THEORY OF THINNING OF FREE VISCOUS FLUID FILMS

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Thin viscous fluid films with free surfaces in the presence of surfactants are considered.

A closed system of nonlinear equations of variable thickness films is formulated taking account of capillary and van der Waals forces, the surface-tension gradients, and the effect of surface viscosity, volume and surface diffusion, and nonlinear adsorption isotherms. The fundamental dimensionless criteria governing the film flow modes are found. A general solution of the surfactant transfer equations is obtained in a quasistatic approximation and also in the opposite weak diffusion limit. A method is proposed for solving problems about thinning films which is based on a quasistatic analysis of the transition domain from the film to the meniscus.

A film-thinning mechanism is found for the case when its surfaces remain almost parallel planes (plane-parallel thinning). Up to now plane-parallel thinning has been observed in many experiments but has not been explained. Several solutions are obtained for the fundamental equations corresponding to plane-parallel thinning, and conditions are determined for which this is possible. A nonzero edge angle can form with the meniscus as the film becomes thinner. It is also shown that films can be destroyed because of the van der Walls force in the narrow domain of passage from the film to a meniscus.

1. Fundamental Equations

Let the viscous fluid film thickness h vary at distances l such that $l \gg h$, i.e., $dh/dx \ll 1$ (x is the coordinate along the layer). As in the hydrodynamic theory of lubrication [1], let us assume that the reduced Reynolds number $R^* = v'h^2/l\nu$ is small (v' is the velocity along the film, and ν is the kinematic viscosity). Moreover, the characteristic time of the process τ is sufficiently large ($\tau\nu \gg h^2$), so that the almost stationary velocity distribution along the layer section is built up in a time much less than τ.

The fluid velocity $\mathbf{v}'$ can be represented as the sum of two solutions, symmetric and antisymmetric relative to the coordinate across the film. Furthermore, only the symmetric solutions are examined. In contrast to the theory of lubrication, the velocity of surface motion $\mathbf{v} \neq$ const. should be taken into account in addition to the mean flow velocity relative to the fixed surface $\mathbf{u}$. The equation of mass conservation is

$$\operatorname{div}(h\mathbf{u} + h\mathbf{v}) = -\partial h / \partial t \tag{1.1}$$

Here and henceforth, equations including quantities which vary just along the plane of film symmetry are considered.

The tangential stresses within a free viscous fluid film can be produced under the influence of surfactants. In many cases of practical interest the tangential viscous stresses exceed the longitudinal viscous stresses by an order of magnitude. Estimates show that the longitudinal stresses cannot be taken into account only under the condition that the change in surface velocity Δv at a distance on the order of l, equal to the scale of the flow under consideration, is not too large ($|\Delta v| \ll ul/h$).

In this case integrating the Navier–Stokes equations across the film yields

$$12\,\mu\mathbf{u} = -h^2\nabla p + h^2\mathbf{F}, \quad 6\mu\mathbf{u} = -h\mathbf{P}_l \tag{1.2}$$

Here p is the pressure within the film, $\mathbf{F}$ is the volume force directed along the film, $\mathbf{P}_l$ is the tangential force on the surface. The quantity p is measured throughout from the pressure in the gas, which is considered constant.

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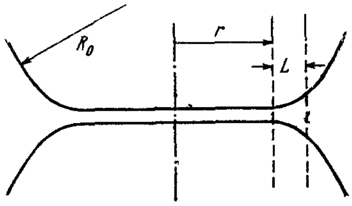

Fig. 1

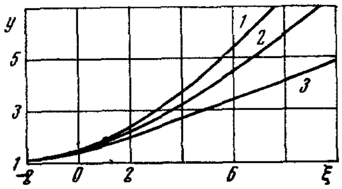

Fig. 2

Locally, the flow with velocity **u** corresponding to (1.2) is the flow in a plane tube subjected to a pressure gradient [2].

The quantity p in (1.2) is determined by the boundary condition for the normal stresses on the film surface, which is associated with a Laplace pressure jump and with the disjoining pressure Π [3],

$$-p = {}^1/_2\, \sigma\Delta h + \Pi, \quad \Pi = -A\,/\,(6\pi h^3) \tag{1.3}$$

Here only the component of the disjoining pressure associated with molecular interaction, which is the reason for the breakdown of liquid films of macroscopic thickness [4, 5], is taken into account, and A is the van der Waals—Hammacher constant [6].

