

Spontaneous Rupture of Thin Liquid Films

BY ELI RUCKENSTEIN* AND RAKESH K. JAIN

State University of New York at Buffalo,
Faculty of Engineering and Applied Sciences,
Buffalo, New York 14214

and Department of Chemical Engineering, University of Delaware, Newark,
Delaware 19711

Received 25th June, 1973

The rupture of a liquid film on a solid surface and of a free liquid film have been studied using hydrodynamic stability theory. The films are not thicker than several hundred Ångström. A small perturbation applied to the free interface generates motions in the film, and the assumption is made that the Navier–Stokes equations can be used to describe them. The difference in forces acting upon an element of liquid in a thin film and in a bulk fluid is accounted for by introducing a body force in the Navier–Stokes equations. This force is calculated from the potential energy per unit volume in the liquid caused by the London–van der Waals interactions with the surrounding molecules of the liquid and with those of the solid. If the perturbation grows, it leads to the rupture of the film. The range of wavelengths of the perturbation for which instability occurs is established and the time of rupture is evaluated. The effect of insoluble and soluble surface active agents is analyzed. Available experimental data concerning condensation on a solid surface and coalescence of bubbles are explained on the basis of the obtained results.

The mechanism of rupture of thin liquid films is of importance for the understanding of flotation, of foams and emulsions, of coalescence of bubbles and droplets, of vapour condensation on a solid surface, and so on. In flotation, for instance, the thinning and the rupture of the liquid film between particles and bubbles might be the rate determining step of the process.¹ Two bubbles may coalesce if the contact time between them is longer than the time needed for the thinning and rupture of the liquid film between them. In water vapour condensation on a shock-tube wall, experiment shows that on a hydrophobic surface a thin film is formed, which breaks up into droplets upon reaching a critical thickness of about 100 Å.²

Scheludko^{3, 4} was the first to relate via a thermodynamic treatment the rupture of thin liquid films to their instability to small surface deformations. Although the surface free energy increases with the increasing surface area associated with these deformations, the total free energy of the film can decrease because of the London–van der Waals forces between molecules. A critical wavelength λ_c is predicted for which the total free energy is not changed by the corresponding perturbation. For a free film this critical wavelength is given by*

$$\lambda_c = \left(\frac{128\pi\sigma}{A_{11}} \right)^{\frac{1}{3}} h_0^2. \quad (1)$$

The film is stable for all wavelengths less than λ_c , and it is unstable for greater wavelengths.

This thermodynamic treatment of the problem gives no information about the

* the nomenclature is given in Appendix 1.

time needed for the occurrence of rupture. Assuming laminar liquid flow parallel to the surfaces of the free film of uniform thickness, h_0 , and no slip at the interfaces, Vrij⁵ has established a kind of diffusion equation for the thickness of the film, which allows one to calculate the growth rate of the perturbation. His results for thin free liquid films are

$$\lambda_c = \left(\frac{4\pi^3\sigma}{A_{11}} \right)^{\frac{1}{2}} h_0^2 \quad (2)$$

and

$$\tau_m \approx 96\pi^2\sigma\mu h_0^5 A_{11}^{-2} \quad (3)$$

where τ_m is a time constant for rupture corresponding to the wavelength for which the rate of growth is maximum.

One can obtain information about the film rupture, including the time of rupture, from a more rigorous procedure than that used in the cited papers, namely hydrodynamic linear stability theory.⁶ Whereas the previously cited authors have solved parts of the problem (using a specific model for each), the stability analysis permits a unified approach leading to the prediction of both the critical wavelength and time of rupture. Felderhof⁷ has applied the hydrodynamic stability analysis to a thin free film accounting for the van der Waals dispersion forces and the double layer forces. His treatment is, however, restricted to the unrealistic situation of inviscid flow. In recent papers, brought to our notice by one of the referees, Lucassen *et al.*⁸ and Vrij *et al.*⁹ have extended the treatment to a free film of a viscous liquid.

In the present paper two situations are treated: (i) stability of a thin layer of liquid on a solid surface and (ii) stability of a thin free film. The emphasis is on the first situation because it was not examined previously. Compared to the previous ones, the present treatment has the advantage of simplicity. Because the thickness of the layer is very small, it is natural to use from the beginning the lubrication approximation of the hydrodynamic equations of motion.¹⁰ This approximation, applied here to pure liquids and to liquids containing surface active impurities, allows one to obtain, in a simple way, information about the critical wavelength λ_c and time of rupture τ_m .

THIN PURE LIQUID LAYER ON A SOLID SURFACE

Consider a thin layer of liquid having a thickness h_0 , not larger than several hundred Ångström. Since the distance over which the London dispersion forces are effective is of the same order of magnitude, the behaviour of the film is strongly influenced by such forces. Small perturbations are applied to the liquid-gas interface (fig. 1). The film is unstable and will rupture if the perturbation grows in time; the film is stable in the opposite case. If the forces of interaction between the molecules of the solid and liquid are stronger than those between the molecules of the liquid, the film will always be stable. In the opposite case it may be unstable. The perturbation generates motion in the film and the assumption will be made that the Navier-Stokes equations can be used to describe the motion. The forces which act upon an element of liquid in a thin layer differ from those in a bulk fluid because the range of intermolecular forces is larger than the thickness of the film. Compared to a bulk liquid, some liquid molecules are replaced by the atoms of the solid or of the gas within the range of intermolecular forces. The difference in forces between the thin layer and the bulk liquid is accounted for in the equations of motion by a body force.

