrease in h), the velocity of thinning increases.

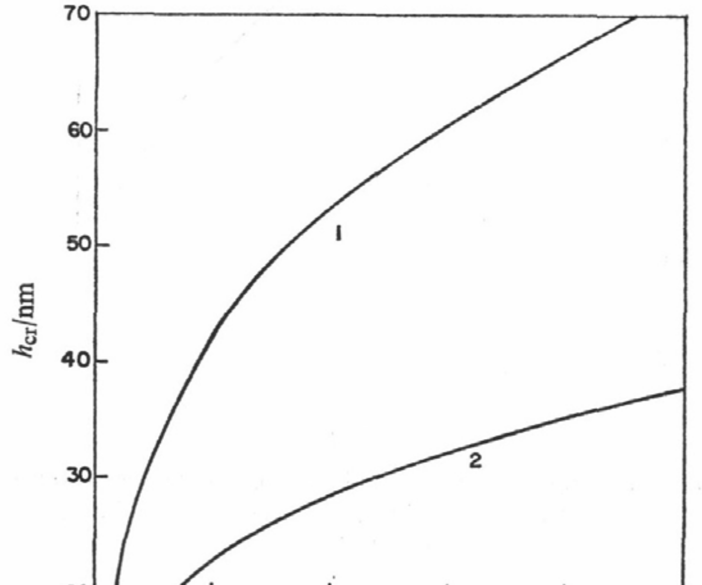

FIG. 4.—Effect of the radius of a plane-parallel film on its critical thickness of rupture (h_{cr}). [$\sigma_0 = 50$ dyn cm^{-1} ; $R_c = 0.2$ cm ; $T = 298$ K ; $\tilde{A} = 10^{-12}(1)$; $10^{-13}(2)$ erg].

RELATIONS BETWEEN h_{cr} AND h_t

Since ΔP has two components P_λ (independent of h) and Π (function of h), it is possible to obtain bounds on the ratio (h_t/h_{cr}) by setting one component equal to zero and integrating eqn (72) analytically. When $|\Pi| \ll P_\lambda$, $h_t/h_{cr} = 1.39$ and when $|\Pi| \gg P_\lambda$, $h_t/h_{cr} = 1.49$. Therefore, in the following analysis, unless indicated, h_t/h_{cr} is taken to equal 1.4.

CRITICAL THICKNESS WITHOUT DIMPLE

Shown in fig. 4 are the typical results of numerical solution of coupled eqn (72) and (75). As in foam films, h_{cr} increases with the radius of film, R, the Hamaker constant, $\tilde{A}$, and the bubble radius, R_c, and decreases with the surface tension σ_0 and temperature, T.

ROLE OF DIMPLE ON CRITICAL THICKNESS

Fig. 5 shows that the critical thickness of rupture, calculated by numerically solving eqn (72) and (75), decreases as R_d increases, and/or width of the ring $(R-R_i)$ decreases. For instance, for $R_{eff} = 10^{-2}$ cm, $\tilde{A} = 10^{-12}$ erg, $\sigma_0 = 50$ dyn cm^{-1}; $R_c = 0.1$ cm, and $T = 298$ K, h_{cr} is 1.11×10^{-5} cm at $\eta = 0$, and it decreases to 5.5×10^{-6} cm for $R_d = 100$ cm and $\eta = 0.99$ $(R-R_i = 10^{-4}$ cm) (fig. 5). These are typical values in critical thickness measurements.

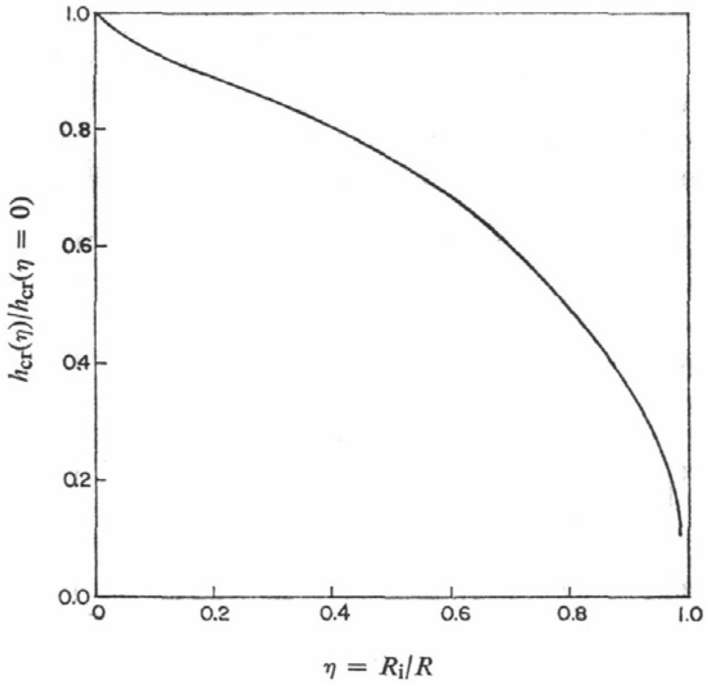

FIG. 5.—Effect of the ratio of the inside to outside radii of ring on the dimensionless critical thickness of rupture. [$\tilde{A} = 10^{-12}$ erg; $\sigma_0 = 50$ dyn cm^{-1}; $R_c = 0.2$ cm; $R_d = 10$ cm; $R_0 = 1.54 \times 10^{-2}$ cm; $h_{cr}(0) = 49.3$ nm].

