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INSTABILITY AND RUPTURE OF THIN LIQUID FILMS

by

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1. Introduction

Thin liquid films sandwiched between two fluids, or between a fluid and a solid surface are encountered in several industrial and biological systems. In flotation, the thinning and rupture of the liquid film between particle and bubble can be the rate determining step of the process.[1] Films of this type are also important in detergency. When an oil covered surface (e.g. a fabric material) is immersed in aqueous surfactant solution, it is necessary to destabilize the oil film by causing it to thin and rupture to form drops on the surface. These drops may be readily removed by hydrodynamic forces when the system is agitated. In water vapor condensation on a hydrophobic shock tube wall, experiments indicate that a thin film is formed that breaks up into droplets upon reaching a critical thickness of about 100 A.[2] The process of coalescence of bubbles and droplets in foams and emulsions also depends on the rupture of intervening thin liquid film. The formation of microvilli in cancer cells can be explained on the basis of the instability of biological membrane to small perturbations, if the membrane is considered as a thin liquid film sandwiched between the extra- and intra-cellular fluids.[3]

One chapter[4] in this book has dealt with the formation and thinning of thin liquid films. The objective of this review is to provide a unified theoretical framework for analyzing the stability of thin liquid films, to review briefly some of the experimental work done to measure the critical thickness of rupture of these films, and finally, to relate the results obtained with some physicochemical phenomena in industrial and biological systems. While a brief historical perspective of the work done in this area is given here, the major emphasis in the present review is on the recent work on the hydrodynamic stability analysis of these films.

2. Rupture Mechanism

Initially, interest in the stability of thin liquid films arose from studies on the coalescence of particles in unagitated colloidal dispersions. As previously remarked, a common phenomenon in such systems is the formation of thin fluid films between elements of the dispersion. Once created, these films gradually thin and may rupture upon attaining a critical thickness (h_{cr}) of approximately several hundred angstroms. As reviewed by Scheludko,[1] early studies attributed this rupture to the onset of a thermodynamically unstable state during the thinning process. In these studies, the usual approach was to calculate the free energy of the film as a function of its thickness and then to examine the thermodynamic stability from the variation of the free energy with thickness (for an example, see Frenkel[5] for the case of a film on a solid surface.

The thermodynamic arguments, however, did not offer any insight into the kinetic mechanism of rupture. de Vries[6] was perhaps the first to supplement the thermodynamic point of view of film stability with a kinetic treatment. de Vries postulated that a film can rupture if a hole (created by thermal or mechanical fluctuations) forms spontaneously in the film. He calculated that the activation energy required to form such a hole is approximately equal to σh^2 (σ and h are the surface tension and thickness of the film, respectively). The film ruptures when the quantity σh^2 is of the order kT (k denotes Boltzmann's constant and T signifies the temperature). For a film at a temperature of 298 K and with a surface tension of 10 dyne/cm, this mechanism predicts a critical thickness of rupture of 10 Å. However, experimentally measured values of the critical thickness for a film at 298 K and with a surface tension of approximately 10 dyne/cm are of the order of several hundred angstroms. Thus, this mechanism yields a critcal thickness of rupture that is an order of magnitude too small.

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In 1960, de Vries[7] modified his "hole" theory in two ways: thermal or mechanical fluctuations can corrugate a deformable interface, and the van der Waals' interaction forces play an important role in the rupture of thin films. Scheludko gave, in 1962, a more detailed thermodynamic treatment to the concept that deformations coupled with interaction forces can lead to film rupture.[8] The existence of corrugation at the film interface has been proven experimentally by light scattering studies.[9] Light incident upon an unperturbed, deformable interface is scattered as well as reflected. The scattering is caused by the unevenness of the surface: A planar interface simply reflects incident light, while a corrugated surface both reflects and scatters it. Scheludko suggested that these natural corrugations, developing on the interfaces of a thin film, increase in amplitude when the growth is accompanied by a decrease in the free energy of the system. Rupture occurs when the enlarging deformations become equal to the thickness of the film.

Scheludko detailed three primary factors that determine the free energy changes of a film subject to growing surface waves: interfacial tension, long range van der Waals interactions and electrical forces. A positive interfacial tension opposes a displacement of the interface because such a displacement increases the surface area and thus raises the free energy of the system.

The long range van der Waals force has an interaction range of the order of 1000 Å. In macroscopic systems, the effect of thickness on this force is usually negligible because characteristic distances are larger than 1000 Å. In thin film systems, however, the role of the thickness is more important because the thickness of the film (at the critical thickness) is of the same order of magnitude. Depending upon the properties of fluids which form the film and bounding media, these forces can be either attractive or reuplsive.[5] When the net force is attractive in nature, it promotes the growth of surface waves.

Electrical forces are significant in the growth of surface waves when ions are present in the liquid from which the film is formed. In this case, double layers are built up at the two interfaces of the film. These double layers oppose the growth of surface waves when their charges have the same sign. This resistance is a consequence of the fact that surface growth is accompanied by a reduction in the thickness of portions of the film and this is energetically unfavorable because it causes an increased overlap of the double layer of the two interfaces and hence an increased repulsion.

Vrij was the first to account for the fact that the growth of surface disturbances occurs in the thinning film.[9] He utilized the corrugation mechanism to develop a theoretical expression for the critical thickness of rupture, suggesting that the thinning and rupture of a film can be viewed as a two stage process.[9,10] In the first stage the uncorrugated film drains from an initial thickness to a thickness h_o. To estimate the time required for this drainage, Vrij considered a circular film thinning under the action of a pressure difference between the film and its border and containing sufficient amounts of surfactant to render the interfaces tangentially immobile. For such films Reynolds' equation relates the dependence of the film thickness (h) on time (t).

$$\frac{d(h^{-2})}{dt} = \frac{4}{3\mu R^2}\Delta p \qquad (1)$$

In Eq. (1), μ is the viscosity of the film, R is the radius and Δp is the pressure difference causing the film to thin.