Since the motion is very slow, the inertial terms can be neglected compared to the viscous terms. Consequently, assuming a two-dimensional motion,

$$\mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) = \frac{\partial p}{\partial x} + \frac{\partial \phi}{\partial x} \quad (4)$$

$$\mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) = \frac{\partial p}{\partial y} + \frac{\partial \phi}{\partial y} \quad (5)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \quad (6)$$

In eqn (4) and (5), ϕ is the potential energy function per unit volume in the liquid accounting for the difference in behaviour between a thin film and a bulk liquid. It is caused by the London-van der Waals interaction with the surrounding molecules of the liquid and with the solid and by the double layer forces. The function ϕ depends on the thickness h of the liquid film and on y .

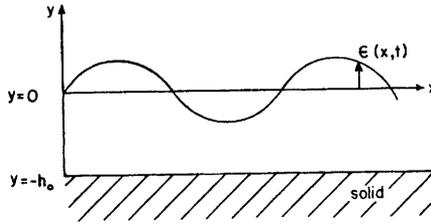


FIG. 1.—Perturbation applied at the liquid-gas interface.

The boundary conditions at the solid-liquid interface are

$$u = v = 0 \quad \text{at} \quad y = -h_0. \quad (7)$$

At the free surface, for deformations of small amplitude, the equality of the normal stresses leads to :

$$-p + 2\mu \frac{\partial v}{\partial y} = -p_0 + \sigma \frac{\partial^2 \epsilon}{\partial x^2} \quad \text{at} \quad y \approx 0, \quad (8)$$

and the equality of tangential stresses leads to

$$\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = 0 \quad \text{at} \quad y \approx 0. \quad (9)$$

For ultra thin films the surface tension may depend on the thickness of the film and consequently the derivative $d\sigma/dx$ has to be introduced in the right-hand-side of the boundary condition (9). Such an effect is, however, ignored here.

The kinematic condition at the interface gives:

$$\frac{\partial \epsilon}{\partial t} \approx v_{y=0}. \quad (10)$$

For wavelengths of the perturbation which are large compared to the thickness of the film, the lubrication approximation of the Navier-Stokes equations can be used.

Consequently, eqn (4) and (5) become

$$\mu \frac{\partial^2 u}{\partial y^2} = \frac{\partial}{\partial x}(p + \phi) = \frac{\partial P}{\partial x} \tag{11}$$

$$0 = \frac{\partial}{\partial y}(p + \phi) = \frac{\partial P}{\partial y} . \tag{12}$$

Using the boundary condition (8), one can write* :

$$P = p_0 + 2\mu \frac{\partial v}{\partial y} + \phi_0 - \sigma \frac{\partial^2 \varepsilon}{\partial x^2} \text{ at } y \approx 0 \tag{13}$$

and since eqn (12) shows that P is independent of y , eqn (11) and (13) lead to :

$$\mu \frac{\partial^2 u}{\partial y^2} = 2\mu \frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} \right)_{y=0} - \sigma \frac{\partial^3 \varepsilon}{\partial x^3} + \frac{\partial \phi_0}{\partial x} . \tag{14}$$

Because $\phi_0 = \phi_0(h) = \phi_0(h_0 + \varepsilon)$

$$\frac{\partial \phi_0}{\partial x} = \left(\frac{\partial \phi_0}{\partial h} \right) \frac{\partial \varepsilon}{\partial x} \approx \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \frac{\partial \varepsilon}{\partial x} \tag{15}$$

and eqn (14) becomes

$$\mu \frac{\partial^2 u}{\partial y^2} = 2\mu \frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} \right)_{y=0} - \sigma \frac{\partial^3 \varepsilon}{\partial x^3} + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \frac{\partial \varepsilon}{\partial x} . \tag{16}$$

The question of interest is whether the surface perturbation grows or decays in time. The stability will be examined with respect to a small periodic perturbation because the effect of any small perturbation can be obtained by superimposing the effects of its Fourier components. Consequently,

$$\begin{bmatrix} u \\ v \\ \varepsilon \end{bmatrix} = \begin{bmatrix} \hat{u}(y) \\ \hat{v}(y) \\ \hat{\varepsilon} \end{bmatrix} e^{ikx} e^{\beta t} . \tag{17}$$

Introducing expressions (17) in eqn (6), (16), (7) and (9), one obtains

$$D\hat{v} + ik\hat{u} = 0 \tag{6a}$$

$$\mu D^2 \hat{u} = ik^3 \sigma \hat{\varepsilon} + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} ik \hat{\varepsilon} + 2\mu ik (D\hat{v})_{y=0} \tag{16a}$$

$$\hat{u} = \hat{v} = 0 \text{ at } y = -h_0 \tag{7a}$$

$$D\hat{u} + ik\hat{v} = 0 \text{ at } y \approx 0. \tag{9a}$$

Eliminating u from eqn (16a), (7a), and (9a) by using eqn (6a), one obtains :

$$D^3 \hat{v} = \frac{1}{\mu} \left[\sigma k^4 + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} k^2 \right] \hat{\varepsilon} + 2k^2 (D\hat{v})_{y=0} \tag{18}$$

$$\hat{v} = D\hat{v} = 0 \text{ at } y = -h_0 \tag{19}$$

$$(D^2 + k^2)\hat{v} = 0 \text{ at } y \approx 0. \tag{20}$$

* The lubrication approximation is applied here only to the Navier–Stokes equations, but not to the boundary conditions. This leads to some smaller order terms in the final results.