Formulas (1.2) and (1.3) are verified by a direct computation of the pressure and mass forces acting in a thin film section in the absence of parallelism of the surfaces [7].

The condition for the tangential stress $\mathbf{P}_l$ on the surface is easily written by forming the surface of some two-dimensional stress tensor P_{ij}:

$$\mathbf{P}_l = \operatorname{div} \mathbf{P} \tag{1.4}$$

The results of numerous experiments [8-10] have proved that the tensor P_{ij} does not reduce to surface tension in the presence of surfactants but depends on the surface strain rate, i.e., anomalously high dissipation energy occurs in a narrow layer near the surface. The linear dependence analogous to the three-dimensional Navier—Stokes law [11] is

$$P_{ij} = \sigma\delta_{ij} + T_{ij}, \quad T_{ij} = \lambda_s \operatorname{div} \mathbf{v}\, \delta_{ij} + \eta_s (\nabla_i v_j + \nabla_j v_i) \tag{1.5}$$

The surface viscosity coefficients η_s and λ_s generally depend on the surfactant concentration Γ in the surface. The surface tension σ depends essentially on Γ.

The concentration Γ is related to the surfactant volume concentration c. Let the adsorption be described by the Langmuir isotherm [12]. Then

$$\sigma - \sigma_0 = -aRT \ln(1 + bc), \quad \Gamma = Hc\,/\,(1 + bc), \quad H = ab \tag{1.6}$$

Here T is the absolute temperature, R is the universal gas constant, and a and b are constants.

To close the system of equations, it is necessary to take account of surfactant transfer because of convection and diffusion. Under the condition $h^2 \ll D\tau$ (τ is the characteristic time, and D is the coefficient of surfactant diffusion in a volume) the concentration gradients across the film can be neglected, and the convective diffusion equation can be written as

$$\operatorname{div}[-hD\nabla c - 2D_s\nabla\Gamma + (\mathbf{u} + \mathbf{v})hc + 2\mathbf{v}\Gamma] = -\frac{\partial}{\partial t}(hc + 2\Gamma) \tag{1.7}$$

Here D_s is the coefficient of surfactant diffusion in a surface.

Let us note that the limit case $hc/\Gamma \to 0$ corresponds to an insoluble surfactant.

Equation (1.7) can be rewritten in the equivalent form

$$2\,\partial\Gamma\,/\,\partial t + h\,\partial c\,/\,\partial t + (\mathbf{u} + \mathbf{v})\, h\nabla c = \operatorname{div}(Dh\nabla c + 2D_s\nabla\Gamma - 2\mathbf{v}\Gamma) \tag{1.8}$$

Formulas (1.1)-(1.7) are a system of six nonlinear partial-differential equations and one algebraic equation in seven unknowns: the film thickness h, the components of the film surface velocity **v** and the mean velocities **u** of fluid motion relative to the surface, the surfactant concentrations in the surface Γ and in the volume c.

Because of the complexity of the system of equations, a general estimate of the role of the diverse effects for an arbitrary flow scale l should first be made.

It is shown in the solution of the problem of thinning a film subjected to capillary forces [13] in the case of a fixed surface that the film becomes thin in an edge domain of width $L \sim (h\sigma/\Delta p)^{1/2}$ as a pressure change Δp c originates from the edges of a section of significant length. If the film dimensions greatly exceed L, then the film certainly loses its plane-parallelism. In the general case of a moving surface, the

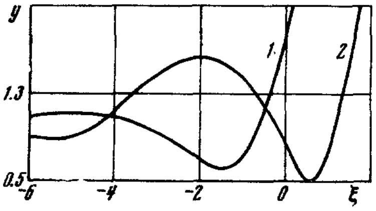

Fig. 3

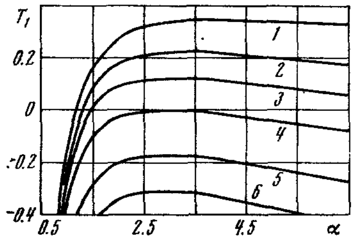

Fig. 4

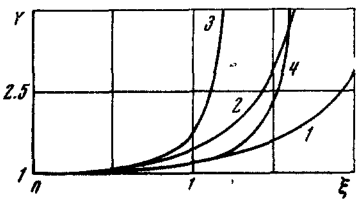

Fig. 5

parameter $S = \Delta p l^2/(h\sigma)$ determines the connection between the pressure drop Δp and the nonuniformity of the thickness for a film section of dimension l.