In the second stage, at a thickness h_o, corrugations develop on the interfaces of the film. Only symmetric varicose disturbances were considered. Using free energy arguments, Vrij has demonstrated that the film is unstable for one of the Fourier components of these disturbances. The film ruptures when the fastest growing component of the subset reaches an amplitude $h_o/2$. The time necessary for this component to cause rupture was estimated by employing a graphical procedure. Vrij identified the critical thickness with the value of h_o that minimized the sum of the drainage and rupture times and introduced a correction for the thinning of the film during the growth of the surface waves. With some additional simplifying assumptions he was also able to derive the following expression for the critical thickness of rupture h or:

$$h_{cr} = 0.267 \left[\frac{A^2 R^2}{f\sigma_o \Delta p} \right]^{1/7} \qquad (2)$$

In Eq. (2), A is the Hamaker constant, σ_o is the surface tension, f is a numerical coefficient approximately equal to six (Δp and R are defined after Eq. (1)). Equation (2) predicts that the critical thickness is independent of the viscosity of the film and varies with the two-sevenths power of the film radius.

The agreement of the elementary calculations of Scheludko and Vrij with experimental observations not only demonstrated the feasibility of the corrugation mechanism but also provided the motivation for a more precise study of the hydrodynamic stability of thin films.

In hydrodynamic stability theory, a geometric perturbation is applied to one or both interfaces of a thin film (Fig. 1). This perturbation produces deformation in the shape of the film as well as initiating fluid motion. If the interfacial perturbations grow in time, the film becomes unstable and may rupture. If the perturbations decay in time, the film is stable with respect to these perturbations. In order to determine the conditions when a film becomes unstable, all the perturbation variables of the system are expressed in the following form:

$$\theta(\vec{R},t) = \hat{\theta}(\vec{R})\, e^{\omega t} \qquad (3)$$

Here, θ is any perturbation variable of the system, and it is a function of both position, $\vec{R}$, and time, t. $\hat{\theta}$ is the time independent component of the perturbed quantity, and ω is the complex frequency of motion (also referred to as the angular velocity). The real component of ω is referred to as the growth coefficient (β). If the growth coefficient is positive, the perturbation, θ, will grow exponentially with time, and will cause the film to be unstable. If the growth coefficient is negative, the perturbation will die out eventually. If the growth coefficient is zero, the film is considered marginally stable, and its dynamics will be determined by the imaginary component of ω. The objective of the linear stability analysis is to obtain an analytical expression or numerical values of ω as a function of various physicochemical parameters that characterize the system, by solving the equations of continuity and motion for the system with appropriate boundary conditions.

Two different approaches have been used to account for the long range van der Waals and electrical double layer forces in the hydrodynamic stability analysis: a disjoining pressure procedure and a body force procedure.

In the disjoining pressure approach, the influence of the van der Waals and double layer forces is incorporated in the normal stress balance at the fluid interface of the film. In these balances, the component of the stress tensor which acts in a direction normal to the interface is required to suffer a discontinuity apart from the Laplace jump. On the other hand, in the body force approach, the influence of these forces is incorporated as a body force in the equations of motion. When applied rigorously, both approaches should lead to the same results.

In the next sections, investigations carried out for both non-thinning and thinning liquid films, using these two approaches, are discussed.

3. Non-thinning Films

a. Inviscid Plane-Parallel Film

Felderhof has developed a detailed electrohydrodynamic study of the surface wave dynamics of thin films. The model system he analyzed consisted of an infinite plane-parallel non-thinning film composed of an inviscid fluid and surrounded by vacuum. Dissolved ions were assumed present in the film volume and the gravitational field was neglected. Felderhof obtained analytical expressions for the motion induced by the onset of low amplitude surface waves by using perturbation theory and normal mode analysis to solve the continuity, Euler and Maxwell equations. The Maxwell equations were solved with the assumption that for each instantaneous shape of the film, the ions in the film volume have achieved thermal equilibrium. This quasi-static assumption restricted the treatment to surface waves with a frequency less than the inverse of the time necessary to establish an ionic equilibrium in the film volume and on the surface.

Felderhof studied the effect of one Fourier component of a perturbation of the film and found that there were two independent modes of vibration of the free film: the symmetric mode (squeezing mode) and the antisymmetric mode (stretching or buckling mode). The symmetric mode is a varicose disturbance of the film; the two interfaces are displaced in sinusoids of equal amplitude and wavelength. For this mode, the sinusoids are 180 degrees out of phase. The antisymmetric mode is a sinuous disturbance of the film; as with the symmetric mode, the two interfaces are displaced in sinusoids of equal amplitude and wavelength. For this mode, however, the sinusoids are in phase (Fig. 1). For each mode, there is a characteristic complex frequency. The response of the system to arbitrary interfacial disturbances is composed through a linear combination (over all wavelengths) of the two modes. Dispersion relations for both modes were obtained. From these relations, the conditions for stability can be determined. The dispersion relations were analyzed in the long-wavelength limit. In this limit, his calculations indicated that the stretching mode, in addition to the squeezing mode, can become unstable to surface waves. Felderhof found that the stability of the stretching mode is determined by the sign of a quantity S defined by

$$S = (\sigma_o - \gamma) + \frac{\alpha}{2} - \frac{A}{8\pi h_o^2} \quad . \qquad (4)$$

In Eq. (4), σ_o is the bulk surface tension of pure fluid which forms the film, γ is the spreading pressure of ions adsorbed on the surface, α is the electric film tension at constant volume, A is the Hamaker constant and characterizes the London-van der Waals dispersion forces present in the film, and h_o is the unperturbed thickness of the film. Physically, α represents the free energy of formation of the double layers, and it decreases the interfacial tension of film. On the other hand, α represents the effect of surface adsorption of ions on the surface tension. The last term arises from the consideration of London-van der Waals dispersion forces, and leads to a decrease in the film tension. If S is zero, the surface waves are stationary with time. Owing to the neglect in this treatment of viscosity and the consequent absence of viscous dissipation, the surface waves cannot be damped out. If S is negative, the surface waves grow with time. Since the stretching mode does not involve variations in the film thickness, this growth may not be accompanied by rupture. However, the growth does cause a kind of buckling of the film. The nature of this change cannot be ascertained from Felderhof's perturbation study, but it could be evaluated from a non-linear analysis.