The solution of eqn (18) has the form :

$$\hat{v} = c_1 + c_2(y + (k^2 y^3)/3) + c_3 y^2 + \frac{\hat{\epsilon}}{6\mu} \left[\sigma k^4 + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} k^2 \right] y^3. \quad (21)$$

The boundary conditions (19) and (20) lead to

$$c_1 = -\frac{h_0^3}{3\mu} \frac{\left[\sigma k^4 + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} k^2 \right] \hat{\epsilon}}{\left[1 + \frac{3}{2}(kh_0)^2 - \frac{1}{6}(kh_0)^4 \right]} \quad (22a)$$

$$c_2 = \frac{c_1}{2h_0} \frac{\left[1 + \frac{5}{6}(kh_0)^2 - \frac{1}{6}(kh_0)^4 \right]}{\left[1 + (kh_0)^2 \right]} \quad (22b)$$

$$c_3 = -\frac{k^2}{2} c_1. \quad (22c)$$

The kinematic condition, eqn (10), leads to the result

$$\beta = \left(\frac{\hat{v}}{\hat{\epsilon}} \right)_{y=0} = \frac{c_1}{\hat{\epsilon}} = \frac{(kh_0)^2}{3\mu h_0} \left[\frac{-\left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} h_0^2 - \sigma (kh_0)^2}{1 + \frac{3}{2}(kh_0)^2 - \frac{1}{6}(kh_0)^4} \right]. \quad (23)$$

Rupture of the film will occur for those wave numbers for which $\beta > 0$.

The lubrication approximation used here is valid only if $h_0/\lambda \ll 1$. Consequently, the denominator in eqn (23) is positive in the range of values for which the above mentioned approximation can be made.

The condition $\beta = 0$ defines a critical wavenumber k_c

$$k_c = \left[-\frac{1}{\sigma} \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \right]^{\frac{1}{2}}. \quad (24)$$

The growth coefficient β has a maximum for the dominant wavenumber k_d , which is given by

$$(k_d h_0)^2 = \frac{6}{9 - k_c^2 h_0^2} \left[\left(1 + \frac{1}{6}(k_c h_0)^2 (9 - k_c^2 h_0^2) \right)^{\frac{1}{2}} - 1 \right]. \quad (25)$$

Since $k_c h_0 \ll 1$, eqn (25) can be approximated by

$$k_d \sqrt{2} \approx k_c. \quad (26)$$

The coefficient for maximum rate of growth, β_m , is therefore given by

$$\beta_m = \frac{\sigma}{3\mu h_0} \frac{(k_d h_0)^4 \left[(k_c/k_d)^2 - 1 \right]}{\left[1 + \frac{3}{2}(k_d h_0)^2 - \frac{1}{6}(k_d h_0)^4 \right]} \approx \frac{h_0^3}{12\mu\sigma} \left[\left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \right]^2. \quad (27)$$

Because the growth of the perturbation is dominated by the fastest growing perturbation, one may expect that the time needed for the rupture of the film will be of the order of $\beta_m^{-1} \approx \tau_m$.

To determine the values of k_c and τ_m , an explicit expression for the potential energy, $\phi_0(h)$, is needed. This potential is due to London-van der Waals dispersion forces and to the double layer forces. Neglecting the double layer forces, one obtains (see Appendix 2)

$$\phi_0(h) = \phi_B + A/6\pi h^3 \quad (28)$$

where $A = A_{11} - A_{12}$ and A_{ij} is Hamaker's constant for the interactions between

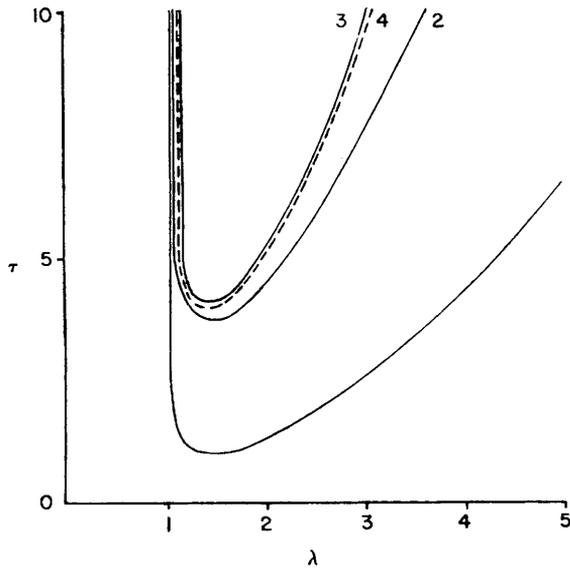


FIG. 2.—Time constant ($\tau = 1/\beta$) as a function of wavelength λ for a thin film on a solid surface. The values of the parameters are given in table 1. The unit of τ is the value of τ_m calculated from eqn (31) and the unit of λ is the value of λ_c calculated from eqn (30). Curve 1, pure liquid film; curve 2, liquid film with gaseous monolayer of insoluble surfactant; curve 3, liquid film with a condensed monolayer of insoluble surfactant; curve 4, liquid film with a gaseous monolayer of soluble surfactant.