For $S \ll 1$ the thickness varies slightly in a distance of the order of l. For $S \gtrsim 1$ the change in thickness is $\Delta h \sim h$, and plane-parallelism does not occur.

In the absence of surface-tension gradients the film surface can be "inhibited" because of the surface viscosity μ_s. The relative role of the surface strain in the mass flux or the degree of surface "solidification" is estimated by the parameter

$$W = \mu_s h / (6 \mu l^2), \qquad \mu_s \sim \lambda_s, \eta_s$$

If $W \gg 1$, then the surface "solidifies" for a flow of scale l, i.e., the change in the surface velocity is negligible as compared with the mean fluid velocity relative to the surface $\Delta v \ll u$.

For $W \lesssim 1$ the strains of the film surface play an essential part. If $W \ll 1$, then the mass flux is produced mainly by surface strain and the change in velocity $\Delta v \gg u$. Hence, the contribution of the fluid velocity u with respect to the surface cannot be taken completely into account in the kinematics. The fluid in each section seems to be "glued" to the deformable film surface.

2. Problem of Thinning of a Film Adjoining a Meniscus

A thin circular film of radius r adjoins a meniscus of radius R_0 (Fig. 1). The meniscus is in equilibrium, and the pressure $(-p_\sigma)$ inside it is independent of the time. The surfactant concentration within the meniscus c_0 is known.

If x is the distance from the center of the film, then the boundary conditions for (1.1)-(1.7) as $x \to \infty$, are

$$u,\ v \to 0, \quad c \to c_0, \quad p \to -p_\sigma \tag{2.1}$$

As the thickness grows $h(x \to \infty)$, the passage to the meniscus is completed rapidly in a distance on the order of $(hR_0)^{1/2}$.

Initial conditions can be appended to (2.1). However, asymptotic laws for thinning of films, which are independent of the initial conditions, are of greatest interest. The problem of determining these laws is considered henceforth.

Let $p_\sigma r^2 \gg h\sigma$ for the film. Then following Sec. 1 it can be shown that in the absence of van der Waals forces the change in pressure p at a distance $x < r - L$ (inner domain) from the center is much less than p_σ, and there is a narrow transition domain to the meniscus in which the main change in the pressure p occurs. The inner domain has a dimension slightly different from the film dimension r. The width of the transition domain $L \sim (h\sigma/p_\sigma)^{1/2} \ll r$ is negligible compared to the film dimension. Let us note that only in the case $p_\sigma r^2 \gg h\sigma$ can the concept of a film dimension be introduced to separate the film from the meniscus. Hence, it is natural that this condition is satisfied well in all experiments [6, 14]. Experiment shows that free films are often made thin while remaining plane-parallel. Then it follows from Sec. 1 that their surface is strained substantially in the longitudinal direction, and the surface velocity is not zero. Otherwise, plane-parallel thinning is impossible.

Because of the presence of the small parameter L/r the problem admits of an effective solution. The build-up time of the transition domain shape τ_1 equals L/v_1 in order of magnitude, where the characteristic fluid velocity in the transition zone is $v_1 \sim -rh^\circ/h$. Hence, the ratio τ_1/τ, where $\tau = |h/h^\circ|$, is the characteristic thinning time, is on the order of $L/r \ll 1$. Therefore, the transition domain is quasistatic, and the derivatives with respect to time therein can be omitted in the equations of motion. The time dependence enters after merger with the solution valid in the inner domain, which can be sought separately.

3. Inner Domain. Taking Account of Diffusion and Adsorption

Let us assume that the surface viscosity in the flow whose scale is r does not suppress the motion of the film surface ($W(r) \leqslant 1$). The surface-tension gradients originating during deformation of the surface must be found.

As is done in many experiments [14, 15], let $D\tau \gg r^2$ (τ is the characteristic thinning time $D \sim D_s$). Then because of diffusion the values of Γ and c vary slightly along the whole film

$$|\Gamma - \Gamma_0| \ll \Gamma_0, \quad |c - c_0| \ll c_0 \tag{3.1}$$

If the velocity of the film surface is not zero $v \geqslant u$, then $v \sim r/\tau$.

