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Hydrodynamics of thin liquid films

Effect of surface viscosity on thinning and rupture of foam films

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With 4 figures

Nomenclature

A_n	maximum amplitude of the nth wave
a	*Szyskowiski*'s constant
a_n	*Fourrier-Bessel*'s coefficients
c	local concentration
c_0	equilibrium concentration
D	bulk diffusion coefficient
D_s	surface diffusion coefficient
h	film thickness
h_{cr}	critical thickness of rupture
h_0	transition thickness
J_0, J_1, J_2	*Bessel*'s functions of first kind; zero, first and second order
k_m	wave number of the critical wave
k_n	$= \lambda_n/R$ – wave number
l_m	critical wave length
l_n	wave length
P	pressure
P_σ	capillary pressure of the meniscus
ΔP	$= P_\sigma - \Pi$
P	equilibrium film pressure
q_n	$\sigma k_n^2 - 2d\Pi/dh$
R	film radius
r	coordinate
T	temperature
t	time
V	$= -dh/dt$ – velocity of film thinning
V_0	*Reynold*'s velocity of thinning
v_r, v_z	velocity components
v_s	tangential surface velocity
v_ζ	$= \partial\zeta/\partial t$ – velocity of local thinning
z	coordinate

$$\alpha = -\frac{3D\mu}{\Gamma_0(\partial\sigma_0/\partial c_0)}\left(1 + \frac{2D_s(\partial\Gamma_0/\partial c_0)}{Dh}\right)$$

Γ	local surface concentration
Γ_0	equilibrium surface concentration
ζ_n	vertical displacement of the surface
λ_n	nth root of the equation $J_0(\lambda_n) = 0$
μ	bulk viscosity
μ_s	surface shear viscosity
Π	disjoining pressure
σ	local surface tension
σ_0	equilibrium surface tension
ω	angular velocity

Already *Plateau* (1) drew attention to the fact, that some surfactants strongly retard liquid drainage from foam films and showed, that in a number of cases this retardation of the draining rate is accompanied by an increase of the foam life-time. *Boussinesq* (2) made a quantitative theory of the effect of surfactant on the hydrodynamic behaviour of dispersion systems, assuming that the interface behaves as a bidimensional fluid with two viscosities: dilational viscosity and shear viscosity.

Later on *Levich* (3) has shown that dilational viscosity originates in *Marangoni-Gibbs'* effect: the moving liquid carries surfactant away, thus disturbing its equilibrium distribution. As a result surface tension gradient and surface-volume exchange of surfactant rise. These effects can be calculated, hence the use of the concept "surface dilational viscosity" becomes superfluous[1]. In his theory *Levich* neglects surface shear viscosity assuming that because of the small thickness of the monolayer, much more energy is dissipated in the volume than in the surface. On this base *Levich* (3) made a theory of the effect of surfactant on the capillary waves. The theory has been confirmed for a number of surfactants (4–6). Concurrently, numerous experimental investigations [see e.g. (7–10)] have shown that in many a case surface shear viscosity can play a substantial role.

Recently, several studies of the influence of the surfactant on the hydrodynamic behavior of thin liquid films have been published (11–16) but none of them takes into account surface shear

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[1] A very clear exposition of this concept is given by *Lucassen-Reynders* and *Lucassen* (4).

viscosity[2]). However, some facts make us think that it can occasionally affect the foam film behaviour. In the first place, we must point out here the correlation between surface viscosity and foam life-time established in many cases. An effect of the same kind is also the so far unexplained dependence of the critical thickness of rupture of the foam films on the surfactant concentration (12).

The theoretical analysis of this effect (12) based on *Levich's* ideas showed that, at least as a first approximation, the critical thickness should not depend on the surfactant concentration. Over the whole concentration interval it should have the same value as for a film with tangentially immobile surface.

In (12) it has been assumed that the discrepancy between theory and experiment can be due to a positive component of the disjoining pressure, not taken into account by the theory. Recently, *Manev* and *Scheludko* (17) have shown, however, that the rise of the critical thickness begins from surfactant concentrations corresponding to the maximum of damping of the surface waves[3]). This result made us think that the basic reason for the increase of the critical thickness of rupture must be sought in the properties of the adsorption monolayer. We show in the present paper that this effect can be due to the surface viscosity.

Most of the initial equations and the methods of their solution used here are the same as in (12), where some questions related to the effect of surfactant on thinning and rupture of foam films are also discussed. Further in the expose we shall therefore consider in detail only the problems in which substantial differences with the previously published results appear.

The basic difference between the theory proposed here and the previously published theories of the kynetics of thinning and rupture of thin films (11–13) consists in the change of the condition for continuity of the tangential component of the stress tensor (see eq. [3c]). We shall calculate the distribution of surfactant and its effect on liquid motion according to *Levich*.

Since in this manner the surface dilational viscosity is automatically taken into account, we shall only use explicitly the surface shear viscosity which (for the sake of brevity) is further called surface viscosity.

