

Possible Mechanism for the Spontaneous Rupture of Thin, Free Liquid Films

BY A. VRIJ

van't Hoff Laboratory, Sterrenbos 19, Utrecht, The Netherlands

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The stability of a free, thin liquid film against small, spontaneous thickness fluctuations is explored. The film is unstable with respect to fluctuations with wavelengths larger than a critical wavelength $\Lambda_c = [-2\pi^2\gamma/(d^2V/dh^2)]^{1/2}$, where γ is the interfacial tension and $V(h)$ the free energy of interaction as a function of the film thickness h . $V(h)$ may include van der Waals attraction and double-layer repulsion. The kinetics of the growing fluctuations is obtained by assuming a laminar liquid flow between rigid film surfaces at a constant viscosity. There are stable fluctuation-modes, which grow exponentially with time, each with a characteristic time constant τ , and modes with certain wavelengths grow faster than all others ($\tau = \tau_m$). If the van der Waals forces predominate Λ_c and τ_m are given by eqn. (4.2) and (4.3) respectively. For $A = 10^{-14}$ – 10^{-12} erg, $\gamma = 30$ dyne/cm and $h = 100$ – 1000 Å, Λ_c ranges from 0.6–600 μ and τ_m from a fraction of a second to several hours. The life-time and critical thickness h_c of an unstable film are also calculated; they depend on the time constant τ_m and on the time of draining. The critical thickness is calculated for microscopic, circular films and compared with measurements of Scheludko and Exerowa. For water and aniline films, the calculated h_c are 410 and 750 Å respectively, whereas the experimental values are 270 and 410 Å.

Studies on the stability of thin, free liquid films are of importance for an understanding of colloidal systems, such as foams and emulsions.¹⁻⁴

The life-time of liquid films is determined by two processes, thinning and breaking. Thinning of a film occurs by draining of the liquid under the influence of gravity and suction at the Plateau-borders. When the thickness is reduced to about 1000 Å, other forces influence the draining; van der Waals attraction increases the draining rate; double layer repulsion decreases it. On further thinning—which often occurs discontinuously—some films become metastable; others, however, collapse between 500 and 100 Å. Metastability is reached when border suction, van der Waals attraction and double-layer (or other) repulsion equilibrate; instability results when the attraction forces predominate.¹

Rupturing of metastable films, if it takes place, seems to occur in an irregular manner because of lack of control over external disturbances such as thermal shocks, vibration, dust, etc.³ Spontaneous rupturing through the formation of a nucleus (hole) requires a high activation energy if the film thickness is larger than 100 Å as shown by de Vries⁵; accordingly, such a process becomes highly improbable. Only for extremely thin films (bimolecular leaflets) may this mechanism become important.⁶

Unstable films (often called transient films), always rupture spontaneously, often at a characteristic “critical thickness”. At present, however, it is still unknown why the critical thickness is usually several 100 Å instead of a few 10 Å necessary for the spontaneous formation of a hole.

Scheludko⁷ proposed that, at its critical thickness, the film becomes unstable with respect to small, spontaneous surface deformations, such that, in spite of an

increase of the free energy through the increase of surface area, the total free energy decreases because of the van der Waals forces. He associated the wavelength Λ of a certain surface deformation with a critical thickness h_c , as follows:

$$h_c = (3K\Lambda^2/64\gamma)^{\frac{1}{2}}. \quad (1.1)$$

Here K is a constant proportional to the Hamaker constant: $A = 6\pi K$, and γ the interfacial tension. The theoretical value of Λ could not be calculated, however. Further, he proposed that the sudden formation of black film from a thicker one occurs by a similar mechanism.

That surface corrugations—due to thermal motion—exist was shown by the author⁸ from the light scattering a liquid film exhibits when placed in an intense light beam. From the intensity of the light scattering and its angular dependence, information on surface forces, operating in the liquid film, can be obtained.

In this paper the stability of these surface corrugations and the kinetics of their diminution and amplification are explored. In an unstable film some of these surface corrugations may grow until they rupture the film. The mechanism is analogous to that proposed by Cahn⁹ for the phase separation by spinodal decomposition in solutions.

FREE ENERGY OF THE CORRUGATED FILM

Consider a free, liquid film (medium 2), with a mean thickness h_0 , between two media 1 and 3. The upper interface (1-2) is in the X — Y plane; the lower interface (2-3) in a plane at a distance h_0 beneath it. The free energy increase ΔF associated with a certain, small corrugation z_{12} in the interface (1-2) and a corrugation z_{23} , in the interface (2-3) is given by⁸

$$\Delta F = \iint \left\{ \frac{1}{2}\gamma [(\partial z_{12}/\partial x)^2 + (\partial z_{12}/\partial y)^2 + (\partial z_{23}/\partial x)^2 + (\partial z_{23}/\partial y)^2] + \frac{1}{2}(d^2V/dh^2)_0(z_{12} - z_{23})^2 \right\} dx dy, \quad (2.1)$$

where γ is the interfacial tension and $V(h)$ the free energy of interaction per unit area. The integral is taken over the surface of a square, a^2 . The first term in eqn. (2.1) is the work associated with the increase of surface area owing to the corrugations; the second term is due to interaction forces such as electrostatic repulsion and van der Waals attraction.