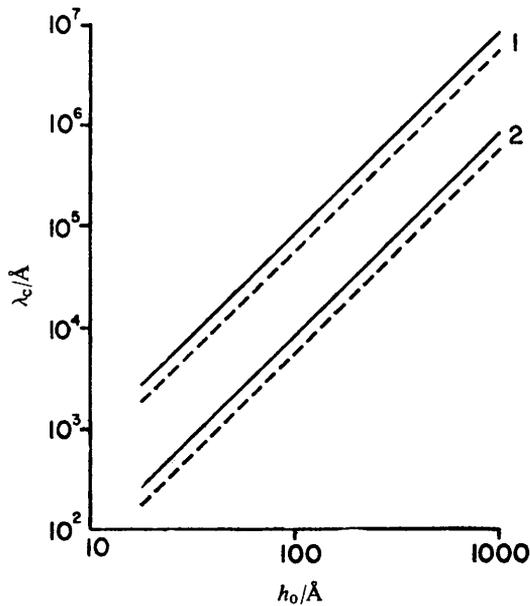


FIG. 3.—Critical wavelength $\lambda_c/\text{\AA}$ as a function of film thickness $h_0/\text{\AA}$. Curve 1, Hamaker constant $A = 10^{-14}$ erg; $\sigma = 30$ dyn/cm; curve 2, Hamaker constant $A = 10^{-12}$ erg; $\sigma = 30$ dyn/cm; —, liquid film on a solid surface; ---, free liquid film.

molecules of type i and j (1 refers to the liquid and 2 to the solid). Interactions with the molecules of the gas are neglected. Using eqn (28), eqn (23), (24) and (27) lead to

$$\beta = \frac{(kh_0)^2}{3\mu h_0} \frac{[(A/2\pi h_0^2) - \sigma(kh_0)^2]}{[1 + \frac{3}{2}(kh_0)^2 - ((kh_0)^4/6)]} \tag{29}$$

$$\lambda_c = \frac{2\pi}{k_c} = \left(\frac{8\pi^3\sigma}{A}\right)^{\frac{1}{2}} h_0^2 \tag{30}$$

$$\tau_m \approx 48\pi^2\sigma\mu h_0^5 A^{-2}. \tag{31}$$

Eqn (29), (30) and (31) are plotted in fig. 2, 3 and 4 respectively.

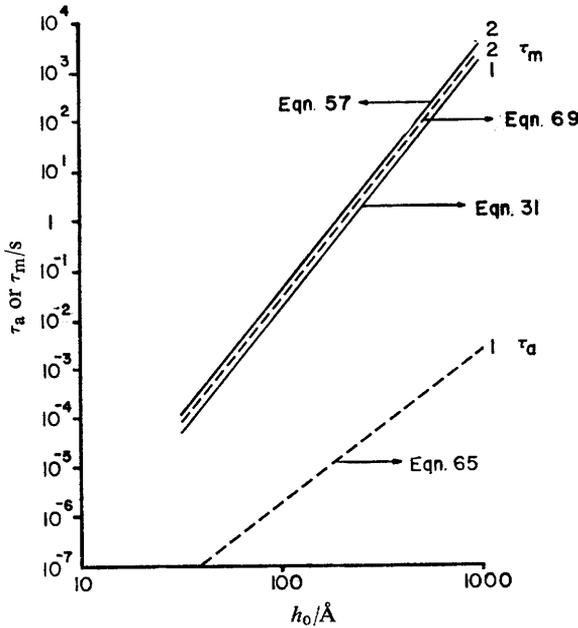


FIG. 4.—Time constant τ_m/s and τ_a/s of the most rapidly growing fluctuations as a function of film thickness $h_0/\text{\AA}$. The values of the parameters are given in table 1. —, Liquid layer on a solid surface; ---, free liquid film. Curve 1, pure liquid film; curve 2, liquid film with a large enough concentration of surfactant. The results are practically the same for a wide range of values of the parameters (including the parameters from table 1), both for soluble and insoluble surfactants. They coincide with those given by eqn (57) for a thin film on a solid surface and by eqn (69) for a thin free film.

EFFECT OF SURFACE ACTIVE AGENTS

Surface active agents generate surface forces which have a damping effect upon the wave motion. Levich¹¹ has developed a hydrodynamic theory of this wave damping for a thick film. Here the case of a thin liquid film on a solid surface is treated using the lubrication approximation. Compared to the case of a pure liquid, the boundary condition (9) at the free surface has to be replaced by

$$\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = \frac{\partial \sigma}{\partial x}, \quad y \approx 0. \tag{9b}$$

Using for the dynamic surface tension σ the expression

$$\sigma = \sigma_0(\Gamma) + \mu_s \frac{\partial u}{\partial x} \quad (33)$$

where μ_s is the surface viscosity, eqn (9b) can be rewritten as

$$\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = \frac{\partial \sigma_0}{\partial \Gamma} \frac{\partial \Gamma}{\partial x} + \mu_s \frac{\partial^2 u}{\partial x^2}, \quad y \approx 0. \quad (33)$$

INSOLUBLE SURFACE ACTIVE AGENTS

In this case the surface concentration Γ of the surface active impurity satisfies the equation

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x}(\Gamma u) = D_s \frac{\partial^2 \Gamma}{\partial x^2}, \quad y \approx 0. \quad (34)$$

Writing $\Gamma = \Gamma_0 + \Gamma'$, where Γ_0 is the surface concentration on the undeformed surface and $\Gamma' \ll \Gamma_0$, eqn (34) becomes

$$\frac{\partial \Gamma'}{\partial t} + \Gamma_0 \frac{\partial u}{\partial x} = D_s \frac{\partial^2 \Gamma'}{\partial x^2}, \quad y \approx 0.$$