The results obtained show that the effect of surface viscosity on the liquid flow strongly depends on the area of the film element on which the liquid motion occurs. Thus the influence of the surface viscosity on the rate of thinning of the film as a whole is substantially weaker than its influence on the velocity of growth of the local concavity caused by the fluctuational capillary waves (see section 3). As a result, for a certain interval of values, the surface viscosity can be simultaneously assumed equal to zero (when calculating the rate of thinning) and infinitely great (when considering the wave motion). This means that with respect to the film thinning only *Marangoni-Gibbs'* effect will be important while with respect to the wave motion the film surface will behave as tangentially immobile elastic membrane. In this way a new formula for the critical thickness is obtained which agrees much better with the experiment than the formulae obtained previously (12) and allows, at least in principle, to explain the dependence of the critical thickness on the surfactant concentration.

1. Rate of film thinning

We shall consider a microscopic thin liquid film, encircled by a meniscus, formed in a capillary (fig. 1)[4]). Because of the natural symmetry of the object we shall use the cylindrical co-ordinate system shown in fig. 2, where R denotes film radius and h is film thickness. With small h/R the flow obeys the simplified *Navier-Stokes'* equations known from the lubrication theory:

$$\frac{\partial^2 v_r}{\partial z^2} = \frac{1}{\mu} \frac{\partial P}{\partial r} \qquad [1a]$$

$$\frac{\partial P}{\partial z} = 0 \qquad [1b]$$

$$\frac{\partial v_z}{\partial z} + \nabla_r v_r = 0; \quad \nabla_r = \frac{1}{r} \frac{\partial}{\partial r} r. \qquad [1c]$$

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[2]) In *Lee* and *Hodgson's* paper (15) surface shear viscosity is taken into account in the initial equations but further on it is assumed to be zero.

[3]) The latter concentration is approximately equal to the constant a in *Szyskowski's* equation [see for instance (18)] for the substances obeying this equation.

[4]) The results obtained are also valid, of course, for a film formed by pressing two bubbles against each other.

v_r and v_z being the corresponding velocity components. The distribution of surfactant in the film volume for small values of *Peclet*'s number is described by the second *Fick*'s law:

$$\frac{\partial^2 c}{\partial z^2} + \Delta_r c = 0; \qquad \Delta_r = \frac{1}{r}\frac{\partial}{\partial z} r \frac{\partial}{\partial r} \qquad [2]$$
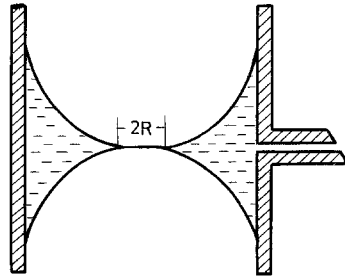

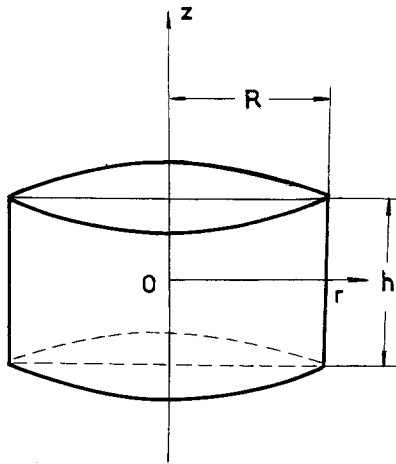Fig. 1. Model of foam film, formed in a cylindrical capillary

Fig. 2. Sketch of the film with the coordinate system

where c is the bulk surfactant concentration. For a plane-parallel film the boundary conditions which the solution of the system of differential equations must obey are:

$$v_z = -V/2 \qquad\qquad \text{at} \quad z = h/2 \quad [3a]$$

$$\nabla_r(v_r\Gamma) - D_s\Delta_r\Gamma = -D(\partial c/\partial z)$$
$$\text{at} \quad z = h/2 \quad [3b]$$

$$\mu(\partial v_r/\partial z) = (\partial\sigma/\partial c)(\partial c/\partial r)$$
$$\qquad + \mu_s(\partial\nabla_r v_r/\partial r) \quad \text{at} \quad z = h/2 \quad [3c]$$