Eqn. (2.1) may conveniently be separated as

$$\Delta F = \Delta F_1 + \Delta F_2, \quad (2.2)$$

$$\Delta F_1 = \frac{1}{2}\gamma \iint \{ [\partial(z_{12} + z_{23})/\partial x]^2 + [\partial(z_{12} + z_{23})/\partial y]^2 \} dx dy \quad (2.3)$$

$$\Delta F_2 = \iint \left\{ \frac{1}{2}\gamma [(\partial h/\partial x)^2 + (\partial h/\partial y)^2] + \frac{1}{2}(d^2V/dh^2)_0(h - h_0)^2 \right\} dx dy, \quad (2.4)$$

where we have substituted $z_{12} - z_{23} = h - h_0$. Thus, the corrugations of the two single surfaces, z_{12} and z_{23} , are replaced by two "normal" corrugations given by the linear combinations $(z_{12} + z_{23})$ and $(z_{12} - z_{23})$. The combination $(z_{12} + z_{23})$, associated with ΔF_1 , depicts fluctuations in the bending of the film as a whole, whereas the combination $(z_{12} - z_{23})$, associated with ΔF_2 , depicts fluctuations in the film thickness.

ΔF_1 is always positive when $\gamma > 0$. ΔF_2 , however, may become negative if $(d^2V/dh^2)_0 < 0$ and the second term in eqn. (2.4) predominates. This means that the film is always stable with respect to fluctuations of the former type, but may

become unstable for some fluctuations of the latter. Because we are only interested in fluctuations that make the film unstable, we restrict the further discussion to fluctuations in $z_{12} - z_{23} = h - h_0$.

To specify such fluctuations further, it is convenient to consider the Fourier components of $h(x, y)$:

$$h - h_0 = \sum_{\rho=-\infty}^{+\infty} \sum_{\sigma=-\infty}^{+\infty} H_{\rho\sigma} \exp[ip(\rho x + \sigma y)], \quad (2.5)$$

where $p = 2\pi/a$. Since h is real the (complex) Fourier coefficients are connected in pairs by the relations:

$$H_{-\rho, -\sigma} = H_{\rho\sigma}^*; H_{\rho, -\sigma} = H_{-\rho, \sigma}^*; H_{-\rho, \sigma} = H_{\rho, -\sigma}^*.$$

Each Fourier component contributes independently to ΔF_2 . For instance, the component $H_{\rho\sigma}$ yields the contribution,

$$a^2 H_{\rho\sigma} H_{\rho\sigma}^* [\frac{1}{4} \gamma p^2 (\rho^2 + \sigma^2) + \frac{1}{2} (d^2 V / dh^2)_0]. \quad (2.6)$$

When $d^2 V / dh^2 < 0$, this component will decrease the free energy if

$$|\Lambda| > |\Lambda_c| = [-2\pi^2 \gamma / (d^2 V / dh^2)_0]^{\frac{1}{2}}, \quad (2.7)$$

where

$$\Lambda = 2\pi/k = (2\pi/p)(\rho^2 + \sigma^2)^{-\frac{1}{2}} \quad (2.8)$$

Λ_c is the wavelength of the critical fluctuation. A fluctuation with $\Lambda < \Lambda_c$ will "fluctuate" around a (meta)stable equilibrium. A fluctuation with $\Lambda > \Lambda_c$, however, will grow in amplitude, making the film unstable. Such a fluctuation can always be found if the dimensions of the film (e.g., a) are larger than Λ_c . Thus,

$$a > \Lambda_c, \quad (2.9)$$

or with eqn. (2.7),

$$(d^2 V / dh^2)_0 < -2\pi^2 \gamma / a^2 \quad (2.10)$$

GROWTH OF THICKNESS FLUCTUATIONS

To obtain the kinetics of the fluctuation process, the mechanism of liquid transport through the film must be specified. Although the fluctuations may be created through a spontaneous process caused by thermal motion, their average decrease or increase in time may be described by macroscopic laws if Λ is large with respect to molecular dimensions. Furthermore, eqn. (2.1) is valid only near equilibrium so that the equation to be derived will only describe the kinetics of the initial stage of the growing process.