Looking for a solution of the form

$$\Gamma' = G e^{ikx} e^{\beta t} \quad (35)$$

one obtains

$$G = \frac{\Gamma_0 (D\hat{v})_{y=0}}{D_s k^2 + \beta}. \quad (36)$$

The boundary condition (9b) leads to

$$(D^2 + k^2)\hat{v} = Mk^2(D\hat{v}), \quad y \approx 0, \quad (20a)$$

where

$$M \equiv \frac{\Gamma_0 (d\sigma_0/d\Gamma)_{\Gamma=\Gamma_0}}{\mu (D_s k^2 + \beta)} - \frac{\mu_s}{\mu}. \quad (37)$$

One obtains, using the same procedure as for pure liquid films,

$$\beta = -\frac{h_0^3}{3\mu} \frac{\left[\sigma k^4 + \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} k^2 \right] \left[1 - \frac{M (kh_0)^2}{h_0 \cdot 4} \right]}{1 + \left(\frac{3}{2} - \frac{M}{h_0} \right) (kh_0)^2 - \frac{(kh_0)^4}{6}}. \quad (38)$$

Using eqn (28) for ϕ , eqn (38) becomes

$$\beta = \frac{(kh_0)^2}{6\mu h_0} \frac{\frac{A}{2\pi h_0^2} - \sigma (kh_0)^2}{1 + \left(\frac{3}{2} - \frac{M}{h_0} \right) (kh_0)^2 - \frac{(kh_0)^4}{6}} \left[1 - \frac{M (kh_0)^2}{h_0 \cdot 4} \right]. \quad (39)$$

The effect of surface active agents is contained in the parameter M .

SOLUBLE SURFACE ACTIVE AGENTS

Neglecting surface diffusion, the perturbation Γ' satisfies the eqn ¹¹

$$-D_b \left(\frac{\partial c'}{\partial y} \right)_{y=0} = \frac{\partial \Gamma'}{\partial t} + \Gamma_0 \frac{\partial u}{\partial x}. \quad (40)$$

The perturbation c' ($c = c_0 + c'$) of the concentration in the film satisfies the diffusion equation

$$\frac{\partial c'}{\partial t} = D_b \left(\frac{\partial^2 c'}{\partial x^2} + \frac{\partial^2 c'}{\partial y^2} \right). \quad (41)$$

Assuming adsorption equilibrium at the free interface and using the Langmuir isotherm

$$\Gamma = \frac{k_1 c}{1 + \frac{k_1}{\Gamma_\infty} c}, \quad (42)$$

one obtains

$$\Gamma' = \theta c', \quad y \approx 0 \quad (43)$$

where

$$\theta \equiv k_1 - 2c_0 k_1^2 / \Gamma_\infty. \quad (43a)$$

Looking for a solution of the form

$$c' = \xi(y) e^{ikx} e^{\beta t}, \quad (44)$$

eqn (41) leads to

$$\frac{d^2 \xi}{dy^2} = \frac{D_b k^2 + \beta}{D_b} \xi. \quad (45)$$

The solution of eqn (45) is

$$\xi(y) = B_1 \exp \left[\left(\frac{D_b k^2 + \beta}{D_b} \right)^{\frac{1}{2}} y \right] + B_2 \exp \left[- \left(\frac{D_b k^2 + \beta}{D_b} \right)^{\frac{1}{2}} y \right]. \quad (46)$$

Eqn (45) has to be solved for the boundary conditions

$$-D_b \frac{\partial c'}{\partial y} = \theta \frac{\partial c'}{\partial t} + \Gamma_0 \frac{\partial u}{\partial x} \quad \text{for } y \approx 0 \quad (47)$$

$$-D_b \frac{\partial c'}{\partial y} = 0 \quad \text{for } y = -h_0. \quad (48)$$

One obtains

$$B_1 = \frac{-\Gamma_0 i k \hat{u}(0)}{(1-B) D_b^{\frac{1}{2}} (D_b k^2 + \beta)^{\frac{1}{2}} + \theta \beta (1+B)} \quad (49)$$

and

$$B_2 = B_1 B \quad (50)$$

where

$$B = \exp \left[-2 \left(\frac{D_b k^2 + \beta}{D_b} \right)^{\frac{1}{2}} h_0 \right]. \quad (51)$$

Hence

$$\Gamma' = \frac{-\Gamma_0 (\partial u / \partial x)_{y=0} (1+B)}{(1-B) D_b^{\frac{1}{2}} (D_b k^2 + \beta)^{\frac{1}{2}} \theta^{-1} + \beta (1+B)}. \quad (52)$$

The boundary condition (9b) leads to

$$(D^2 + k^2) \hat{\theta} = N k^2 (D \hat{\theta}), \quad y \approx 0, \quad (53)$$

where

$$N = \frac{1}{\mu} \left[\frac{\Gamma_0 (\partial \sigma_0 / \partial \Gamma)_{\Gamma_0} (1+B)}{D_b^{\frac{1}{2}} (D_b k^2 + \beta)^{\frac{1}{2}} (1-B) \theta^{-1} + \beta (1+B)} - \mu_s \right]. \quad (54)$$

The equation obtained for β is identical to eqn (38) if M is replaced by N .

The growth coefficient β has a maximum for the dominant wavelength. The time of rupture τ_m of the film can be evaluated from the maximum growth coefficient $\tau_m \approx \beta_m^{-1}$. The curves $\beta = \beta(k)$ (eqn (39)) and the minimum time of rupture as function of h_0 are presented in fig. 2 and 4. The values of various parameters are given in table 1.