Taking these estimates into account, (1.8) can be simplified to

$$\operatorname{div}(hD\nabla c + 2D_s\nabla\Gamma - 2\mathbf{v}\Gamma) = 0 \tag{3.2}$$

It hence follows that the change in Γ caused by surface strain is compensated by the diffusion flux. In the plane or axisymmetric case, the expression in the div sign in (3.2) equals a constant which is zero because of symmetry:

$$hD\nabla c + 2D_s\nabla\Gamma = 2\mathbf{v}\Gamma$$

Hence, taking account of (1.6) there follows

$$\mathbf{grad}\ \sigma = -K\mathbf{v}, \qquad K = cHRT\,/\,(D_s + D\,(1 + bc)^2\,h\,/\,2H) \tag{3.3}$$

Here c is a constant because of (3.1), and $K = K(h)$ along the film.

The coefficient $K = 0$ in the limit of large and small surfactant concentrations and has the maximum value

$$K_{\max} = \frac{H^2RT}{Dhb}\frac{c}{1+bc}, \quad c = \frac{1}{b}\sqrt{1 + 2\frac{D_s}{D}\frac{H}{h}}$$

Neglecting μ_s from (1.2), (1.5), and (4.3), we obtain

$$\mathbf{u} = (K\,/\,6\mu)\,h\mathbf{v}, \qquad h\ \mathbf{grad}\ p = -2K\mathbf{v} \tag{3.4}$$

The coefficient K governs the possibility of film surface deformation without the origination of substantial pressure changes and substantial thickness changes. As $K \to 0$ the gradients of p and σ vanish; the film surface is deformed freely. For large values $K \gg 6\,\mu/h$ the surface is incompressible. Small values of K are achieved because of the large value of the diffusion coefficient and also because of the small content of surfactants in the surface with respect to the volume. The coefficient K is lowered substantially in the adsorption saturation domain $c \gg 1/b$.

From (1.1), (1.3), (3.4) we obtain an equation for the film thickness in the plane or axisymmetric case:

$$\operatorname{div}\left\{\left(\frac{h^2}{4K(h)} + \frac{h^3}{24\mu}\right)\mathbf{grad}\left(\sigma\triangle h - \frac{A}{3\pi h^3}\right)\right\} = -\frac{\partial h}{\partial t} \tag{3.5}$$

For $A = 0$ and small changes in the film thickness, (3.5) agrees in form with the equation investigated in [13]. Equation (3.5) is valid everywhere if the surface viscosity is so small that it does not affect the flow in the transition domain. The thickness hence varies considerably in the inner domain, and plane-parallel thinning is impossible.

For $v \geqslant u$ the role of the change in σ and the surface viscosity can be compared by forming the appropriate ratio u/v of the velocities of motion with the surface and relative to it. For $W \ll kH/6\,\mu$, or $\mu_s \ll Kl^2$, the surface viscosity is negligible as compared with σ, since for the same u it admits much too large values of v. In the inverse limit case, the surface viscosity plays a main role.

Equation (3.5) admits of the particular solution

$$h(x,t) = h_0 - \frac{h_0^{\cdot}}{16\sigma h_0^2}\frac{K(h_0)}{1 + h_0K(h_0)\,/\,6\mu}x^4 \tag{3.6}$$

which is valid for $|h - h_0| \ll h_0$. Here x is the distance along the axis. The thinning of the film is almost plane-parallel with edges thicker than in the center. The nonuniformity in the thickness is greatest at $K = K_{\max}$. The condition for plane-parallelism of the inner domain $|h^{\circ}|r^4K \ll 16\sigma h^3$ follows from (3.6).

If the role of diffusion is negligible $Dr^2 \ll \tau$, and, moreover, the mean velocity of fluid motion relative to the surface is considerably less than the velocity of the surface $u \ll v$, then the transfer equation (1.7) has the integral

$$c + 2\Gamma / h = f(\xi_i), \quad i = 1, 2 \tag{3.7}$$

Here ξ_i are Lagrange coordinates. The surface tension is found easily as a function of the Lagrange coordinates and the film thickness $\sigma = \sigma(\xi_i, h)$. It is hence seen that for large film thicknesses $h \gg 2\Gamma/c$ the thickness changes result in relatively small changes in σ.