For simplicity, we assume a laminar liquid flow parallel to the surfaces of the film (of uniform thickness h_0); this assumption is reasonable if $\Lambda \gg h_0$ and $h - h_0 \ll h_0$. It is further assumed that the liquid in the film has a constant viscosity up to the interfaces, and that no slip occurs at the interfaces.¹⁰ Then we may write for the liquid flux per unit length,¹¹

$$\mathbf{Q} = -(h_0^3 / 12\eta) \text{grad } \Delta P, \quad (3.1)$$

where η is the viscosity of the liquid and ΔP is the extra pressure on the film due to the fluctuation. For ΔP , one may write¹²

$$\Delta P = \Delta P_\gamma + \Delta(dV/dh). \quad (3.2)$$

Here ΔP is the capillary pressure counteracting this fluctuation whereas $\Delta(dV/dh)$ is due to intermolecular forces in the film. For small fluctuations one may write for eqn. (3.2),

$$\Delta P = -\frac{1}{2} \gamma (\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2) + (d^2 V / dh^2)_0 (h - h_0). \quad (3.3)$$

To describe the dependence of h on time we need the law of conservation of volume :

$$\partial h / \partial t = -\operatorname{div} \mathbf{Q}. \quad (3.4)$$

Combining eqn. (3.1), (3.3) and (3.4) yields the equation of motion :

$$\partial h / \partial t = (h_0^3 / 12\eta) \{ (d^2 V / dh^2)_0 (\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2) - \frac{1}{2} \gamma (\partial^4 h / \partial x^4 + 2 \partial^4 h / \partial x^2 \partial y^2 + \partial^4 h / \partial y^4) \}. \quad (3.5)$$

This equation is formally equivalent to the equation of Cahn,⁹ which describes concentration fluctuations in solution as a function of time.

The solution of eqn. (3.5) is ⁹ :

$$h - h_0 = \sum_{\rho} \sum_{\sigma} H_{\rho\sigma}(t) \exp[ip(\rho x + \sigma y)], \quad (3.6)$$

with

$$H_{\rho\sigma}(t) = H_{\rho\sigma}(0) \exp[t/\tau(\rho, \sigma)] \quad (3.7)$$

and

$$1/\tau(\rho, \sigma) = 1/\tau(k) = (h_0^3 / 12\eta) [- (d^2 V / dh^2)_0 k^2 - \frac{1}{2} \gamma k^4]. \quad (3.8)$$

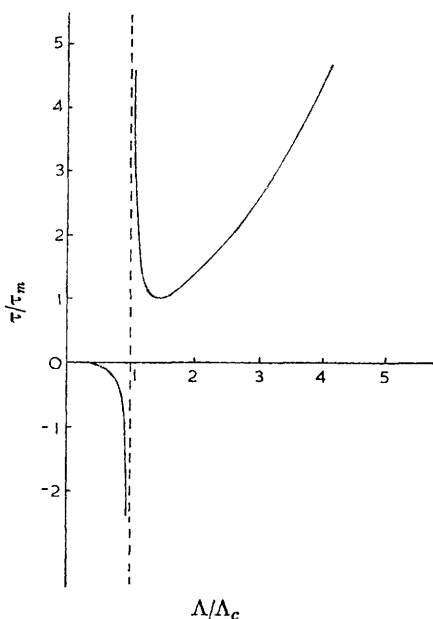


FIG. 1.—Relative time constant τ/τ_m as a function of relative wavelength Λ/Λ_c .

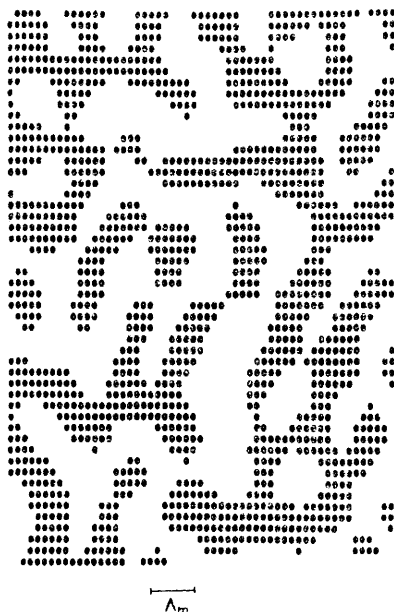


FIG. 2.—Schematic representation of thickness fluctuations in a liquid film which result in breaking. Λ_m is the wavelength of the most rapidly growing thickness fluctuation.

Eqn. (3.6) is an extension of eqn. (2.5). It describes the thickness fluctuation as the sum of independent stationary sinewaves, the amplitudes of which are exponential functions of time. The initial amplitudes and phases, represented by the (complex) $H_{\rho\sigma}(0)$ are defined by the initial fluctuation at $t = 0$.