b. Viscous Plane Parallel Films (Foam and Emulsion Type)

The stability of an infinite plane parallel non-thinning viscous film was analyzed independently by Lucassen et al.[13,14] and Ruckenstein and Jain.[15] In the former analysis, the thin film was bounded by two different semi-infinite fluids. The semi-infinite phases and the film were assumed to contain surface active agents whose effect on the wave motion was accounted for by assuming that the surfaces were viscoelastic. Diffusional exchange of the surfactant from the film and bulk phases to the interfaces was, however, neglected. These authors used the disjoining pressure approach. The analysis of Ruckenstein and Jain differed from the former in these ways: (i) these authors used the body force approach; (ii) their treatment included a systematic analysis of the effect of surfactants, and (iii) the film was bounded by a vacuum.

While Lucassen and coworkers derived the dispersion equation for a film bounded by two different fluids, they examined in detail the dynamics of a system consisting of a film bounded by two identical semi-infinite phases. For such a system, similar to Felderhof, they found that if gravity is neglected these are two independent modes of vibration of the film; the symmetric mode and the antisymmetric mode. Since only the symmetric mode leads to film rupture due to local thinning of the film, Vrij et al.[14], in a companion paper, examined the conditions for growth of surface waves for the symmetric mode in the long-wavelength limit (i.e. when the wavelength of perturbation is much larger than the unperturbed thickness of the film).

Considering only London-van der Waals dispersion forces, Vrij et al. and Ruckenstein and Jain showed that the growth coefficient, β (the real part of ω), for the symmetric mode is given by a simple expression:

$$\beta = -\sigma_{eff} f_1 \tag{5}$$

where

$$\sigma_{eff} = \sigma_o - \frac{A}{\pi h_o^4} \frac{\lambda^2}{4\pi^2} \tag{6}$$

and f_1 is a positive definite function of the system parameters. (The expressions for f_1 are different in references 14 and 15.) In this equation σ_o is the interfacial tension, A is the Hamaker constant, h_o is the unperturbed film thickness, and λ is the wavelength of perturbation. The sign of β, which in turn determines the stability of the system, depends only on the sign of σ_{eff}. An inspection of Eqs. (5) and (6) suggests that it is possible to find the value of a wavelength that corresponds to zero growth rate (condition for marginal stability). This wavelength is referred to as the critical wavelength, λ_c, and is given by:

$$\lambda_c = 2\pi(\pi\sigma_o/A)^{1/2} h_o^2 \tag{7}$$

If the wavelength of a perturbation is greater than λ_c, the film will become unstable. For each wavelength greater than λ_c, the value of β is positive and can be calculated from Eq. (5). The wavelength with the largest value of growth coefficient is the most rapidly growing fluctuation. This wavelength dominates the rupture kinetics of the film, and is referred to as the dominant wavelength (λ_d). Furthermore, if one assumes that the linear stability analysis is valid up to the point when the two surfaces come into contact, it is possible to estimate the time constant of rupture (τ_m) as the reciprocal of the growth rate corresponding to the dominant wavelength.

These studies have shown that when the bounding medium is vacuum, a dominant wavelength does not exist in a surfactant free film.[15] However, when large amounts of surfactants are present in the system, the dominant wavelength is given by the following expression:

$$\lambda_d \approx \sqrt{2}\,\lambda_c \tag{8}$$

When the viscosity of the bounding media is non-zero, dominant wavelength exists even for systems without surfactants, and its value is given by

$$\lambda_d \approx \sqrt{3}\,\lambda_c \tag{9}$$

Vrij et al. and Ruckenstein and Jain also examined the effect of the surfactants on the growth coefficient of the symmetric mode in the long wavelength limit. Their detailed numerical calculations demonstrated that the maximum growth rate is essentially a step function of the surface elasticity. For films with a surface elasticity less than a critical value, the maximum growth rate is virtually independent of the elasticity. At the critical value this growth rate is reduced sharply in absolute value. For surface elasticities larger than the critical value, the maximum growth coefficient is again independent of elasticity. Since the time of rupture is approximately the inverse of the maximum growth coefficient, films with elasticities less than the critical value rupture more quickly than those with elasticities greater than this value. Vrij et al. also found that numerical values for this critical surface elasticity are low. They therefore concluded that only small amounts of surfactant need be adsorbed at the interface to render it tangentially immobile. In the limit of large surfactant concentration, the time constant of rupture is given by the following expression:

$$\tau_m = 96\pi^2\sigma_o\mu\, h_o^5\, A^{-2} \tag{10}$$

The analysis of thin viscous films mentioned above did not include detailed analysis of the double layer forces. Recently, Sche and Fijnaut have extended the electrohydrodynamic analysis of Felderhof to viscous thin films surrounded by a vacuum.[17] The dispersion relations they have obtained are complicated because of the inclusion of these effects, and thus detailed calculations have been undertaken only for the simplified case of a tangentially immobile surface. For this case, the criteria for growth of both the squeezing and stretching modes, in the long-wavelength limit is found to be independent of the viscosity of the film and identical to the criteria established by Felderhof for inviscid flow.

Maldarelli et al.[18] have recently extended the analysis of Felderhof to the general case when the liquid film is bounded by two different viscous phases. In addition to obtaining analytical results for the squeezing and stretching modes for a symmetric film (i.e. film bounded by the same fluid), these authors have studied the role of asymmetry on the growth of perturbations numerically, especially the asymmetry of interfacial tension.