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LIST OF SYMBOLS

a_1–a_4 = integration constants [eqn (19), (2), (27), (28)]
$\tilde{A}$ = Hamaker constant
A, B = constants defined by eqn (30) and (38)
c = perturbed bulk concentration
C, C_i, C_o = surfactant concentration within, inside and outside the ring, respectively
D, D_s = bulk and surface diffusion coefficients
$E_{n,m}$ = constant given by eqn (54)
F_b = normal force at the upper surface [eqn (33)]
h = film thickness
h_0, h_{cr} = initial and critical thickness, respectively
h_d = maximum thickness of the film
J_n, Y_n = Bessel functions of the first and second kind
k = wavenumber
k_r = wavenumber of rupturing wave
k_c, k_d = critical and dominant wave numbers, respectively
k_B = Boltzmann constant
p = perturbation in the base pressure
P, P_i, P_o = pressures within, inside and outside the ring
P_λ = pressure defined by eqn (76)
$P_\sigma = 2\sigma_0/R_c$ = Laplace jump across a curvature of radius R
ΔP = driving pressure [eqn (36)]
Q_i, Q_0, Q_{net} = flow rates given by eqn (38)-(40)
R_i, R = inner and outer radii of the ring, respectively (cm)
R_c, R_d = radii of bubble and dimple, respectively
R_r = average radius of the barrier ring
R_{eff} = effective radius defined by eqn (34)
t = time
T = absolute temperature
U = radial velocity at the upper interface
v_r, v_θ, v_z = perturbation velocities in r, θ and z directions, respectively
V_o = velocity of thinning
V_r, V_z = radial and axial velocity components
V_{Re} = Reynolds' velocity of thinning

α_1, α_2 = parameters defined by eqn (32) and (59)
β = growth coefficient
γ = perturbed surface concentration
Γ_0 = equilibrium surface concentration (mol cm^{-2})
Γ_p = perturbation surface concentration due to thinning
Δ_H = surface Laplacian
ε = geometrical perturbation at the upper interface
$\eta = R_i/R$ = ratio of inner to outer radii of the ring
μ = bulk viscosity
μ_d, μ_s = surface viscosities
Π = disjoining pressure
σ_0 = equilibrium surface tensions (dyn cm^{-1})
σ^f = film tension (dyn cm^{-1})
σ_{eff} = quantity defined by eqn (60)
τ = time constant of rupture
ϕ = parameter defined by eqn (24)

APPENDIX 1

In the analysis presented above, we neglected the coupling terms between the drainage flow and the disturbance flow. We shall estimate these terms for a tangentially immobile film on a sloid substrate and demonstrate that these terms are negligible for a film which is very thin. The thickness H of a film with deformable interfaces can be described by the following general equation: [13]

$$-\frac{\partial H}{\partial t} = \nabla_r\left[\frac{H}{2}(U^A+U^B)-\frac{H^3}{12\mu}\frac{\partial P}{\partial r}\right] \tag{A1.1}$$

where U^A and U^B are the radial velocities at the upper and lower interfaces of the film. The base case can be obtained by setting $H = h$ into eqn (A1.1). Substituting also $U^A = U^B = 0$ (tangential immobility), we obtain

$$\frac{\partial h}{\partial t} = \nabla_r\left(\frac{h^3}{12\mu}\frac{\partial P}{\partial r}\right). \tag{A1.2}$$

Subtracting eqn (A1.2) from (A1.1), making use of eqn (48) and neglecting terms $O(\varepsilon^2)$ and smaller leads to the following dispersion equation:

$$\beta = \frac{\sigma_{eff}h^3k_m^4}{12\mu}+\delta \tag{A1.3}$$

where the coupling term, δ, is given by:

$$\delta = -3\frac{V_0}{h}\frac{\Delta_r(r\varepsilon)}{\varepsilon} = -3\frac{V_0}{h}\left(2+\frac{\partial \ln \varepsilon}{\partial \ln r}\right). \tag{A1.4}$$

For an aqueous film of the thickness $O(10)$ nm and radius (10^{-2}) cm, thinning under a driving pressure $\Delta P \sim 500$ dyn cm^{-2}, V_0/h is $O(10^{-3})$ s^{-1}. Therefore, δ is negligible compared to the growth coefficient β, after the onset of instability when $\beta = 0$.