$$\partial v_r/\partial z = 0 \qquad\qquad \text{at} \quad z = 0 \quad [3d]$$

$$\partial c/\partial z = 0 \qquad\qquad \text{at} \quad z = 0 \qquad [3e]$$

$$c = c_0 \qquad\qquad\qquad \text{at} \quad r = R \qquad [3f]$$

$$P = P_0 \qquad\qquad\qquad \text{at} \quad r = R \qquad [3g]$$

Here $V = -dh/dt$ (t denotes time) is the velocity of film thinning, D and D_s are the coefficients of bulk and surface diffusion respectively, $\Gamma = \Gamma(r)$ is the surface concentration of surfactant (*Gibbs'* excess), c_0 is the equilibrium bulk concentration of surfactant, and P_0 is the pressure in an equilibrium film of the same thickness. The film symmetry with respect to the plane $z = 0$ (see the conditions [3d] and [3e]) allows us to write the conditions [3a]–[3c] only for the upper surface $z = h/2$. Eq. [3b] expresses the condition for surfactant conservation and eq. [3c] differs from the corresponding eq. [28a] in (12) by the presence of a second term on the right-hand side which takes into account surface viscosity [see (19)]. When writing the first term on the right-hand side of [3c] we have assumed that adsorption equilibrium exists between the surface and the liquid sublayer – i.e. that $\sigma = \sigma [c(r, z = h/2)]$. Eqs. [3f] and [3g] follow from the assumption that the volume of the film is much smaller than that of the meniscus, so that the liquid drained out from the film does practically not disturb the equilibrium in the meniscus. All functions representing the solution of eqs. [1] and [2] must obviously be finite at $r = 0$. The surface concentration Γ can be represented as a sum of its equilibrium value $\Gamma_0(c_0)$ and the perturbation Γ_1, due to the flow:

$$\Gamma = \Gamma_0 + \Gamma_1 \qquad\qquad [4]$$

In (11) it has been shown that in practice $\Gamma_1 \ll \Gamma_0$ which allows $\partial\sigma/\partial c$ and $\partial\Gamma/\partial c$ to be replaced by their equilibrium values $\partial\sigma_0/\partial c_0$ and $\partial\Gamma_0/\partial c_0$.

From [1] and the corresponding boundary conditions one easily obtains:

$$v_r = \frac{z^2}{2\mu}(\partial P/\partial r) + B(r) \qquad [5]$$

and

$$\partial P/\partial_r = \frac{12\mu}{h^3}(Vr - 2Bh) \qquad [6]$$

where $B(r)$ is an integration constant. Since $z \leqslant h/2 \ll R$, the solution of [2] can be written in the form (see also [3f]):

$$c - c_0 = \sum_{n=1}^{\infty} a_n \left[1 + \frac{(k_n z)^2}{2}\right] J_0(k_n r). \qquad [7]$$

Here J_0 is *Bessel*'s function of first kind, zero order, a_n are *Fourier-Bessel*'s coefficients and $k_n = \lambda_n/R$, where λ_n is the nth root of the equation $J_0(\lambda_n) = 0$. When [7] is not differentiated with respect to z the term $k_n^2 z^2/2$ can be neglected. From [3b] and [7] we obtain:

$$\nabla_r v_s = \frac{\alpha h(\partial\sigma_0/\partial c_0)}{6\mu} \sum_{n=1}^{\infty} a_n k_n^2 J_0(k_n r) \qquad [8]$$

where $v_s = v_r(z = h/2)$ and

$$\alpha = -\frac{3D\mu}{\Gamma_0(\partial\sigma_0/\partial c_0)}\left[1 + \frac{2D_s(\partial\Gamma_0/\partial c_0)}{Dh}\right]. \qquad [9]$$

Eq. [5], [6], and [8] after integration on r allow us to determine the constant B:

$$B = \frac{\alpha(\partial\sigma_0/\partial c_0) h}{12\mu} \sum_{n=1}^{\infty} a_n J_0'(k_n r) \qquad [10]$$

where $J_0' = dJ_0/dr$. From [3c], [5]–[8], and [10] after integration from r to R we obtain:

$$V(R^2 - r^2) = \frac{2h^2}{3\mu}\frac{\partial\sigma_0}{\partial c_0}$$
$$\times \sum_{n=1}^{\infty}\left(1 + \alpha + \frac{\mu_s k_n^2 \alpha h}{6\mu}\right)$$
$$\times a_n J_0(k_n r). \qquad [11]$$

Expanding the right-hand side of [11] in *Fourier-Bessel*'s series we obtain expressions for the coefficients a_n:

$$a_n = \frac{VR^2 J_2(\lambda_n)}{\lambda_n^2 J_1^2(\lambda_n)}$$
$$\times \left[\frac{h^2}{6\mu}\frac{\partial\sigma_0}{\partial c_0}\left(1 + \alpha + \frac{\mu_s k_n^2 \alpha h}{6\mu}\right)\right]^{-1}. \qquad [12]$$

The assumption that the film is plane-parallel does not allow us to use the condition for continuity of the normal component P_{zz} of the stress tensor on the film surface. So we shall replace this condition with the approximate integral condition for equality of the force F_f with which the film liquid acts upon the surface, and the external force F_0 causing the drainage. Since at $h/R \ll 1$; $P_{zz} \approx -P$, from [3f], [6], and [10] we obtain:

$$F_f = 2\pi \int_0^R Pr\,dr = \frac{4\pi R^2}{h}\cdot\frac{\partial\sigma_0}{\partial c_0}$$
$$\times \sum_{n=1}^{\infty}\left(1 + \frac{\mu_s k_n^2 \alpha h}{6\mu}\right)\frac{a_n J_1(\lambda_n)}{\lambda_n}$$
$$+ \pi R^2 P_0. \qquad [13]$$