Substitution of the eqn. (2.7) and (2.8) into eqn. (3.8) shows that $\tau < 0$ when $\Lambda < \Lambda_c$ and that $\tau > 0$ when $\Lambda > \Lambda_c$. Thus, fluctuations of the first kind ($\tau < 0$) will decrease exponentially with time and return to metastable equilibrium, whereas

fluctuations of the second kind ($\tau > 0$) will *increase* exponentially with time and move away from equilibrium.

τ depends on k . It shows a sharp minimum at $\Lambda_m = \Lambda_c 2^{\frac{1}{2}}$; see fig. 1. This minimum appears because, when Λ is only slightly larger than Λ_c , the driving force, and thus also the liquid flow speed, is small, whereas, when Λ is much larger than Λ_c the time required to produce the fluctuation is large, because the liquid must be transported over a larger distance. The minimum is equal to

$$\tau_m = (24\gamma\eta/h_0^3)(d^2V/dh^2)_0^{-2}. \quad (3.9)$$

Because the amplitudes of fluctuation modes have τ in the exponent, the amplitude of the modes with wavelength Λ_m will grow faster than all others.

To visualize the thickness fluctuation ($h-h_0$) of the film we refer to pictures obtained by Cahn.⁹ He used a computer to calculate the Fourier sum with random selections of directions, phases and amplitudes. One of these is redrawn and given in fig. 2. It shows a pattern of interconnected "hills and gullies" with dimensions of the order of Λ_m . It seems reasonable to assume that the rupturing starts along one of the gullies.

STABILITY CONDITIONS AND TIME CONSTANT OF THICKNESS FLUCTUATIONS

To determine values for Λ_m and τ_m , we need $V(h)$ which is believed to contain van der Waals attraction and electrostatic repulsion terms. Graphs of $V(h)$ representing the first two contributions have been discussed elsewhere.^{1, 13} Schematic plots of $V(h)$ and also of d^2V/dh^2 are given in fig. 3(A, B).

The stability of the film against thickness fluctuations can now be read from fig. 3B. According to eqn. (2.10), instability will occur if $d^2V/dh^2 < -2\pi^2\gamma/a^2$. Large films (for instance, $a = 1$ cm) are practically unstable in the regions $h < OP$ and $h > OQ$. For smaller films the instability region at $h > OQ$ is reduced and for the smallest ones it will disappear altogether. The instability region at $h < OP$, however, will remain, although this does not imply that the film can reach such thicknesses because of the potential barrier in $V(h)$.

Let us digress on the important case where the van der Waals forces predominate (at least in some region of h), and formulate $V(h)$ as follows¹ (no retardation):

$$V(h) = -A/12\pi h^2. \quad (4.1)$$

A is the Hamaker constant. Using this equation to calculate d^2V/dh^2 and substituting the result into eqn. (2.7) yields

$$\Lambda_c = h_0^2(4\pi^3\gamma/A)^{\frac{1}{2}}. \quad (4.2)$$

This equation is the equivalent of eqn. (1.1) of Scheludko. The numerical constant, however, is different because of his approximate treatment.

Λ_c as a function of h_0 is plotted in fig. 4 with $\gamma = 30$ dynes/cm and with $A = 10^{-14}$, 10^{-13} and 10^{-12} erg (plot 1, 2 and 3). Applying the stability condition $a > \Lambda_c$ (see eqn. (2.9)) it follows that films with a equal to about 0.1 mm should be stable at least down to a thickness of about 1000 Å. Much smaller films, for instance, those separating oil globules in a creamed emulsion (say, $a = 1\mu$), should be stable even down to a thickness of about 100 Å. For τ_m one deduces from the eqn. (3.9) and (4.1):

$$\tau_m = 96\pi^2\gamma\eta h_0^5 A^{-2}. \quad (4.3)$$

In fig. 5, τ_m is plotted against h_0 with $\gamma = 30$ dynes/cm; $\eta = 0.01$ poise and $A = 10^{-14}$, 10^{-13} and 10^{-12} erg (plot 1, 2 and 3).