When electrical double layers are absent, the expression for the growth coefficient, β, for the antisymmetric mode is given by the following expression:

$$\beta = -\left(\sigma_o - \frac{A}{8\pi h_o^2}\right) f_2 \tag{11}$$

Here, all the quantities have the usual meaning, and f_2 is a positive definite function of system parameters. Therefore, instability of this type will occur only in low tension systems, i.e. when

$$\sigma_o < \frac{A}{8\pi h_o^2} \tag{12}$$

Biological membranes provide an example of such a system.[3] When a film becomes unstable in this mode, it is possible to estimate the dominant wavelength, λ_d, for systems where $\mu_{media}/\mu_{film} \ll 1$. Its value is:

$$\lambda_d \cong 2\pi h_o/(6\mu_{media}/\mu_{film})^{1/3} \quad . \tag{13}$$

It must be pointed out here that while the value of the quantity $(\sigma_o - A/8\pi h_o^2)$ may be negative during the kinetic process, this quantity must be positive eventually for a system to be stable mechanically and thermodynamically. In addition, reactions at the interface[41] lead to additional terms in Eq. (11) causing the film to be unstable even at positive values of $(\sigma_o - A/8\pi h_o^2)$.

When the film is surrounded by different fluids, it is not possible to obtain an analytical expression for the growth coefficient. These authors[18] however have numerically examined such a system in detail, and have found that for a given wavelength and viscosities, the primary factor that determines the ratio of amplitudes of perturbation at two interfaces is the surface tension. In the antisymmetric mode, the amplitude ratio remains close to unity, but in symmetric modes, the amplitude ratio is inversely proportional to the ratio of surface tensions. One would also expect this on the basis of physical arguments, because the larger the value of surface tensions, the more difficult is it for the surface to deform.

c. Spherical Film

Patzer and Homsey,[19] in an analysis similar to the above, have examined the stability of a thin film bounded by two spherically concentric fluid phases. Such a system can be considered as a mathematical model of a soap bubble or a biological cell. The focus of their study was the calculation of the marginally stable thickness of the spherical film as a function of the physiochemical parameters of the system. The base state was assumed to be one of zero flow. Two types of interfaces, tangentially immobile (large surface concentration of surfactant) and completely free (zero surface concentration of surfactant) were considered. Patzer and Homsey found numerically that increasing the surface tension or decreasing the Hamaker constant decreases markedly the marginally stable thickness of the thin film. Their numerical calculations also indicated that the marginal thickness is independent of the type of interface considered (either tangentially immobile or completely free).

d. Film on a Solid Substrate (Wetting Film)

All the aforementioned studies on surface wave dynamics analyzed liquid films that were surrounded by either a viscous fluid or a vacuum. Ruckenstein and Jain[15] and Jain and Ruckenstein[20] have treated the case of a film on a solid substrate. The model system they studied consisted of an infinite plane-parallel non-thinning film situated on top of a solid and bounded from above by a semi-infinite fluid. The surrounding fluid and the film were assumed to contain surface active materials. The lower (film-solid) interface was considered rigid and impenetrable to surfactant. At the upper (film-semi-infinite fluid) interface, the authors formulated a surfactant mass balance to account for the effects on the wave motion of surface diffusion, surface shear viscosity and elasticity and the diffusional exchange of surfactant from the film and the semi-infinite fluid to the interface. Both London dispersion and double layer forces were included in their analysis.

These investigators analyzed the stability of the film with respect to infinitesimal displacements of the upper deformable interface by using perturbation theory and normal mode analysis. Their calculations indicated the existence of only one mode of vibration of the film. This result is a consequence of the assumed rigidity of the lower interface. Explicit expressions for the growth coefficient for the cases of completely free (zero surface concentration of surfactant) and tangentially immobile surfaces were obtained.

In both cases, the growth coefficient, β, is given by the following expression:

$$\beta = - n\,\sigma_{eff} \times f_3 \,, \qquad (14)$$

where:

$$\sigma_{eff} = \sigma_o - \left(\frac{A}{2\pi h_o^4}\right)\frac{\lambda^2}{4\pi^2} \qquad (15)$$

and f_3 is a positive definite function of system parameters. Here n=1 for a tangentially immobile surface, and n=4 for a free surface. These authors obtained the following expressions for λ_c and λ_d for systems with and without surfactants:

$$\lambda_c = 2\pi(2\pi\sigma_o/A)^{1/2}\, h_o^2 \qquad (16)$$

and

$$\lambda_d \approx \sqrt{2}\,\lambda_c \qquad (17)$$

When the system has no surfactants, the following expression for the time constant of rupture was obtained:

$$\tau_m \approx 48\pi^2 \sigma_o \mu\, h_o^5\, A^{-2} \qquad (18)$$

On the other hand, when surfactants are present in large amounts the time constant increases by a factor of four:

$$\tau_m \approx 192\pi^2 \sigma_o \mu\, h_o^5\, A^{-2} \qquad (19)$$

Their calculations further indicated that for completely free surfaces, the growth coefficient decreases slightly with increasing viscosity of the upper phase, while for tangentially immobile surfaces, the growth coefficent is virtually independent of this viscosity. Jain and Ruckenstein also analyzed numerically the influence of surface elasticity and surface shear viscosity on the growth rate. They obtained a step profile for the behavior of the maximum growth coefficient as a function of the surface elasticity. Their numerical results also demonstrated that for films with reduced surface elasticities, the presence of surface shear viscosity can markedly decrease the maximum growth rate.

4. Thinning Films

a. Foam Films

The studies discussed in Section 3 were devoted to infinite plane-parallel or spherical non-thinning films. However, the films that occur naturally in dispersions are radially bounded structures draining under the influence of capillary suction and negative disjoining pressure. Thus the previous studies, though instructive in detailing the fundamental physiochemical aspects of thin film dynamics, needed to be extended to incorporate the effects of a circular geometry and drainage flow. On the basis of Scheludko's and Vrij's ideas, a systematic analytical approach for thinning films was developed by Ivanov et al.[21] The model system they employed consisted of a plane-parallel circular draining foam film. Symmetric varicose disturbances were superimposed on the thinning and the focus of the analysis was to determine the critical thickness at which the film ruptures as a result of these disturbances.