The force F_0 is calculated according to (20). If the gas pressure above the meniscus is P_g, the external force will be $F_0 = \pi R^2 P_g$. Taking into account that $P_\sigma = P_g - P_m$ and $P_0 = P_m + \Pi$ [see (20)], where P_m is the pressure in the meniscus and P_σ and Π are respectively capillary and disjoining pressure, from the condition $F_0 = F_g$ we obtain:

$$V = \frac{h^3 \Delta P}{24\mu R^2}$$
$$\times \left[\sum_{n=1}^{\infty}\frac{(6\mu + \mu_s k_n^2 \alpha h) J_2(\lambda_n)}{(6\mu + 6\mu\alpha + \mu_s k_n^2 \alpha h)\lambda_n^3 J_1(\lambda_n)}\right]^{-1} \qquad [14]$$

where

$$\Delta P = P_\sigma - \Pi \qquad [15]$$

is the pressure difference causing the drainage. The velocity V can be compared to *Reynolds*' velocity V_0 [see (21)] with which a film between two solid planes, under the same pressure difference, would thin:

$$V_0 = \frac{2h^3 \Delta P}{3\mu R^2}. \qquad [16]$$

Taking into account [12], from [14] and [16] we obtain:

$$\frac{V_0}{V} = 16\sum_{n=1}^{\infty}\frac{(6\mu + \mu_s k_n^2 \alpha h) J_2(\lambda_n)}{(6\mu + 6\mu\alpha + \mu_s k_n^2 \alpha h)\lambda_n^3 J_1(\lambda_n)}. \qquad [17]$$

Since with increasing n the roots λ_n also rapidly increase, eq. [17] can be writen in a simpler form. Thus for low surface viscosity we obtain:

$$\frac{V_0}{V} = \frac{1}{1 + \alpha}\left[1 + \frac{4\mu_s h\alpha^2}{3\mu R^2(1 + \alpha)^2}\right] \qquad [18]$$

and for high surface viscosity:

$$\frac{V_0}{V} = 1 - \frac{6\mu R^2}{5\mu_s h}. \qquad [19]$$

2. Critical thickness of film rupture

According to *Scheludko* (14) the rupture of thin films is due to thermal fluctuations which lead to corrugation of the film surface. The shape of the surface at any moment can be presented as a superposition of an infinite number of fluctuation waves with various lengths and amplitudes. Let us suppose for simplicity that

there is only one wave with wave-number k_n. The vertical displacement of the film surface at a given point from its position in the absence of waves (i.e. in a plane-parallel film) we shall denote by ζ_n (fig. 3).
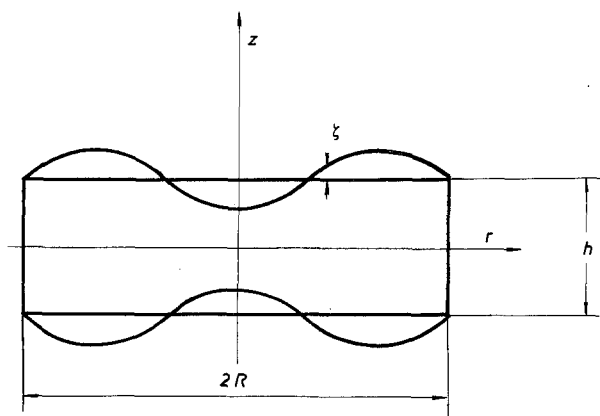

Fig. 3. Fluctuation waves on the film surface

We shall only consider the case of symmetrically situated waves (see fig. 3) which are responsible for the rupture (16). Thus the local film thickness will be $h + 2\zeta_n$. For simplicity we shall assume that the wave has a cylindrical symmetry.

The corrugation of the surface give rise to two forces: the first one caused by the local capillary pressure tends to smooth the film surface while the second one due to the increase of the negative disjoining pressure (with respect to its value in the plane-parallel film), tends to increase ζ_n. If h is large the first effect prevails, if it is small the second one, so that for a given wave a transition thickness h_0 exists at which the character of wave motion changes. While at $h > h_0$ the surface performs oscillations around the equilibrium position $\zeta_n = 0$, at $h < h_0$ the oscillations cease and liquid is transfered continuously into the thicker parts of the film. Thus ζ_n continuously grows until the film breaks or a black spot is formed (14).

The mean thickness h at which the rupture occurs (critical thickness h_{cr}) depends not only on the wave motion but also on the translational velocity V, with which the two surfaces approach each other. The latter effect has been taken into acount by *Vrij* (16), who has used an ingenious procedure for combining the two motions. However, *Vrij*'s theory is only valid in the case

where there is no tangential motion on the film surface ($v_s = 0$) and, besides, leads to a correct result for h_{cr} because of a certain compensation of errors (22). Thus in (12) a more consistent and complete hydrodynamic theory of the phenomenon has been worked out which we shall use now.