RUPTURE OF LIQUID FILMS

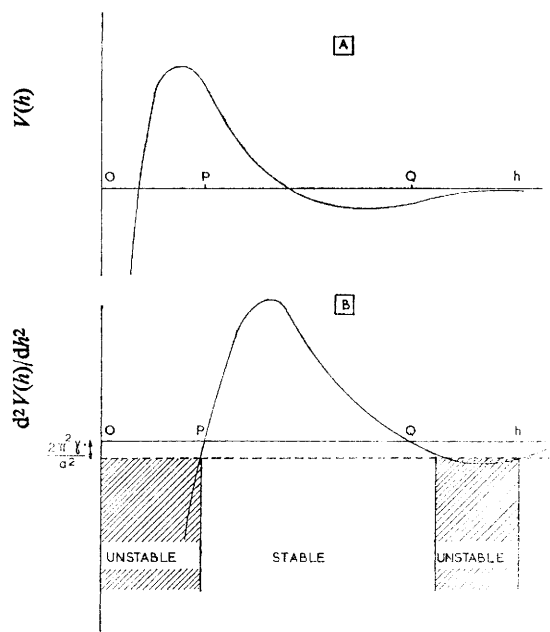


FIG. 3.—Schematic graphs of the free energy $V(h)$ of interaction and its second derivative, $d^2V(h)/dh^2$, as a function of film thickness h . The stable and unstable regions are marked. γ is the interfacial tension and a the linear dimension of the film.

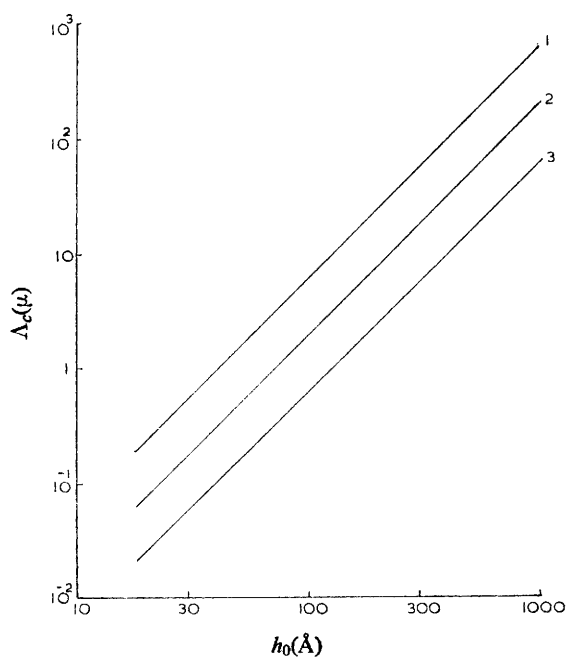


FIG. 4.—Wavelength $\Lambda_c(\mu)$ of the critical fluctuation as a function of film thickness $h_0(\text{\AA})$. Plots 1, 2, and 3 for Hamaker constant's $A = 10^{-14}$, 10^{-13} and 10^{-12} erg respectively. $\gamma = 30$ dyne/cm.

To calculate the time needed for the fluctuations to increase to values about equal to h_0 , i.e., the time needed to break the film, the initial values of the thickness

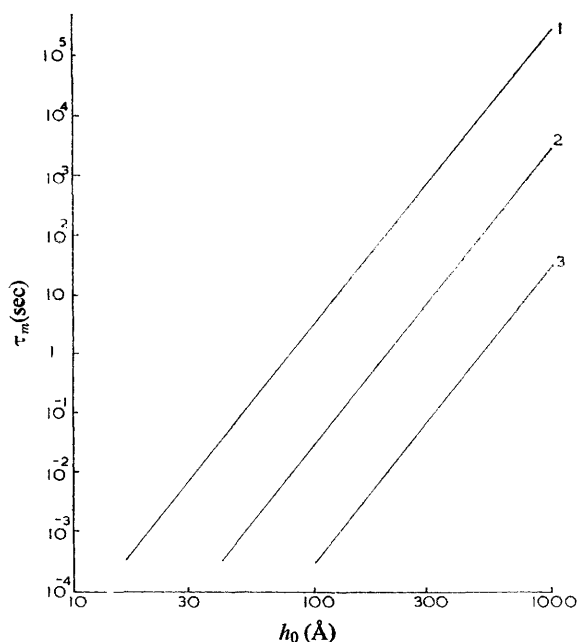


FIG. 5.—Time constant τ_m (sec) of the most rapidly growing fluctuation as a function of film thickness h_0 (Å). Plots 1, 2 and 3 for Hamaker constant's $A = 10^{-14}$, 10^{-13} and 10^{-12} erg respectively. $\gamma = 30$ dyne/cm; $\eta = 0.01$ poise.

fluctuations have to be specified. In the draining film, i.e., a film in which h_0 is a function of t , the breaking time also depends on the draining rate. We consider first the simpler case of a stationary film in which h_0 is constant with time.

BREAKING TIME OF A STATIONARY FILM

The breaking time t_b of an unstable film will depend on h_0 , τ_m and the initial fluctuations of the film at $t = 0$: i.e., the values of $H_{\rho\sigma}H_{\rho\sigma}^*(t = 0)$. The values of these last quantities, however, are generally unknown and different for different film samples. Therefore one may expect to have not just one value for t_b , at a certain h_0 , but a whole distribution of t_b , because only one deep gully somewhere in the film may lead to breaking. At present, we content ourselves with the calculation of an approximate, mean value for t_b , assuming that the initial fluctuations are generated by thermal motion.