To obtain analytical expressions for the motion induced by the drainage and surface fluctuations, Ivanov et al. assumed that the velocity vector of this motion can be decomposed into two terms. The first is the velocity due to the drainage of the film. This velocity was obtained by solving the continuity and Navier-Stokes equations in the lubrication approximation for an unperturbed circular draining film. Thus an expression for the velocity of thinning $V = -dh/dt$ was derived. For details see references 4 and 22. The second term is the velocity caused by the surface waves. This velocity was obtained by a quasi-static procedure: The film was assumed to have a fixed thickness and the velocity vector resulting from a symmetrical varicose disturbance, ξ, of the film was calculated as a function of this thickness using the approach employed in the non-thinning films. The drainage was then coupled to the surface growth by assuming that ξ during the thinning is a function of time through the thickness h. Mathematically, the motions due to thinning and the present perturbations can be combined in the following manner:

$$V_\xi = \frac{\partial\xi}{\partial t} = \beta \cdot \xi = \left(\frac{\partial\xi}{\partial h}\right)\left(\frac{dh}{dt}\right) = -V\left(\frac{\partial\xi}{\partial h}\right) \qquad (20)$$

where ξ is the applied perturbation, β is the growth coefficient (real part of the frequency of motion ω), and h is the average film thickness at time t. Due to this assumption, all time-dependent quantities depend on t only via h. Integration of Eq. (20) leads to:

$$\xi(h) = \xi(h_t)\ \exp\left[-\int_{h_t}^{h} \frac{\beta}{V}\,dh\right] \qquad (21)$$

where h_t is the transition thickness at which the wave becomes marginally unstable.

The film will rupture when the amplitude of the fastest growing perturbation, ξ_m, is equal to the half thickness of the film at that time, i.e. $h_{cr} = 2|\xi_m|$. Using this condition, and a set of simplifying, but physicall consistent, assumptions, Ivanov et al.[21] obtained the following expression for the initial thickness of rupture of foam films with tangentially immobile interfaces:

$$h_{cr}^2 = \left(\frac{4kT}{R^2\pi_t'}\right)\left[\ln\frac{P_c - \pi_{cr}}{P_c - \pi_t}\right]^{-1} \times$$
$$\exp\left[\frac{R^2\pi_t'}{4\sigma_o}\ln\frac{P_c - \pi_{cr}}{P_c - \pi_t}\right] \qquad (22)$$

where k is the Boltzmann's constant, T is the absolute temperature, R is the radius of film, P_c is the capillary pressure, σ_o is the interfacial tension, π_t and π_{cr} are the disjoining pressures at the transition thickness, h_t, and the critical thickness, h_{cr}, respectively. The transition thickness, h_t, is obtained by getting the growth coefficient, β, equal to zero in the dispersion equation.

Using this procedure, Ivanov et al. were able to calculate theoretical values of the critical thickness of rupture for films with tangentially immobile surfaces. Their results were in satisfactory agreement with experimentally measured values of critical thicknesses for films with large concentrations of surfactant when theoretical isotherm for disjoining pressure was used[22] (Fig. 21). The authors also studied films that containe small amounts of surfactant. For these films, they utilized a surfactant mass balance at the interface to account for the effect of surface elasticity on the thinning and surface motion. However, surface shear viscosity was neglected. The theoretically calculated critical thicknesses of rupture were found to be independent of the amount of surfactant present, contrary to the experimentally observed decrease in critical thickness with increasing surfactant concentration. In a later study, Ivanov and Dimitrov[23] extended the analysis of Ivanov et al. to include the effects of surface shear viscosity. In this analysis, they demonstrated that the observed decrease in critical thickness with increasing surfactant concentration can be due to surface shear viscosity.

Interesting physical conclusions about thinning films can also be reached, if Eq. (20) is integrated in the form[24]:

$$\xi(h_{cr}) = \xi(h_t) + \int_{h_t}^{h_{cr}} \frac{v_\xi}{V}\, dh \qquad (23)$$

It follows from this equation that each factor which effects both β and V to the same extent, will not alter h_{cr}. For example, h_{cr} for films with tangentially immobile interfaces does not depend on μ (see (22)), because both β and V are inversely proportional to μ. On the contrary, if β is decreased more than V, this will result in decreasing h_{cr}, because the growth of perturbations will be hindered and the surfaces will "touch" each other at a smaller mean thickness. This can be observed in the presence of a long-range positive (e.g. electrostatic) disjoining pressure; if it is not large enough to prevent rupture, it will primarily slow down the drainage from the thinnest part of the film without substantially affecting V. If, however, the positive disjoining pressure is a short range one, it will appear and abruptly increase only when the surfaces "touch" each other and thus will not affect h_{cr}. This is the case of formation of black spots — according to the above concept they should appear at the same thickness at which the film would rupture at small surfactant concentrations. These conclusions are in agreement with the experimental results of Manev et al.[25]

b. Emulsion Films

Using the approach discussed above, Ivanov and coworkers have studied the influence of a surfactant on the capillary waves in a symmetrical emulsion system, and have derived expressions for the critical thickness of rupture.[26,27] Using their results, these investigators suggest that the critical thickness of an emulsion film can be reduced by decreasing the value of v_ξ more than that of V. This can be achieved in two different ways: either by increasing the viscosity of drop (because $v_\xi \to 0$ as $\mu_{drop}/\mu_{film} \gg 1$) or by adding surfactants to the drops (because a large surfactant concentration reduces v_ξ considerably, but does not alter the velocity of thinning).