We shall assume that:

$$\zeta_n \ll h \ll k_n^{-1}. \tag{20}$$

The first inequality [20] allows us to accept that all the quantities characterizing the flow in the film can be presented as a sum of two effects: the effect related to the drainage of the plane-parallel film with a thickness h and the effect related to the wave motion in this film. Since at small *Reynolds'* number *Navier-Stokes'* equations are linear, in this case they split into two systems of equations. The first one describes the thinning of the plane-parallel film and at $h/R \ll 1$ coincides with eq. [11]. Since the boundary conditions are similarily transformed the first effect is described by the theory developed in section 1 of the present paper [see also (11)]. From the second inequality [20] it follows that for the wave motion, equations analogous to [1] are also valid but in this case a term $\varrho(\partial v_r / \partial t)$ appears on the left-hand side of [1a]. However, setting

$$\zeta_n = \zeta_{0n}(r) e^{\omega_n t} \tag{21}$$

(ω_n is angular velocity) it is readily shown [see (12)] that at (v is kinematic viscosity)

$$\omega_n h^2 / v \ll 1 \tag{22}$$

this term and the similar terms appearing in eqs. [2] and [3] can be dropped, so that the wave motion is also described by eqs. [1] and [2] and the boundary conditions [3]. The only difference is that the condition [3a] must be replaced by

$$v_z = v_\zeta = \partial \zeta / \partial t \quad \text{at} \quad z = h/2. \tag{23}$$

Since the solution of [2] in this case has the form

$$c - c_0 = \left[1 + \frac{(k_n z)^2}{2} \right] \Psi_n(R) \tag{24}$$

where $\Psi_n(r)$ satisfies the equation

$$\Delta_r \Psi_n = -k_n^2 \Psi_n; \quad \Psi_n(R) = 0 \tag{25}$$

ζ_n must also satisfy a similar equation:

$$\Delta_r \zeta_n = -k_n^2 \zeta_n; \quad \zeta_n(R) = 0. \tag{26}$$

On the other hand for the pressure in the film

at $\zeta_n \ll h$ and $\partial P / \partial z = 0$ we can write (12):

$$P = P_g - \sigma \Delta_r \zeta_n + \Pi(h) - 2\Pi'(h)\zeta_n \qquad [27]$$

where σ is surface tension and $\Pi' = d\Pi/dh$. From [1a], [3d], [26], and [27] we obtain:

$$v_r = \frac{q_n z^2}{2\mu} \frac{\partial \zeta_n}{\partial r} + C_n(r) \qquad [28]$$

where

$$q_n = \sigma_0 k_n^2 - 2\Pi' \qquad [29]$$

and $C_n(r)$ is integration constant. Eqs. [3b] and [24] yield:

$$\nabla_r v_s = \frac{h\alpha}{6\mu} \frac{\partial \sigma_0}{\partial c_0} k_n^2 \Psi_n. \qquad [30]$$

The last equation together with [3c] and [24] after integration on r gives

$$q_n h \zeta_n = 2 \frac{\partial \sigma_0}{\partial c_0} \left(1 + \frac{\mu_s \alpha k_n^2 h}{6\mu}\right) \psi_n. \qquad [31]$$

Eqs. [28], [30], and [31] allows us to eliminate $C_n(r)$:

$$\nabla_r C_n = \frac{k_n^2 \zeta_n q_n h^2}{8\mu} \left(1 + \frac{4\alpha\mu}{6\mu + \mu_s \alpha k_n^2 h}\right). \qquad [32]$$

Eqs. [1c], [23], and [28] yield:

$$v_\zeta = -\frac{q_n h^3}{24\mu}\left[k_n^2 + \frac{6\alpha\mu}{6\mu + \mu_s \alpha h}\right]\zeta_n. \qquad [33]$$

Since at $h = h_0 v_\zeta$ must be zero, from the last equation we can obtain an expression determining the value of the transition thickness:

$$q_n(h_0) = \sigma_0 k_n^2 - 2\Pi_0 = 0 \qquad [34]$$

where $\Pi_0 = \Pi(h_0)$. Since from [21] we have

$$v_\zeta = \partial \zeta_n/\partial t = \omega_n \zeta_n \qquad [35]$$

from [33] and [35] we can calculate the angular velocity:

$$\omega_n = -\frac{q_n h^3}{24\mu}\left[k_n^2 + \frac{6\alpha\mu}{6\mu + \mu_s \alpha h}\right]. \qquad [36]$$