To this end let us suppose that the film will break when $\overline{(h-h_0)^2}$ becomes of the order of h_0 , where the bar means an average over the film area, thus,

$$a^{-2} \iint (h-h_0)^2 dx dy \simeq h_0^2. \quad (5.1)$$

Substitution of eqn. (3.6) into the integral yields

$$h_0^2 \simeq \sum_{\rho} \sum_{\sigma} \exp(2t/\tau) H_{\rho\sigma} H_{\rho\sigma}^*(t = 0). \quad (5.2)$$

This is a rough approximation because eqn. (3.6) was derived for fluctuations which are small with respect to h_0 .

To obtain an approximate value of this sum we may take advantage of the fact that for $t \gg \tau_m$ only those terms closest to $k = k_m$, ($k^2 = p^2(\rho^2 + \sigma^2)$), are important. Therefore we replace $H_{\rho\sigma}H_{\rho\sigma}^*(t=0)$ by their average value at k_m and use, instead of the full expression for τ given by eqn. (3.8), its expansion around the minimum $\tau = \tau_m$:

$$1/\tau = 1/\tau_m - (4/k_m^2 \tau_m)(\Delta k)^2, \quad (5.3)$$

where $\Delta k = k - k_m$, and replace the sum by an integral from $\Delta k = -\infty$ to $+\infty$. This yields

$$h_0^2 \simeq (HH^*)_{0m} \exp(2t/\tau_m) \int_{-\infty}^{+\infty} (2\pi k_m/p^2) \exp[-(8t/\tau_m k_m^2)(\Delta k)^2] d(\Delta k), \quad (5.4)$$

where $(HH^*)_{0m}$ is written for $H_{\rho\sigma}H_{\rho\sigma}^*(t=0; k=k_m)$. Furthermore, $(HH^*)_{0m}$ is replaced by a mean value, to be obtained with the help of the principle of equipartition that states that the mean free energy of each fluctuation-mode, given by eqn. (2.6), should be equal to $kT/2$; thus

$$\overline{H_{\rho\sigma}H_{\rho\sigma}^*} = \alpha^{-2} [\frac{1}{4}\gamma k^2 + \frac{1}{2}(d^2V/dh^2)_0]^{-1} (kT/2). \quad (5.5)$$

Application of this equation, at $k = k_m$, however, makes $H_{\rho\sigma}H_{\rho\sigma}^* < 0$; this is impossible: indeed, eqn. (5.5) becomes invalid at $k < k_c$. To circumvent this difficulty we assume that the interaction forces are "turned on" at $t = 0$, and drop the term $(d^2V/dh^2)_0$. Then $(HH^*)_{0m}$ becomes

$$(HH^*)_{0m} = 2kT/\gamma k_m^2 a^2. \quad (5.6)$$

Substituting eqn. (5.6) into eqn. (5.4) and performing the integration then yields

$$h_0^2 \simeq (kT/2\gamma\pi^{\frac{1}{2}}) [\exp(2t/\tau_m)] / (2t/\tau_m)^{\frac{1}{2}}. \quad (5.7)$$

Solving this equation for t yields an approximate value for t_b . One finds that t_b is a small multiple of τ_m :

$$t_b = \tau_m f(h_0, \gamma) \quad (5.8)$$

For instance, f ranges from 4.5 to 6.9 for $h_0 = 100$ to 1000 \AA , using $\gamma = 30 \text{ dynes/cm}$. After a time approximately equal to t_b , the unstable film either ruptures or abruptly decreases its thickness to form a thinner metastable film, depending on the shape of $V(h)$. This mechanism may explain the sudden formation of black film from a much thicker one, which is often observed.

LIFE TIME AND CRITICAL THICKNESS OF A DRAINING FILM

The life time t_l of a draining film will not only depend on the time of breaking t_b , but also on the time of draining. When the film is still thick the draining usually proceeds rapidly and the thickness fluctuations grow slowly or not at all. When the film becomes thinner, however, the rate of draining slows down, whereas the stable fluctuations (if present) grow faster and faster until a critical thickness h_c is reached at which one of the fluctuations grows so fast that the film breaks.