Recently, Dimitrov and Ivanov[28] have obtained the following expression for the rate of thinning of emulsion films with deformable interfaces using the lubrication approximation.

$$-\frac{\partial H}{\partial t} = \nabla_r \left[\frac{H}{2}(v_r^A + v_r^B) - \frac{H^3}{12\mu}\frac{\partial P}{\partial r} \right] \qquad (24)$$

where H is the local film thickness, t is time, P is pressure, μ is viscosity, r is the radial position in film, v_r^A and v_r^B are the radial velocities of the upper and lower interfaces, respectively, and $\nabla_r = \frac{1}{r}\frac{\partial}{\partial r} r$. When the interface is tangentially immobile (presumably due to large surfactants concentration), $v_r^{A,B}$ is zero. When the interface is tangentially mobile, $v_r^{A,B}$ is calculated by solving the Navier-Stokes' equation and the diffusion equation for the drop phase and the film along with the appropriate boundary conditions (see the review article by Ivanov and Jain in this book). Note that all hydrodynamic variables, i.e. H, $v_r^{A,B}$ and P in Eq. (24) have two components: one which accounts for the thinning of uncorrugated film, and the other that accounts for the flow induced in the non-thinning film due to corrugations. By neglecting the coupling terms, it is possible to obtain expressions for both v_ξ and V in a straightforward manner. Once the expressions for v_ξ and V are available, the procedure described above can be used to obtain the critical thickness of rupture (unpublished results).

c. Estimation of Coupling Terms

In all the published works of Ivanov and coworkers, the effect of drainage on the wave-motion has been assumed to be negligible. In an attempt to estimate these terms, Gumerman and Homsey[29] also have examined the stability of a plane-parallel circular free draining film subject to surface displacements. Their study, however, was restricted to films containing enough surfactant to render the interfaces tangentially immobile. These authors studied the marginal stability of film and found that hydrodynamic variables of the perturbed state (for example, the pressure and the velocity vector) should, in contrast to the assumptions of Ivanov et al., be dependent upon the drainage. The coupling terms were also estimated by Ivanov.[22]. Based on previous studies suggesting that the length of the wave, dominating the process of rupture, was approximately one tenth of the film radius, he concluded that those terms can be neglected.

We have recently calculated these coupling terms systematically using Eq. (24) for films with tangentially immobile interfaces, and we have derived an analytical expression for the coupling term similar to that found by Gumerman and Homsey. We also found numerically that these terms are negligible for thin films with non-zero surfactant concentrations.

d. Film on a Solid Substrate with Dimple

When a small drop or bubble approaches a solid or liquid interface, the intervening liquid film between the bubble and the interface is usually plane-parallel. However, when the bubble is large, it readily acquires a reverse curvature in its center so that some fluid is entrapped by a thinner ring.[30] The central lens of liquid is usually referred to as "dimple" and the surrounding circular film as "barrier" ring (Fig. 3).

In order to study the role of dimple, we have recently analyzed a model system as shown in Fig. 3: the liquid "barrier" ring of thickness h, and external and internal radii R and R_i formed between a bubble and a solid substrate.[31] The fluid outside the film is considered 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 the surfactants soluble in the film. Furthermore, the analysis includes the Gibbs-Marangoni effects, and both the surface constitutional dilational viscosity (μ_d) and the surface shear viscosity (μ_s). In the limit $R_i \to 0$, the results reduce to those obtained previously for plane-parallel radially bounded film, and in the limit $R_i \to 0$ and $R \to \infty$, the result for unbounded thin film can be obtained.

It must be pointed out here that in reality the slopes at the boundary of the ring are continuous. In addition the pressure gradients outside the ring may not be zero as assumed here. The model system considered here makes it possible to obtain the exact solution to the problem, as well as retains the essential features of the real system, if the pressures inside and outside the ring p^i and p^ℓ, are calculated by incorporating the geometry of the real system, i.e. the radii of bubble (R_c) and dimple (R_d), respectively (Fig. 3).

Having made these assumptions the problem falls in the realm of hydrodynamic stability theory. The first step is to solve the base case 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, the following expression for the critical thickness of rupture is calculated using the approach outlined in Section 4-a:

$$h_{cr}^2 = \frac{2kT}{R_{eff}^2 \Pi_t'} \left[\frac{(R - R_i)^2}{R^2 - R_i^2} \right] \left[\int_{h_{cr}}^{h_t} \frac{\Pi'}{\Delta P} \, dh \right]^{-1} \times$$
$$\exp \left[\frac{R_{eff}^2 \Pi_t'}{8\sigma_o} \int_{h_{cr}}^{h_t} \frac{\Pi'}{\Delta P} \, dh \right] \tag{25}$$

with

$$R_{eff}^2 = (R^2 + R_i^2) - (R^2 - R_i^2)/\ln (R/R_i) \tag{26}$$

and

$$\Delta P = P_c \left[\frac{1}{1 - (R_i/R)^2} + \frac{1 + R_c/R_d}{\ln (R_i/R)} \right] - \Pi \tag{27}$$

where ΔP is the driving pressure, $P_c = 2\sigma_o/R_c$ is the capillary pressure of the bubble and $R_d \approx 2R_i^2/(h_d - h)$ is the radius of curvature of the dimple, obtained by assuming the dimple to be the cap of a sphere of radius R_d. The maximum elevation of the dimple, h_d, above the solid surface can be calculated from[32]:

$$h_d = 0.285 \, (R + R_i) \sqrt{h/R_c} \quad .$$

It must be mentioned here that as $R_i \to 0$, the results for a plane-parallel film can be obtained. In the limit $R_i \to 0$ and $R \to \infty$, the results of Jain and Ruckenstein for a plane-parallel radially unbounded film can be obtained. Since the presence of a dimple does not alter the expression for the growth coefficient, β, the changes in critical thickness are mainly governed by the changes in the velocity of thinning. Velocity of thinning increases when the width of the ring $(R - R_i)$ is reduced or the radius of dimple, R_d, is increased. Indeed, the critical thickness of rupture, calculated numerically by solving Eq. (25), decreases as the width of the ring decreases and/or as R_d increases.

5. Applications

a. Industrial Systems

As mentioned in Section 1, quantitative understanding of the dynamics of thin liquid films is of importance in several industrial processes, such as flotation,[1] coalescence of bubbles and droplets in foams and emulsions, detergency, condensation,[2] and power coating. In what follows, the results discussed in previous sections are used to interpret some of the available experimental information.