At $\omega_n h^2/\nu \ll 1$, ζ_n depends on t only through h. Therefore we can write in [33] $v_\zeta = (\partial\zeta_n/\partial h)dh/dt$. Substituting here $dh/dt = -V$ from [18] and integrating the resulting equation on h we shall obtain the sought dependence of ζ_n on h. In order to simplify the formulae we shall put, however, $\mu_s = 0$ in the expression for V. This is possible because the effect of the surface viscos-

ity on the film drainage is much weaker than on the wave motion (see section 3). Thus we obtain

$$\zeta_n = \zeta_{0n} \exp\left[-\frac{k_n^2 R^2}{16} \times \int_h^{h_0} \frac{(\mu_s k_n^2 h\alpha + 6\mu + 6\mu\alpha)}{(1+\alpha)(\mu_s k_n^2 h\alpha + 6\mu)} \times \frac{q_n}{\Delta P} dh\right] \qquad [37]$$

where $\zeta_{0n} = \zeta_n(h_0)$. Since the exponent in [37] is independent on r, from [26] and [37] it follows

$$\zeta_{0n} = A_n J_0(k_n r). \qquad [38]$$

It has been shown in [12] and [14] that the constant A_n can be determined from *Einstein's* theorem (23) (see also [38]):

$$kT = \pi \sigma_0 k_n^2 \int_0^R \zeta_{0n}^2 r\, dr$$
$$= \pi \sigma_0 k_n^2 A_n^2 R^2 J_1^2(\lambda_n). \qquad [39]$$

On the basis of eq. [37] an expression for h_{cr} can be derived. Since at this, however, very complicated and inconvenient formulae are obtained, we prefer to consider here only one important case. In section 3 it will be shown that in some cases $\dfrac{\mu_s h k_n^2}{6\mu} \gg 1$. This means that in such cases $\mu_s = \infty$ can be set in [37] [α is of the order of a unit-see (11)]. Thus from [37] we obtain the approximate expression:

$$\zeta_n = \zeta_{0n} \exp\left[-\frac{k_n^2 R^2}{16} \int_h^{h_0} \frac{q_n}{(1+\alpha)\Delta P} dh\right]. \qquad [40]$$

In cases where the surface viscosity is great, instead of [18], eq. [19] must be used for V and in [33] again $\mu_s = \infty$ must be assumed. Thus in the same way we have derived [40] in this case we obtain

$$\zeta_n = \zeta_{0n} \exp\left[-\frac{k_n^2 R^2}{16} \int_h^{h_0} \left(1 - \frac{6\mu R^2}{5\mu_s h}\right)\frac{q_n}{\Delta P} dh\right]. \qquad [41]$$

If the disjoining pressure is negative the film will break when its two surfaces touch. This will take place at a certain thickness h_n at which

$$h_n = 2|\zeta_n|. \qquad [42]$$

If we consider a set of waves with various k_n, the condition [42] will be realized at different thicknesses for the different waves and to a given wave with a wave-number k_m a maximum thickness h_m will correspond. This wave will play, of course, a determining role for the film rupture and we shall call it critical wave. The value of k_m can be determined from the equation

$$\partial h_n / \partial k_n = 2(\partial |\zeta_n| / \partial k_n) = 0. \qquad [43]$$

Together with [40] eq. [43] yields:

$$k_m^2 = \frac{1}{\sigma_0} \int_{h_{0m}}^{h_{cr}} \frac{\Pi'}{(1+\alpha) \Delta P} dh \left[\int_{h_{cr}}^{h_{cr}} \frac{dh}{(1+\alpha) \Delta P} \right]^{-1} \qquad [44]$$

(when deriving [44] the weak dependence of ζ_{0n} on k_n has been neglected).

So far we have presumed that on the film surface there is only one wave with a wave-number k_n while in fact the shape of the surface is determined by superposition of an infinite number of waves:

$$\zeta = \sum_{n=1}^{\infty} \zeta_n \approx R \int_0^{\infty} \zeta_n dk_n. \qquad [45]$$

Since the function $\zeta_n(k_n)$ has a very sharp maximum at $k_n = k_m$ (16) the calculation of the integral in [45] can be carried out by the method of steepest descents. The condition [42] for the film rupture in this case will have the form

$$h_{cr} = 2|\zeta| \qquad [46]$$

where h_{cr} is the looked-for critical thickness i.e. the mean thickness of the film at the moment of rupture. In order to minimize the error which we make with the assumption for cylindrical symmetry of the wave we shall substitute $\sqrt{\overline{\zeta^2}}$ for ζ in [46], $\overline{\zeta^2}$ being determined by

$$\overline{\zeta^2} = \frac{2}{R^2} \int_0^R \zeta^2 r \, dr. \qquad [47]$$

With the aid of the described procedure we finally obtain

$$h_{cr}^2 = N \exp \left[\frac{R^2 \Pi'(h_0)}{4\sigma_0} \int_{h_{cr}}^{h_{0m}} \frac{\Pi'}{(1+\alpha) \Delta P} dh \right] \qquad [48]$$

where h_{0m} is the value of h_0 for the critical wave and

$$N = \frac{2kT}{R^2 \Pi'_{0m}} \left[\int_{h_{cr}}^{h_{0m}} \frac{\Pi' dh}{(1+\alpha) \Delta P} \right]^{-1}. \qquad [49]$$

Eq. [48] must be solved together with eqs. [34] and [44] (at $k_n = k_m$ and $h_n = h_{cr}$) which give the dependence of h_{0m} on h_{cr}[5]).