4. Transition Domain for $KL^2 \ll \mu_s$

In the quasistatic approximation (Sec. 2), the main equations in the transition domain are

$$hu + hv = h_0 v_0, \quad -\frac{12\mu u}{h} = 2\mu_s \frac{d^2 v}{dx^2} = h \frac{d}{dx}\left(-\frac{\sigma}{2}\frac{d^2 h}{dx^2} + \frac{A}{6\pi h^3}\right) \tag{4.1}$$

$$\mu_s = \lambda_s + 2\eta_s \tag{4.1}$$

Here because of the condition $L \ll r$ small terms in the equations, corresponding to axial symmetry, are omitted. To analyze the transition domain it is sufficient to consider the plane problem.

The conditions

$$h \to h_0, \; v \to v_0, \; x \to -\infty \tag{4.2}$$

$$v \to 0, \; \sigma d^2 h / dx^2 \to 2p_\sigma, \; x \to \infty \tag{4.2}$$

are given at infinity.

The solution of (4.1) under the conditions (4.2) is determined to the accuracy of translation. The asymptotic solution of the linearized equations (4.1) as $x \to -\infty$ can be used to determine the initial data of the numerical computations just as has been done in [16] in the solution of the problem of motion of a film with an incompressible surface.

In dimensionless notation

$$x = l\xi, \; h = h_0 y, \; l = (\sigma / 24\,\mu v_0)^{1/3} h_0 \tag{4.3}$$

there follows from (4.1) for values of y as $x \to -\infty$

$$Wy''' - y' + W(y - 1) = 0, \; W = h_0 \mu_s / 6\mu l^2$$

The equation

$$W\lambda^3 - \lambda + W = 0$$

corresponding to a solution of the form $1 + \exp(\lambda\xi)$, has two positive real roots for $W < \frac{1}{3}2^{2/3}$. For $W > \frac{1}{3}2^{2/3}$ there are two complex roots $\mathrm{Re}\lambda > 0$. Correspondingly, for $W < \frac{1}{3}2^{2/3}$ the asymptotic solution is monotonic and for large values of W has the form of a wave with rapidly damping amplitude. The monotonic solution is characteristic for a tensile surface, while the waveform solution is characteristic for an incompressible surface. The passage from one solution to the other occurs for $\mu_s \sim \mu R_0$. The asymptotic investigation of (4.1) for the case $\mu_s \gg \mu R_0$ as $x \to \infty$ yields

$$v \sim x^{-\lambda}, \quad \lambda = 12\,\mu R_0 / \mu_s$$

which corresponds to a passge to the limit of a constant surface velocity. Viscous tension hence decreases as $1/x$.

5. Transition Domain for $KL^2 \ll \mu_s \ll R_0\mu$. Edge Angle of a Film with a Meniscus

In this case $u \ll v$, and integration of (4.1) taking account of (4.2) yields

$$h\frac{d^2 h}{dx^2} = \frac{1}{2}\left(\frac{dh}{dx}\right)^2 + \frac{4\mu_s h_0 v_0}{\sigma h^2}\frac{dh}{dx} - \frac{A}{2\pi\sigma}\left(\frac{1}{h_0^2} - \frac{1}{h^2}\right) \tag{5.1}$$

In the dimensionless notation

$$x = l\xi, \; h = h_0 y, \; l = \sigma h_0^2 / (4\mu_s v_0)$$

$$B = Al^2 / (\pi\sigma h_0^4), \; \alpha = 2p_\sigma l^2 / (\sigma h_0) \tag{5.2}$$

the problem of analyzing the transition domain is

$$2yy'' = y'^2 + 2y'y^{-2} - B(1 - y^{-2});\quad y \to 1,\ x \to -\infty;\quad y'' \to \alpha,\ x \to \infty \tag{5.3}$$

For B = 0 Eq. (5.3) admits of solution in quadratures. Integrating (5.3), we obtain

$$y' = {}^2/_5 (\sqrt{y} - y^{-2}) \tag{5.4}$$

Hence, for the value of α in (5.2) there follows: $\alpha = {}^2/_{25}$. Curve 1 (Fig. 2) corresponds to the solution for B = 0. The transition-domain dimension L can be determined approximately by taking it to be the distance at which y changed from 1.14 to 2. Then $L \approx 3l$, and there follows from (5.2)

$$p_\sigma L^2 = 0.36\ h_0\sigma,\quad L^2 = 0.18\ h_0 R_0 \tag{5.5}$$

which confirms the general estimate $p_\sigma L^2 \sim h\sigma$ well.