TABLE 1

	gaseous monolayer	condensed monolayer
μ	0.01 P	0.01 P
μ_s	10^{-3} g/s	10 g/s
Γ_0	8.3×10^{-12} mol/cm ²	8.3×10^{-10} mol/cm ²
$(\partial \sigma_0 / \partial \Gamma)_{\Gamma_0}$	-2.4×10^{10} erg/mol	-1.34×10^{12} erg/mol
σ_0	30 dyn/cm	30 dyn/cm
D_s	10^{-5} cm ² /s	10^{-5} cm ² /s
D_b	10^{-5} cm ² /s	10^{-5} cm ² /s
θ	2×10^{-4} cm	2×10^{-4} cm
A	10^{-13} erg	10^{-13} erg
h_0	100 Å	100 Å

If $|\Gamma_0 (\partial \sigma_0 / \partial \Gamma)_{\Gamma_0}|$ is large enough, the parameters $-M$ (for insoluble) and $-N$ (for soluble) become large and β can be approximated as for $-M$ (or $-N$) $\rightarrow \infty$: one obtains

$$\beta = \frac{(kh_0)^2}{12\mu h_0} \left(\frac{A}{2\pi h_0^2} - \sigma (kh_0)^2 \right) \quad \text{for } -M \rightarrow \infty. \quad (55)$$

In this case the dominant wavenumber is given by

$$k_d \approx 2^{-\frac{1}{2}} k_c = (4\pi)^{-\frac{1}{2}} A^{\frac{1}{2}} \sigma^{-\frac{1}{2}} h_0^{-2} \quad (56)$$

and an explicit expression is obtained for τ_m

$$\tau_m \approx 192\pi^2 \mu \sigma h_0^5 A^{-2} \quad -N \text{ (or } -M) \rightarrow \infty. \quad (57)$$

For pure systems M (or N) = 0 and eqn (39) reduces to eqn (29). The time of rupture can be evaluated in this case by eqn (31). One may observe that the ratio of times of rupture in the extreme cases $-M$ (or $-N$) $\rightarrow \infty$ and M (or N) = 0 is about 4.

THIN FREE LIQUID FILMS

This situation was treated previously by Lucassen *et al.*⁸ for free films of all thicknesses. The present approach is simpler, but restricted to thin films. The effect of surface active impurities is treated here in more detail.

The perturbation can be created in this case at both free surfaces. If the wave numbers of the perturbations at both the interfaces are equal, then two extreme cases of perturbations are possible, namely spatially in phase (asymmetric) and 180° out of phase (symmetric). The latter leads to the most rapid rupture. Therefore, the analysis which follows is based on the 180° out of phase perturbations.

PURE SYSTEMS

The equations of motion (4) and (5), the continuity eqn (6) and the boundary conditions (8) and (9) still hold for this situation. New boundary conditions specific to this case are,

$$v = 0 \quad \text{at } y = -h_0/2 \quad (58)$$

$$\partial u / \partial y = 0 \quad \text{at } y = -h_0/2. \quad (59)$$

Now $h = h_0 + 2\varepsilon$, then eqn (15) must be replaced by

$$\frac{\partial \phi_0}{\partial x} = 2 \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \frac{\partial \varepsilon}{\partial x} \quad (60)$$

and eqn (16) takes the form

$$\mu \frac{\partial^2 u}{\partial y^2} = 2\mu \frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} \right)_{y=0} - \sigma \frac{\partial^3 \varepsilon}{\partial x^3} + 2 \left(\frac{\partial \phi_0}{\partial h} \right)_{h=h_0} \frac{\partial \varepsilon}{\partial x}. \quad (61)$$

The same procedure as that used for thin film on a solid surface leads in this situation to

$$\beta = \frac{1}{6\mu h_0} \left[\frac{A}{\pi h_0^2} - \sigma (kh_0)^2 \right] \quad (62)$$

and

$$\lambda_c = \left(\frac{4\pi^3 \sigma}{A} \right)^{\frac{1}{2}} h_0^2. \quad (63)$$

One may observe that in this case no dominant wavelength exists. For sufficiently large wavelengths, however, β becomes independent of the wavelength

$$\beta_a = \frac{A}{6\pi\mu h_0^3}. \quad (64)$$

The time needed for the rupture of the film is in this case of the order of

$$\tau_a \approx \frac{1}{\beta_a} = \frac{6\pi\mu h_0^3}{A}. \quad (65)$$

The constant A is equal to the difference $A_{11} - 2A_{13}$, where A_{11} is Hamaker

constant for the interaction between the molecules in the film and A_{13} is the Hamaker constant for the interaction between the molecules in the film and the molecules of the other phase. Eqn (63), (64) and (65) are plotted in fig. 5, 3 and 4 respectively.

EFFECT OF SURFACE ACTIVE AGENTS ON THIN FREE LIQUID FILMS

For insoluble surface active agents one obtains

$$\beta = \frac{1}{6\mu h_0} \frac{\frac{A}{\pi h_0^2} - \sigma(kh_0)^2}{1 - \frac{2M}{3h_0} \frac{(kh_0)^2}{18}} \left[1 - \frac{M}{h_0} \frac{(kh_0)^2}{6} \right] \tag{66}$$

where M is given by eqn (37).