3. Discussion

The theory developed above suffers from an essential and, unfortunately, hard to avoid defect. This is the assumption that the surface viscosity μ_s does not depend on the surfactant concentration and on the flow velocity. Because of the extreme difficulties connected with the solution of the hydrodynamic equations in the case of variable surface viscosity, in all theoretical studies in which this effect is taken into account μ_s is assumed constant [see e.g. (2) and (19)]. Still, in order to be able to take into account, although roughly, the change of the surface viscosity when the surfactant concentration changes, we shall admit that at high concentrations the surface viscosity has a finite constant value and at a certain concentration c_0^* it sharply drops to zero. Since the surface viscosity is due to molecular interactions in the adsorption monolayer, it is logical to presume that the concentration c_0^* is close to the bulk surfactant concentration corresponding to $\Gamma_0 / \Gamma_\infty = 1/2$, Γ_∞ being the maximum surface concentration. Therefore for surfactant obeying *Szyskowski*'s equation c_0^* is close to the constant a.

The formulae derived in the present paper for the velocity of film thinning (see [18] and [19]) give as limiting cases the expressions obtained before: from [18] at $\mu_s = 0$, $V/V_0 = 1 + \alpha$ is obtained [see (11)], and at $\mu_s = \infty$ [19] transforms into *Reynolds*' formula.

The effect of surface viscosity on the hydrodynamic behaviour of the thin films strongly depends on the length scale of the flow (in [18] and [19] the term with μ_s includes R^2 and in [37] $-k_n \approx (2\pi/l_n)^2$, where l_n is the wavelength). On the bases of [44] it can be shown that for aniline films $l_m \approx 2\pi/k_m \approx 0.1 R$. So it is

[5]) When calculating the dependence h_{cr} vs. R the values of h_{0m} obtained from the combined numerical solution of [34] and [44] for a chosen value of h_{cr} are used. Since the result is insensitive to N, an arbitrary (but reasonable) value for R can be put in [49]. Thus, from [48] the film radius R corresponding to the chosen criterical thickness h_{cr} is obtained. This value of R is then substituted in [49] and with the new value of N again R is calculated, etc. As a rule, one iteration is sufficient.

possible that μ_s affects the behaviour of the fluctuation waves without changing significantly the rate of thinning. Thus for the ratio of the respective terms in [18] and [37] at $l_m = 0,1 R$ we obtain

$$\frac{\mu_s h}{\mu R^2} : \frac{\mu_s k_m^2 h}{6\mu} \approx \frac{l_m^2}{6R^2} \approx 2 \cdot 10^{-3}. \qquad [50]$$

For instance, if $h = 5 \cdot 10^{-6}$ cm and $R = 5 \cdot 10^{-3}$ cm [these are typical values in critical thickness measurements (12)] we obtain

$$\mu_s k_m^2 h/6\mu \approx 10^4 \mu_s$$

while

$$\mu_s h/\mu R^2 \approx 20\mu_s.$$

That is why, if $\mu_s = 10^{-3}$ s.p., it is possible to neglect its effect on the rate of thinning, while with respect to the fluctuation waves μ_s can be assumed to be infinitely great and the surface considered as an infinitely elastic membrane. This, actually, allows to put $\mu_s = \infty$ when deriving eq. [40]. The fact that surface viscosity can affect the velocity v_ζ of the wave motion in a different way from the way it affects the velocity V of film thinning is the basic difference between the proposed here theory of the critical thickness and the theory published before.

Since the velocity V of thinning of films stabilized with soluble surfactant is always higher than *Reynolds*' velocity V_0 the theoretical critical thickness calculated according to eq. [48] is in better agreement with the experiment. In fig. 4 the dependence of h_{cr} on the radius R of aniline films is shown. As a surfactant lauryl alcohol is used. Curves 1 and 4 [borrowed from (12)] give respectively the theoretical dependence, calculated on the basis of eqs. [26] from (12) and the experimental values measured in (12). Curves 2 and 3 are calculated on the basis of eq. [48] in the present paper at $D_s = 0$ and $D_s/D = 10$ respectively. The comparison of curves 2 and 3 shows that surface diffusion can substantially affect the film rupture.