The coupling term (A1.4) can also be estimated by using a Taylor series expansion around $z = h$ on the boundary condition: [21]

$$v_r+V_r = 0 \qquad \text{at } z = h+\varepsilon. \tag{A1.5}$$

Following the analysis discussed above, we find that the coupling term, δ^*, for a foam film (thin film between two bubbles) is one-half that δ [see eqn (A1.4)] for a wetting-foam (thin film on a solid substrate).

APPENDIX 2

Implicit in the estimation of h_{cr} is the assumption that the linear stability is valid up to the point of rupture. In order to check this assumption, ε/h was calculated as a function of h from the initial thickness, h_0, to the critical thickness of rupture, h_{cr}, using eqn (70) and (74). ε/h was <0.1 until the film was about to rupture ($h \approx 1.2\ h_{cr}$) (see fig. 6).

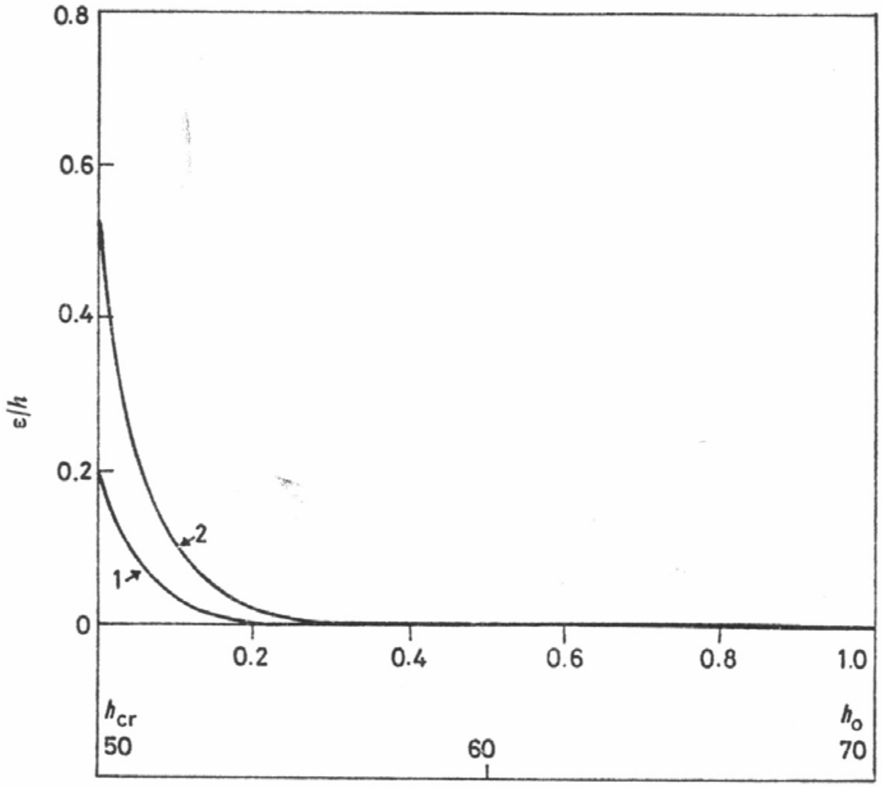

FIG. 6.—Ratio of the wave amplitude to film thickness (ε/h) as a function of film thickness. [$\tilde{A}$ = 10^{-13}(1); 10^{-12}(2) erg].

APPENDIX 3

While using the wave-superposition principle to compute the shape of the disturbance, we employed the well-known formula:

$$\sum_{m=0}^{\infty}{}' f(m) = \int_0^\infty f(m)\,dm + \frac{1}{12}f'(0) - \frac{1}{30.4!}f'''(0) + \ldots \qquad (A3.1)$$

and kept only the first term in eqn (73). This term was later computed by the method of steepest descent. Numerically, we calculated the error due to these assumptions to be $<10\ \%$ for typical values of parameters: $\tilde{A} = 10^{-12}$ erg; $\sigma_0 = 50$ dyn cm^{-1}; $h = 50$ nm; $R_c = 0.2$ cm and $T = 298$ K.

APPENDIX 4

In the present analysis, the root mean square amplitude $\sqrt{(\bar{\varepsilon}^2)}$ was used instead of $|\varepsilon|$ to calculate the critical thinness of rupture. Using eqn (70) and (74), we obtain that:

$$\left|\frac{\varepsilon_m(r)}{\sqrt{(\bar{\varepsilon}_m^2)}}\right| = \left|\frac{J_0[\lambda_m(r/R)]}{\sqrt{2}J_1(\lambda_m)}\right| \tag{A4.1}$$

where, λ_m is the mth zero of the Bessel function, J_0. Depending upon the radial position, r, the right hand side of eqn (A4.1) may vary between 0 and 1 for given values of R and λ_m. If ε_m is averaged over the film $(0 \leqslant r \leqslant R)$, the ratio $|\varepsilon_m/\sqrt{(\bar{\varepsilon}_m^2)}|$ is $O(1)$.

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