For soluble surface active agents the growth coefficient can be calculated from eqn (66) if M is replaced by

$$N' = \frac{1}{\mu} \left[\frac{\Gamma_0(\partial\sigma_0/\partial\Gamma)_{\Gamma_0}}{D_b^{\frac{1}{2}}(D_b k^2 + \beta)^{\frac{1}{2}}(1 - B')\theta^{-1} + \beta(1 + B')} - \mu_s \right] \tag{67}$$

where

$$B' = \exp \left[- \left(\frac{D_b k^2 + \beta}{D_b} \right)^{\frac{1}{2}} h_0 \right]. \tag{68}$$

Eqn (66) is plotted in fig. 5 for both soluble and insoluble surfactants using for the parameters the values from table 1. The time of rupture τ_m is evaluated as the reciprocal of β for the dominant wavenumber. Some numerical values are plotted in fig. 4.

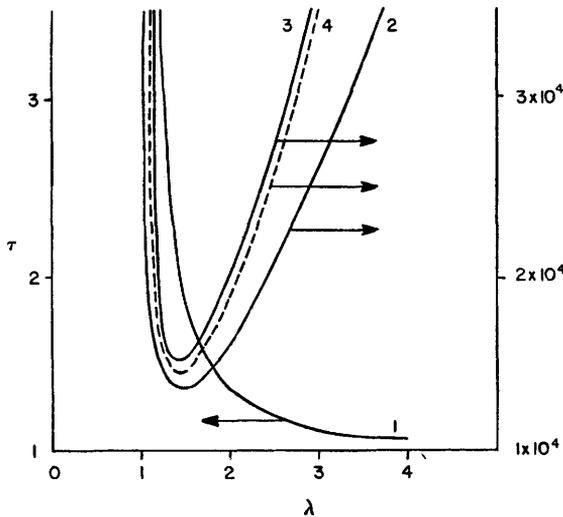


FIG. 5.—Time constant ($\tau = 1/\beta$) as a function of wavelength λ for a thin free film. The values of the parameters are given in table 1. The unit of τ is the value of τ_a calculated from eqn (65) and the unit of λ is the value of λ_c calculated from eqn (63). Curve 1, pure liquid film; curve 2, liquid film with gaseous monolayer of insoluble surfactant; curve 3, liquid film with condensed monolayer of insoluble surfactant; curve 4, liquid film with a gaseous monolayer of soluble surfactant.

Several effects, which are important under certain conditions,^{1,2} have not been included in the present treatment: (i) the double layer forces (ii) the influence of surface active agents on the van der Waals interaction forces and (iii) the effect of the thickness of the layer on the surface tension.

DISCUSSION

The hydrodynamic stability analysis allows us to interpret some of the available experimental information.

Concerning the rupture of a thin film on a solid surface, the present treatment gives some understanding of the results obtained by Goldstein² in a study of water vapour condensation on a shock-tube wall. For condensation on a clean hydrophobic surface, Goldstein reports that a continuous film of condensate is formed, which, after reaching a thickness of about 100 Å in about 10 μs after the compression, begins to break up into many small droplets. In all mechanical systems there are perturbations of various wavelengths; consequently the rupture of the film can be considered in this case to be a consequence of hydrodynamic instability. It is also of interest to mention that if Hamaker's constant A is taken to be of the order of 10^{-12} erg and h_0 of the order of 50 Å, then the time of rupture computed from eqn (31) with $\sigma \approx 70$ dyn/cm and $\mu \approx 10^{-2}$ P is of the order of 10 μs, as was found experimentally.

Concerning the rupture of a free thin film, it is important to stress that in any real system there are surface active impurities. Minute quantities of them have a strong stabilizing effect, damping the waves which occur at a free surface. For this reason eqn (65), which is valid for the time of rupture in a pure liquid, gives a lower bound of the time of rupture. In the presence of surface active impurities the time of rupture can be several orders of magnitude longer than for a pure liquid (fig. 4). An upper bound for the time of rupture can be obtained from eqn (66) if $|\Gamma_0(\partial\sigma/\partial\Gamma)_{\Gamma_0}|$ is large enough so that one may assume that $-M$ (for insoluble surfactants) or $-N$ (for soluble surfactants) tends to infinity. One obtains Vrij's result⁵

$$\tau_m \approx 96\pi^2 \sigma \mu h_0^5 A^{-2}, \quad -M(\text{or } -N') \rightarrow \infty. \quad (69)$$

The coalescence time between two bubbles in contact in a pure liquid is indeed very short.^{1,3} In the presence of surface active impurities the coalescence time is much longer, of the order of 10^{-1} s.^{1,3} If one assumes, as suggested by Marucci, that the drainage time is negligible and hence that the rupture of a thin film of some hundred Ångström thick, is the mechanism that controls the rate of coalescence, eqn (69) and (65) give an upper and lower bound of the coalescence time. One may verify that indeed the value 10^{-1} s is bounded by these equations (fig. 4).