The experimental investigations show that the critical thickness of rupture increases when the surfactant concentration becomes small (12). This fact cannot be explained by the theory in (12) only the influence of *Marangoni-Gibbs* effect at $\mu_s = 0$ has been studied, the theoretical result can be explained with the compensation of two reversely acting effects. The exchange of
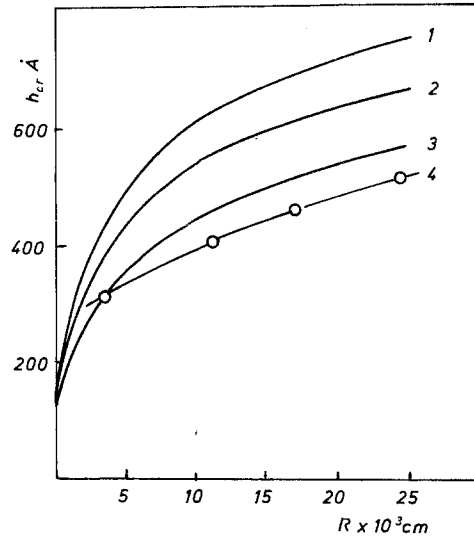

Fig. 4. Dependence of the critical thickness h_{cr} on the radius R for an aniline film stabilized with lauryl alcohol $(T = 292^\circ; \; D = 10^{-5} \text{ cm}^2/\text{sec}; \; c_0 = a = 2.56 \cdot 10^{-5} \text{ mol}/\text{cm}^3; \; \Gamma_\infty = 6.5 \cdot 10^{-11} \text{ mol/cm}^2; \; \mu = 4.4 \cdot 10^{-2} \text{ g/cm} \cdot \text{sec})$

surfactant between the surface and the film volume increases both the velocity of film thinning V and the velocity of wave motion v_ζ. The first effect leads to reduction of the critical thickness and the second to its increase but within the limits of the employed linear theory of the waves the two effects cancel each other. As we have already seen, at certain values of the surface viscosity $(\mu_s \approx 10^{-3}$ s.p.) the second effect ceases to depend on *Marangoni-Gibbs*' effect. This excludes the possibility of compensation of the two effects, mentioned above and leads to reduction of the critical thickness. Since in this concentration region $(c_0 > c_0^* \approx a)\alpha$ slightly depends on c_0 [see (11)], h_{cr} will be practically independent on the surfactant concentration.

When the surfactant concentration drops under c_0^* the surface viscosity must vanish. Putting $\mu_s = 0$ in [37] we than obtain a formula for ζ_n which coincides with the analogous expression [20] for ζ_n in (12). Thus, in this case h_{cr} can be calculated from formula [26] of (12). (The values of h_{cr} calculated in this way for aniline films are given by curve 1 in fig. 4.) Therefore, for an aniline film with a given radius advanced in (12) according to which the critical thickness should be constant at any surfactant concentration and have the same value as for a

film with tangentially immobile surface[6]). Since R at $c_0 \approx c_0^* \approx a$, h_{cr} steeply increases its value from this corresponding to curve 3 in fig. 4 (or a similar curve, depending on D_s/D ratio) to a value corresponding to curve 1 in the same figure. This is a possible explanation of the fact, established by *Manev* and *Scheludko* (17), that the concentration of surfactant at which the increase of the critical thickness starts coincides with the concentration corresponding to the maximum of damping of the capillary waves. The hypothesis put forward here needs, of course, a serious experimental verification[7])[8]).

Summary

The influence of surface viscosity on the rate of thinning and on the critical thickness of rupture of foam films has been studied. It is shown that this effect depends strongly on the length-scale of the flow. Therefore it is possible to neglect it when calculating the rate of thinning, but to assume for the wave motion, caused by the thermic fluctuations, that the surface viscosity is infinitely great. The expression for the critical thickness, obtained in this way, agrees relatively well with the experimental results. A possible explanation of the dependence of critical thickness on surfactant concentration is suggested.

Zusammenfassung

Der Einfluß der Oberflächenviskosität auf die Verdünnungsgeschwindigkeit und die kritische Zerreißdicke von Schaumfilmen wird untersucht. Es zeigt sich, daß dieser Effekt stark von der charakteristischen Flußgröße abhängt. Folglich kann man bei der Berechnung der Verdünnungsgeschwindigkeit die Oberflächenviskosität unberücksichtigt lassen und sie bei der von den thermischen Fluktuationen verursachten wellenartigen Bewegung als unendlich groß annehmen. Die auf diese Art erhaltenen Gleichungen für die kritische Dicke stimmen verhältnismäßig gut mit den experimentellen Daten überein. Eine mögliche Erklärung der Abhängigkeit der kritischen Dicke von der Konzentration des Tensids wird vorgeschlagen.

[6]) In (12) the effect of surface diffusion has not been taken into account, however, it can easily be shown that with $\mu_s = 0$ this effect does not influence h_{cr} as well.

[7]) The present paper had already been prepared for printing when *Manev* et al. (24) completed another investigation of the effect of surfactant on the critical thicknesses. In it they put forward the hypothesis that the effect is due to the damping of non-fluctuational non-uniformities of the film thickness. This hypothesis does not contradict the basic ideas of our work which considers a plane-parallel film, corrugated by fluctuational waves. However, the possibility of a phenomenon to be explained, though qualitatively, in several ways, shows that it needs further clarification.

[8]) Recently two new theoretical investigations on the critical thicknesses of rupture of foam films have been completed (25, 26). In some aspects they are close to the ideas of the present paper.

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