Taking account of $\alpha = {}^2/_{25}$, we find the velocity of the inflowing film from (5.2):

$$v_0 = (5 / 4\ \mu_s)\, h_0^{3/2} \sqrt{\sigma p_\sigma} \tag{5.6}$$

The condition for which (5.6) is valid is $W(L) \ll 1$, which, taking (5.5) into account, is equivalent to $\mu_s \ll R_0\mu$.

The solution with the van der Waals force taken into account ($B \neq 0$) is found numerically. The solution which decreases most rapidly as $x \to -\infty$ is of interest. The scale of the change in another possible solution is considerably greater and this solution will not be discussed.

The $y(\xi)$ curves 2 and 3 in Fig. 2 correspond to the values B = 0.08 and 0.16. The dependence $\alpha(B)$ is hardly different from the linear

$$\alpha = 0.08 - 0.5B$$

which yields a correct result for B = 0 and 0.16, and the difference in slope does not exceed ~12%. The fact that $\alpha = 0$ at B = 0.16 is important. Since from (5.2)

$$3\, p_m / p_\sigma = B / \alpha \quad (p_m = -\Pi = A / 6\,\pi h_0^3)$$

then $[p_m \gg p_\sigma]$ as $[B \to 0.16]$ and the van der Waals forces play a major part in the transition domain. The asymptotic $y(\xi)$ as $\xi \to \infty$ has the following form for B = 0.16: $y = 0.4\xi$. The dimension of the transition domain is already not determined by the quantity p_σ, but by p_m ($L^2 \approx \sigma h_0/2p_m$). Hence, $L \ll \sqrt{h_0 R_0}$. Therefore, for $p_m \gg p_\sigma$, the film makes the edge angle

$$\theta = (A / \pi\sigma)^{1/2} h_0^{-1} \tag{5.7}$$

with the meniscus.

The velocity of film influx determined from (5.2)

$$v_0 = (5 / 8\ \mu_s) \sqrt{A\sigma / \pi} \tag{5.8}$$

is independent of the thickness if B ~ 0.16.

The approximate formula

$$v_0 = \frac{5}{4\mu_s} h_0^{3/2} \sqrt{\sigma\left(p_\sigma + \frac{A}{4\pi h_0^3}\right)} \tag{5.9}$$

agrees with the exact formulas (5.6) and (5.8) in the limits $h_0 \to \infty$ and $h_0 \to 0$ and has an error not exceeding 4% for intermediate values of h_0 when $p_\sigma \sim A/(4\pi h_0^3)$.

6. Transition Domain for $\mu_s \gg R_0\mu$. Breakdown under the Effect of the Van der Waals Force

In the case under consideration, the surface behaves as an incompressible surface in the transition domain. The velocity $v \approx v_0$ and the Eqs. (4.1) simplify to

$$\sigma \frac{d^3h}{dx^3} + \frac{A}{\pi h^4}\frac{dh}{dx} = \frac{24\mu v_0}{h^3}(h_0 - h) \tag{6.1}$$

This equation has been examined in [16] for A = 0, where the influx to the meniscus has been investigated of a film whose surface is incompressible because of σ. Let us note that such a situation is not possible for films being thinned. When the surface is incompressible because of σ in the transition domain, then it is incompressible everywhere, and the velocity is $v = 0$.

The viscous tension of the T_{xx} component of the viscous-stress tensor in the surface defined by (1.5) is important. In addition to the conditions $h \to h_0$ as $x \to -\infty$, $\sigma h'' \to 2p_\sigma$, as $x \to \infty$, the condition for the difference in the viscous tension $T_{xx}^{(-)}$ as $x \to -\infty$ and the viscous tension $T_{xx}^{(+)}$ as $x \to \infty$ should be satisfied. The tensions $T_{xx}^{(-)}$ and $T_{xx}^{(+)}$ produced because of the surface viscosity can be substantial only when $W(L) \gg 1$. Their values can be found from the solution of the problem in the exterior of the transition domain.