The quantitative treatment of this process is complex because h_0 depends on t and, in turn, Λ_c , Λ_m and τ_m on h_0 . Where h_0 decreases with increasing t , there is a corresponding decrease in Λ_c , Λ_m and τ_m . To take this into account a greater number of terms should be included in the sum (5.2) than for the analysis of a stationary film, where h_0 was constant and only the fastest growing fluctuation, at that h_0 , had to be included. Therefore, a simplified, graphical treatment is proposed which may be applied to films where the dependence of h_0 on t is relatively

simple and known, e.g., the small circular films investigated by Scheludko ^{7, 10, 12, 14-16} and others.¹⁷⁻¹⁹

In fig. 6, the breaking time t_b and the time of draining t are plotted, schematically, as a function of h_0 —within that range of h_0 for which modes with $\Lambda_m < a$ exist—for an unstable film (fig. 6A) and for an unstable film thinning to a metastable one (fig. 6B). Also, $t + t_b$ is plotted as a function of h_0 (dashed curve). t_b is obtained from eqn. (5.8) and (3.9). For unstable films, eqn. (4.3) for τ_m may apply

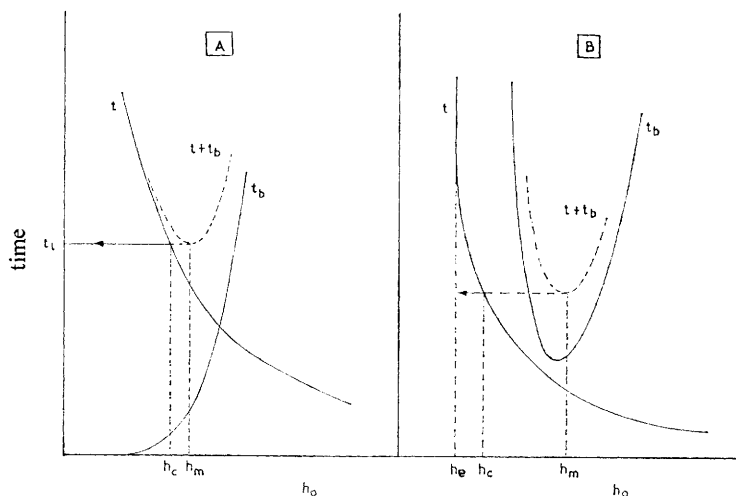


FIG. 6.—Schematic plot of the time t of draining and the time t_b of breaking as a function of film thickness h_0 . Part A: only van der Waals forces; part B: both van der Waals forces and double-layer forces. t_l is the lifetime of the film, h_c and h_e the critical and equilibrium thicknesses; h_m is the thickness at the minimum in $t + t_b$.

and, consequently t_b will increase continuously with h_0 (see fig. 6A). For an unstable film thinning to an equilibrium film with thickness h_e , $V(h)$ may be of the form displayed in fig. 3A, with h_e near the minimum and the transient unstable region at $h_0 > OQ$.

Now the life time of a draining film with a thickness h_0 is always smaller than the corresponding value of $t + t_b$. For smaller h_0 , also $t + t_b$ becomes smaller until a minimum is reached at $h_0 = h_m$. This minimum value of $t + t_b$ is taken equal to the life-time of the film; thus,

$$\tau_{t_l} = (t + t_b)_{\min}. \quad (6.1)$$

is obtained with the relation

$$dt/dh + dt_b/dh = 0. \quad (6.2)$$

The critical thickness h_c corresponds to the thickness on the drainage line where $t = t_l$ (see fig. 6). According to this procedure it should be considered a minimum value. In fig. 6A rupturing takes place at h_c ; in fig. 6B the thickness suddenly changes from h_c to h_e , the equilibrium thickness.

TEST OF EQUATIONS ON DATA OF MICROSCOPIC FILMS

Scheludko and Exerowa ^{7, 10, 14-16} have investigated the draining and rupturing of circular microscopic aniline and water films in air. Some surfactant had been added to prevent local thinning (Gibbs-Marangoni effect) in the earlier stages of drainage and to allow the films to drain gradually and regularly with the opposing

interfaces nearly parallel until breaking occurs at a thickness of a few 100 Å. According to Scheludko¹² the drainage of the circular free films is governed by the equation

$$dh_0^{-2}/dt = \alpha P, \quad (7.1)$$

where P is the pressure applied on the outside of the film and

$$\alpha = 4/3\eta r^2. \quad (7.2)$$

r is the radius of the film and η the viscosity of the liquid. (For a further discussion of these equations, see Frankel and Mysels²⁰ and Platikanov.²¹)

P is equal to

$$P = P_0 - \Pi_w - \Pi_{el}. \quad (7.3)$$

P_0 is the capillary suction at the Plateau border, Π_w is the contribution of the van der Waals forces, given by

$$\Pi_w = -dV/dh = -A/6\pi h_0^3, \quad (7.4)$$

and Π_{el} is the electrostatic repulsion between the film surfaces. Π_{el} may be neglected if double layers are absent or if the electrolyte content is sufficiently high.