APPENDIX 1

NOMENCLATURE

A	A_{11} - A_{12} for a film on a solid surface and A_{11} - $2A_{13}$ for a free film
A_{ij}	Hamaker constant for the interaction between molecules of type i and j . $\pi^2 \alpha_i n_i n_j$
B, B'	quantities defined by eqn (51) and (68)
B_1, B_2	integration constants given by eqn (49) and (50)
c	bulk concentration of surfactants
c_0	concentration of surfactant in the undeformed film
c'	$c - c_0$
c_1, c_2, c_3	integration constants

D	$\partial/\partial y$
D_b	diffusion coefficient in the bulk
D_s	surface diffusion coefficient
G	constant defined by eqn (36)
h_0	average film thickness
h	actual film thickness ($h = h_0 + \varepsilon$ for a film on a solid surface and $h = h_0 + 2\varepsilon$ for a free film)
k	wavenumber of the perturbation
k_c	critical wavenumber
k_d	dominant wavenumber
k_1	constant in eqn (42)
M, N, N'	quantities defined by eqn (37), (54) and (67)
n_1	molecular density of the liquid
n_2	molecular density of the solid
p	hydrostatic pressure
p_0	external pressure on the film
P	$(p + \phi)$
r	distance between two molecules
t	time
u	velocity component in the x direction
u_{ij}	interaction potential between two molecules of type i and j separated by the distance r
U_{ij}	potential energy of one molecule of type i due to all molecules of type j
v	velocity in the y direction
V	volume of the solid
x, y	cartesian coordinates
Y	$h - y$
α_{ij}	London-van der Waals parameter for interaction between molecules of type i and j
β	growth parameter
β_m	maximum value of β for a thin film
β_a	maximum value of β for free films of pure liquids
ε	perturbation of the film thickness ($\varepsilon = h - h_0$ for a film on a solid surface and $2\varepsilon = h - h_0$ for a free film)
$\hat{\varepsilon}$	maximum amplitude of perturbation ε
λ	wavelength = $2\pi/k$
λ_c	critical wavelength
λ_d	dominant wavelength
μ	viscosity of the liquid
μ_s	surface viscosity
σ	liquid-gas surface tension
σ_0	static liquid-gas surface tension
τ	$1/\beta$, characteristic time
τ_m	$1/\beta_m$
τ_a	$1/\beta_a$
ϕ	interaction potential per unit volume at a point in the liquid
ϕ_0	interaction potential per unit volume at the free surface of liquid
ϕ_B	interaction potential per molecule of the liquid situated at the free surface in a semi-infinite liquid
ϕ_B	$n_1\phi_B$
Γ	surface concentration of surfactants

Γ_0	value of Γ for undeformed film
Γ'	$\Gamma - \Gamma_0$
Γ_∞	constant in eqn (42)
θ	quantity defined by eqn (43a)

APPENDIX 2

The potential energy of a molecule in the liquid film due to the molecules of the semi-infinite solid is given by ¹⁴

$$U_{12}(Y) = \iiint_V n_2 u_{12}(r) 2\pi r^2 dr \sin \theta d\theta$$

where n_2 is the number of molecules per unit volume of solid and u_{12} is the potential energy due to the interaction between two molecules at distance r . V is the lower half space. For London-van der Waals type interaction

$$u_{ij} = -\alpha_{ij}/r^6$$

consequently

$$U_{12}(Y) = -\left(\frac{\pi n_2 \alpha_{12}}{6}\right) \frac{1}{Y^3}.$$

If the molecule is located at the free surface, $Y = h$ and

$$U_{12}(h) = -\left(\frac{\pi n_2 \alpha_{12}}{6}\right) \frac{1}{h^3}.$$

Similarly, the potential due to the molecules of the liquid film on one molecule situated at the free surface of the liquid is given by

$$U_{11}(h) = \phi'_B + \left(\frac{\pi n_1 \alpha_{11}}{6}\right) \frac{1}{h^3}.$$

Therefore the total potential energy per unit volume of liquid acting at the free surface is given by:

$$\begin{aligned} \phi_0 &= n_1 [U_{11}(h) + U_{12}(h)] \\ &= \phi_B + \frac{A_{11} - A_{12}}{6\pi h^3} \end{aligned}$$

where A_{ij} is the Hamaker constant (subscript 1 refers to the liquid and 2 to the solid)

$$A_{ij} = \pi^2 \alpha_{ij} n_i n_j$$

and

$$\phi_B = n_1 \phi'_B.$$

We are grateful to the referees for bringing ref. (8) and (9) to our attention. This work was supported in part by the National Science Foundation.

¹ A. Scheludko, *Kolloid Z.*, 1963, **191**, 52.

² R. Goldstein, *J. Chem. Phys.*, 1964, **40**, 2763.

³ A. Scheludko, *Proc. K. Ned Akad., Wet.*, 1962, **B65**, 76.

⁴ A. Scheludko, *Adv. Colloid and Int. Sc.*, 1967, **1**, 391.

⁵ A. Vrij, *Disc. Faraday Soc.*, 1966, **42**, 23.

⁶ S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability* (Oxford Univ. Press, Oxford, 1961).

⁷ B. V. Felderhof, *J. Chem. Phys.*, 1968, **49**, 44.

- ⁸ J. Lucassen, M. van den Tempel, A. Vrij and F. Th. Hesselink, *Proc. K. Ned. Akad. Wet.*, 1970, **B73**, 109.
- ⁹ A. Vrij, F. Th. Hesselink, J. Lucassen and M. van den Tempel, *Proc. K. Ned. Akad. Wet.*, 1970, **B73**, 124.
- ¹⁰ G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, 1967), p. 219.
- ¹¹ V. G. Levich, *Physico-Chemical Hydrodynamics* (Prentice-Hall, N.J., 1962).
- ¹² E. Ruckenstein and R. K. Jain, to be published.
- ¹³ G. Marrucci, *Chem. Eng. Sci.*, 1969, **24**, 975.
- ¹⁴ J. Frenkel, *Kinetic Theory of Liquids* (Dover, N.Y., 1955).