There follows from (1.2) and (1.5) for the difference in tensions

$$T = 2T_{xx}^{(-)} - 2T_{xx}^{(+)} = {}^1/_2\, \sigma\, (hh'' - {}^1/_2\, h'^2)_\infty + A\, /\, (4\pi h_0^2) \tag{6.2}$$

Here $T > 0$ always, since in the interior domain the surface is stretched ($T_{xx}^{(-)} > 0$), but is compressed ($T_{xx}^{(+)} < 0$), on the meniscus above the transition domain. Here the subscript ∞ denotes the limit value $x \to \infty$. Replacement of the variables (4.3) results in the problem of finding solutions $y(\xi)$ of the equation

$$y^4 y''' + By' + y\,(y - 1) = 0 \tag{6.3}$$

under the conditions

$$\begin{gathered} y \to 1 \quad \text{as} \quad \xi \to -\infty \\ y'''_\infty = \alpha, \ (yy'' - {}^1/_2 y'^2)_\infty + {}^1/_2\, B = \alpha T_1 \\ \alpha = \frac{2p_\sigma l^2}{h_0 \sigma}, \quad B = \frac{3\alpha p_m}{p_\sigma}, \quad p_m = \frac{A}{6\pi h_0^3}, \quad T_1 = \frac{T}{p_\sigma h_0} \end{gathered} \tag{6.4}$$

The asymptotic of the solution of (6.3) as $\xi \to -\infty$ is

$$y = 1 + \exp\ (a_1 \xi) \cos\,(a_2 \xi + \varphi) \tag{6.5}$$

to the accuracy of translation.

The constants a_1 and a_2 here are determined from the solutions of the cubic equation

$$\lambda^3 + B\lambda + 1 = 0,\ \lambda = a_1 + ia_2,\ a_1 > 0,\ a_2 > 0$$

Assigning a value of the phase angle φ in (6.5) between 0 and 2π, and continuing the solution having the form (6.5) for $-a_1\xi \gg 1$, numerically, in the domain $\xi > 0$, we obtain all the solutions of the problem (6.3), (6.4).

The characteristic modes of the transition domain are represented in Fig. 3 for the values $B = 0$ and 1 (curves 1 and 2, respectively) and $T_1 = 0$. The limit $T \ll p_\sigma h_0$ corresponds to the value of the dimensionless tension $T_1 = 0$. As should be expected from an analysis of the asymptotic, the solution in the transition domain is of wave nature.

Numerical computations yield the dependence of the quantities α, T_1, B in parametric form as the functions $T_1(B, \varphi)$ and $\alpha(B, \varphi)$. The function $T_1(\alpha, B)$ is shown in Fig. 4 for the values $B = 0$, 0.5, 0.8, 1.105, 1.5, 1.8 (curves 1-6, respectively). The quantity max T_1 decreases monotonically from 0.346 at $B = 0$ to 0 at $B = 1.105$, while max $T_1 < 0$ in the domain $B > 1.105$.

In the absence of van der Waals forces ($B = 0$) and for the viscous tension $T \ll p_\sigma h_0$ we have the quantity $\alpha = 1.185$. Hence, it follows from (4.3) and (6.4) that

$$v_0 = 0.092\ (p_\sigma h_0)^{3/2}\, /\, (\mu \sigma^{1/2}) \tag{6.6}$$

The maximum value of the ratio $p_m/p_\sigma = 0.18$ for $T_1 = 0$ is reached for $B = 0.9$.

For $B > 1.105$ or $p_m > 0.18\, p_\sigma$ no stationary solution exists in the transition domain which will satisfy the condition $T > 0$. For $p_m \ll p_\sigma$ the lack of solutions means the transition to a flow with a frozen surface when it is necessary to take account of the change in thickness to the transition domain in the interior domain of the film. The disappearance of stationary solutions means that a much more rapid thinning of the film has started in the transition domain than in the interior.

For $p_m \sim 0.18\, p_\sigma$ the disappearance of a stationary solution at $h = h_*$ is accompanied by rapid breakdown of the film. The wavy nature of the solution (Fig. 3) contributes to this since the pressure p in thinner film sections is elevated substantially because of the molecular forces and grows sharply as the thickness diminishes. Therefore, if $\mu_S \gg R_0\mu$, then breaks in the film in the transition domain occur, as follows from the conditions $p_m < 0.18\ p_\sigma$ and (6.4), at a thickness greater than or equal to

$$h_* = 0.66\ (A\ /\ p_\sigma)^{1/3}$$

7. Plane-Parallel Thinning

The film surfaces remain parallel planes with a variable distance $h_0(t)$ between them if the velocity distribution has the form $v = v_0 x/r$. The film and its surface hence undergo uniform strain. The film is compressed in a direction perpendicular to the surface; its surface broadens. This is pure shear, the exact solution of the Navier–Stokes equations.