The most extensive series of experiments to measure the lifetime and critical thickness of rupture of this liquid film have been carried out by Scheludko and his coworkers. In these experiments a radially bounded thin film is formed by either pressing a bubble (or droplet) against a solid substrate, or by sucking out the liquid I from a biconcave meniscus formed by the "drops" or "bubbles" of phase II (Fig. 4). Several variations of these two basic set-ups have been used by various investigators in this area of research;[33] an excellent exposé of the work is given in a comprehensive review by Scheludko.[1] Most of the results obtained from these studies can be explained by the theoretical results reported in Section 4.

Another set of interesting experiments where a thin film is formed on a solid substrate have been conducted by Goldstein[2] in a study of water vapor condensation on a clean hydrophobic shock tube wall. Goldstein reports that in these experiments a continuous film of condensate is formed, which, after reaching a thickness of about 100 Å in about 10μs 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.[15] It is also of interest to mention here that if Hamaker's constant A is taken to be order of 10^{-12} erg and h_o of the order of 50 Å, then the time constant of rupture computed from Eq. (18) with $\sigma_o \approx 70$ dyne/cm and $\mu \approx 16^{-2}$ P is of the order of 10μs, as was found experimentally.[2,15]

Several investigators have measured the coalescence time in foams and emulsions. While these "gross" measurements do not provide accurate information about the time constant of rupture of an individual film, they do provide an order of magnitude. Marucci,[34] for example, has reported that in the presence of surface active impurities the coalescence time in foams is of the order of 10^{-1} sec. One may verify that indeed the value 10^{-1} sec can be obtained from Eq. (10) for an aqueous film about 500 Å thick.

b. Biological Systems

The biological cell provides a different example of a system in which a thin film plays a cruical role.[3] The cell membrane is a highly viscous lamella bounded by two (approximately) spherically concentric liquid phases (i.e. the intra- and extra-cellular fluids). In certain cell mobility processes and in phagocytosis and microvilli formation, the membrane deforms considerably from its approximately spherical configuration. Reasons for the onset of these membrane deformation processes have not been fully elucidated, and it is hoped that a theoretical study of the stability of thin liquid films may provide insight into the origins of such processes.

An inspection of cells with microvilli suggests that microvilli can be considered as the filopodial protusions of the cell membrane.[35] We suggest that intra- or extra-cellular events occurring in living cells cause small fluctuations in the membrane configuration, and under some conditions these fluctuations become unstable in the antisymmetric (or buckling or stretching) mode to form villi.[3] The diameter of microvilli can be estimated from the wavelength of the fastest growing perturbation. Substituting in Eq. (13), $h_o \approx 100$ Å, $\mu_{bulk} \approx 10^{-2}$ P, and $\mu_{film} \approx 10^4$ P, one obtains the value dominant wavelength to be of the order 0.1μm, which is the experimentally measured value of microvilli diameter.[35] Furthermore, Eq. (13) suggests that λ_d is proportional to $\mu_{film}^{1/3}$, i.e. a membrane with a lower viscosity will have a lower value of microvilli diameter, and, hence, a greater number density of microvilli. Indeed, experiments have suggested that a cancer cell membrane is more "fluid" (i.e. less viscous) than a normal cell membrane.[36] This observation in light of the present theoretical framework explains the greater density of microvilli in cancer cells as compared to in normal cells.[37]

The thin film model of a cell membrane can be used to explain the fusion of cells and vesicles, and engulfment of viruses and macromolecules by cells (phagocytosis). In these processes, the cell membrane becomes unstable in the symmetric (or squeezing) mode, and ruptures ultimately so that two cells in contact can fuse. In phagocytosis, the membrane may engulf a particle by bending (stretching mode) as the particle approaches the membrane. Furthermore, in the symmetric mode instability of the membrane thins locally at several spots (Fig. 1). This reduced thickness of membrane may cause the membrane to be more permeable during the onset and progession of instability.

While the present analysis is simple, it describes the available data qualitatively. It can be improved considerably by the inclusion of non-uniform charge density, a more precise analysis of the double-layer interactions, a viscoelastic model of the membrane, a spherical configuration of the cell and chemical reactions.[38,39,40] Inclusion of some of these factors in the stability analysis of thin films is the subject of our current investigations.[41]

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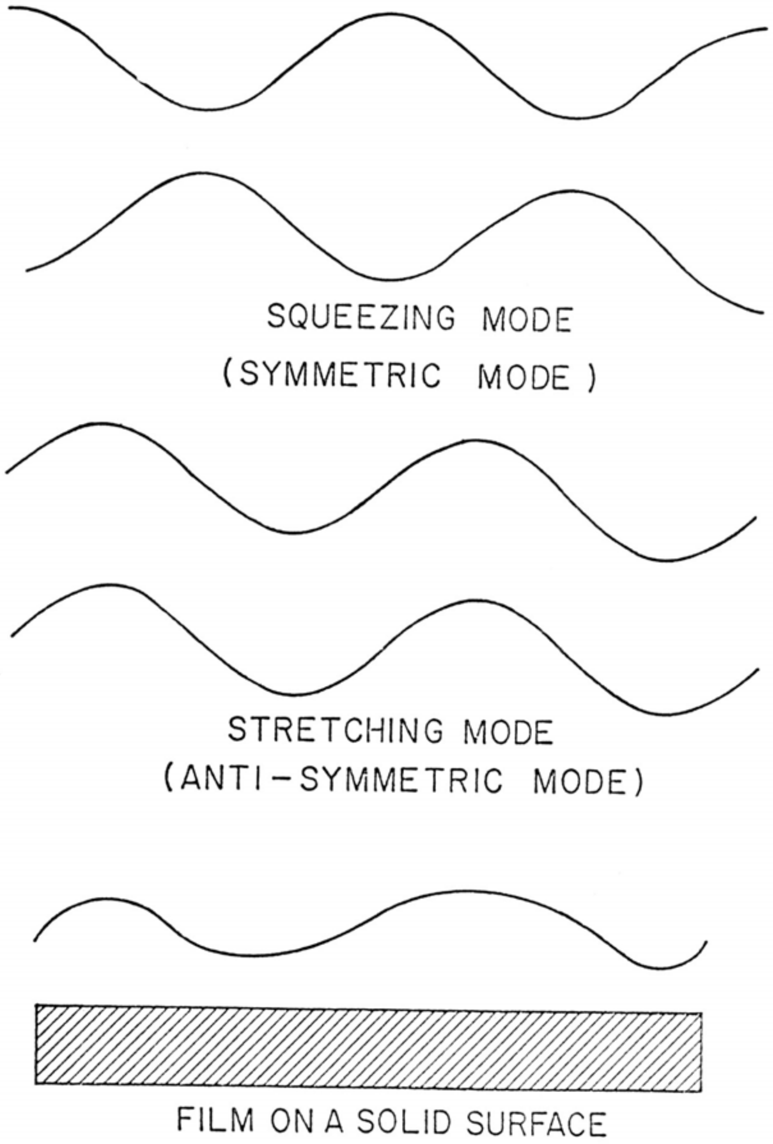