A useful approximate analytical expression for h_c may be obtained if P_0 and Π_{el} are neglected with respect to Π_w , which is a reasonable approximation for small h_0 and high salt concentrations. It applies only to the last stage of the draining process. Then one may write

$$dh_0/dt \simeq -A/9\pi\eta r^2. \quad (7.5)$$

Further, dt_b/dh may be obtained from eqn. (5.8) and (4.3). Neglecting the dependence of f on h_0 and using (7.5) and (6.2) one obtains:

$$h_c \simeq 0.222(Ar^2/f\gamma)^{\frac{1}{2}}. \quad (7.6)$$

According to this equation, h_c does not depend on η . A more general analysis, including the term P_0 , does not change this conclusion perceptibly. Experiments on films with varying η would show if this conclusion is correct.

It is also of interest to calculate the approximate value of Λ_c at h_c . Substituting eqn. (7.6) into eqn. (4.2) yields

$$\Lambda_c(h=h_c) \simeq 0.55rf^{-\frac{1}{2}}. \quad (7.7)$$

Taking $f = 7$, one finds that $\Lambda_c \simeq 0.21r$.

Scheludko and Exerova measured the $h_0(t)$ curve for aniline films stabilized with 0.5 % dodecylalcohol and obtained $A \simeq 7 \times 10^{-12}$ erg ($P_0 = 430$ dynes cm^{-2} and $r = 10^{-2}$ cm). The experimentally obtained critical thickness of aniline films stabilized with decylalcohol was about 420 Å to within a small variation. Assuming that the draining rates of films stabilized with dodecyl- and decyl-alcohol are equal, h_c is calculated to be 750 Å using the graphical procedure and $\gamma = 39.4$ dynes/cm and $\eta = 0.044$ poise. Eqn. (7.6) gives the more approximate value 890 Å ($f = 7$).

From the $h_0(t)$ curve for films of 0.1 M aqueous KCl solutions, stabilized with 5×10^{-4} % saponin the same authors obtained $A \simeq 10^{-12}$ erg ($P_0 = 730$ dynes cm^{-2} ; $r = 10^{-2}$ cm). Critical thicknesses of films containing 0.1 M KCl and stabilized with propionic and butyric acid were also measured. They found $h_c \simeq 270$ Å. The distribution of values of h_c , however, was broader than for aniline. Assuming that the drainage of these films is the same for all stabilizers, and carrying out the same procedure as for aniline with $\gamma = 65$ dyne/cm and $\eta = 0.01$ poise, we calculate $h_c = 410$ Å. Eqn. (7.6) yields $h_c = 485$ Å ($f = 6.5$).

The analysis shows that the experimental values of h_c for aniline and water are about 1.8 and 1.5 times smaller than the theoretical values. This result seems reasonable considering the number of approximations that has to be made. The

discrepancy may be due to additional stabilizing mechanisms not included in the theory. Any film elasticity will damp fluctuations in h , especially if they tend to become larger. Consequently, the thickness at which the film breaks is smaller than that calculated here because then the van der Waals force outweighs those arising from the Gibbs-Marangoni effect. Reducing the constant A of aniline by a factor of 8 and that of water by a factor of 3 would also remove the discrepancy. An 8-fold difference for aniline is outside the limit of experimental error, although the reported value of A seems high with respect to that of water. A 3-fold difference for water, however, is still in the limit of accuracy of which this value is known.

The influence of the electrolyte concentration on the breaking process is marked. Scheludko⁷ found a continuous draining to the equilibrium thickness with KCl concentrations lower than 10^{-2} M and a formation of black holes or rupturing at concentration of about 10^{-1} M. These facts may be explained qualitatively from fig. 6B: decreasing the salt concentration decreases $|-d^2V/dh^2|$ and thus increases t_b . In the time corresponding to the minimum value of $t+t_b$ the film has already drained continuously to a thickness close to the equilibrium thickness h_e , which means that no sudden thinning to the equilibrium thickness occurs. There are indications, however, that the stability of the film against black spot formation or rupturing cannot be explained from the shape of the d^2V/dh^2 curve only.²²

The theory given above has been applied to the relatively simple, small, circular film. It should be, however, also a valuable starting point for the consideration of more complicated systems such as macroscopic films in a foam, very small films in a creamed emulsion, and films on a solid support.

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Note added in proof. Eqn. (7.5), obtained by neglecting P_0 and Π_{el} with respect to Π_w , is a poor approximation in the range of h_0 in which it is applied. Neglect of Π_w and Π_{el} with respect to P_0 gives a better approximation. Then eqn. (7.6) becomes $h_c \simeq 0.268 (A^2 r^2 / P_0 f \gamma)^{1/2}$ and eqn. (7.7) $\Lambda_c(h = h_c) \simeq 0.80 (Ar^3 \gamma^3 / P_0^4 f^4)^{1/4}$.