Figure 1. Modes of Instability of a Thin Liquid Film.

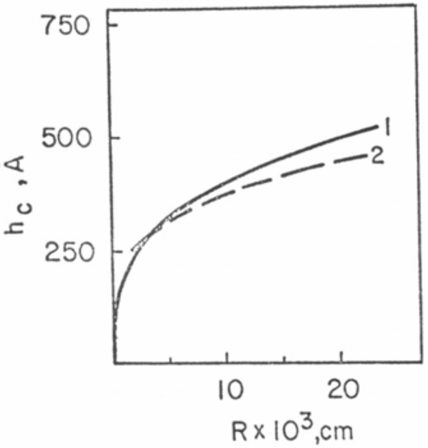

Figure 2. Experimental results (curve 2) and theoretical predictions (curve 1) for the critical thickness of aniline films with tangentially immobile surfaces.

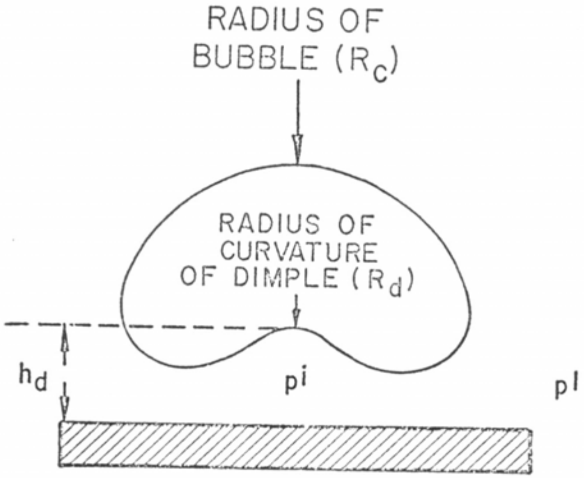

Figure 3(a). Schematic of a "dimple" formed during the approach of a bubble to a solid substrate.

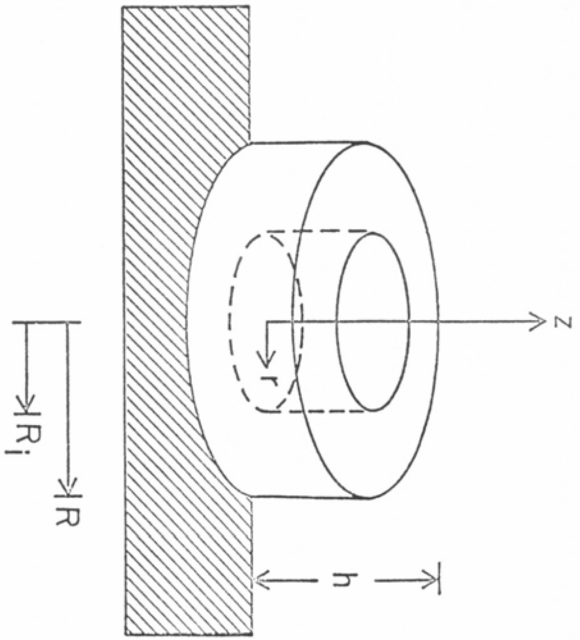

Figure 3(b). Schematic of the ring shaped film and the coordinate system.

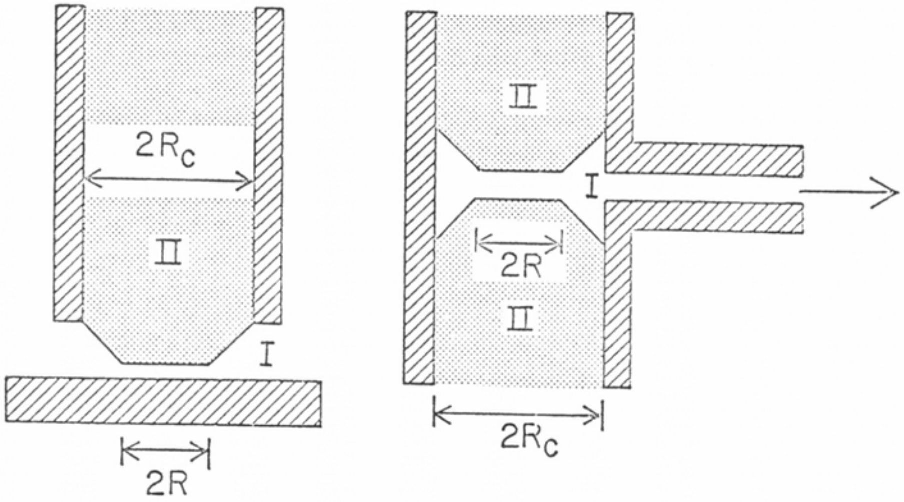

Figure 4. Schematic of experimental set-ups to study the stability of thin liquid films.