When viscous tension in the inner domain is small compared with the tension in the transition domain, the two solutions at $x \approx r$ are merged in the film thickness and velocity, since the corresponding problems in the transition domain are solved taking account of the viscous tensions being zero as $x \to \pm\infty$. The merger permits finding the thinning law.

The dependence of the thinning rate on the film dimension r for plane-parallel thinning is

$$dh_0\ /\ dt = -\ 2h_0 v_0(h_0)\ /\ r$$

where the function $v_0(h_0)$ is determined by the fluid and surfactant properties and depends on the pressure in the meniscus p_σ.

For the case $\mu_S \ll R_0\mu$ and in the absence of van der Waals forces, there follows from (5.6) and (1.1)

$$dh_0\ /\ dt = -\ 2.5\ h_0^{5/2}\ \sqrt{\sigma p_\sigma}\ /\ (\mu_s r), \quad \mu_s = \lambda_s + 2\eta_s \tag{7.1}$$

Hence, $h_0 \sim t^{-2/3}$ as $t \to \infty$.

For $\mu_s \ll R_0\mu$, $p_\sigma \ll A\ /\ (6\pi h_0^3)$ we obtain from (5.9)

$$dh_0\ /\ dt = -1.25\ h_0 \sqrt{A\sigma}\ /\ (\mu_s r \sqrt{\pi}) \tag{7.2}$$

The film thickness decreases exponentially with time.

The thinning law

$$dh_0\ /\ dt = 0.18\ p_\sigma^{3/2} h_0^{5/2}\ /\ (r\ \mu\sigma^{1/2}) \tag{7.3}$$

follows from (6.6) for the case $\mu_S \gg R_0\mu$ when the surface behaves as an incompressible surface in the transition domain.

The time dependence is analogous to (7.1).

Compliance with the conditions found in Sec. 3 is necessary for the validity of (7.1)-(7.3).

As μ_S grows in the domain $\mu_S \gg R_0\mu$ the formula (7.3) ceases to be valid when the viscous tensions outside the transition domain turn out to be substantial.

In order to take account of the viscous tensions outside the transition domain, let us consider the motion in the surface separately from the fluid motion in the volume by assuming that their interaction is essential only in the transition domain which we replace by a tension jump. Analysis of the asymptotic outside the transition domain shows that such an approach is justified in the limit $\mu_S \gg R_0\mu$. Moreover, we assume in the derivation that the film radius r is much less than the meniscus radius R_0. Then the surface of the meniscus is slightly different from a plane at a distance of the order of several r.

Equation (1.4) taking account of (1.5) under the assumptions made yields

$$\frac{d^2v}{dx^2} + \frac{1}{x}\frac{dv}{dx} - \frac{v}{x^2} = 0$$

Hence, taking account of the condition $v = v_0$ at $x = r$, we find that

$$v = v_0 x\ /\ r \ \text{ for } \ x \in [0,\ r],\ v = v_0 r\ /\ x \ \text{ for } \ x > r$$

The viscous tensions in (6.2) hence equal

$$T_{xx}^{(-)} = 2\,(\lambda_s + \eta_s)\,v_0\,/\,r, \quad T_{xx}^{(+)} = -\,2\eta_s v_0\,/\,r, \quad T = 4\,(\lambda_s + 2\eta_s)\,v_0\,/\,r \tag{7.4}$$

Analogously, in the plane case

$$v = v_0 x / r \text{ for } x \in [0, r],\ v = v_0 \text{ for } x > r$$
$$T = 2(\lambda_s + 2\eta_s)\, v_0 / r \tag{7.5}$$

Equating the values of the outer tension jump (7.4) or (7.5) to the inner jump determined from (6.4), we find

$$q\,\frac{\lambda_s + 2\eta_s}{6\mu r}\left(\frac{2p_\sigma h_0}{\sigma}\right)^{1/2} = \alpha^{3/2} T_1(\alpha) \tag{7.6}$$

Here q = 1, 2 in the axisymmetric and plane cases, respectively. The tensions in the inner domain can be neglected if the left side of (7.6) is much less than one. Both $\alpha \approx 1.185$ and the thinning law (7.3) correspond to this. As the left side of (7.6) grows, the parameter α increases monotonically as follows from Sec. 6, and hence the rate of thinning drops.

8. Thinning of a Film under the Effect of van der Waals Forces

When the role of surface diffusion is small as compared to the role of volume diffusion

$$D_s \ll D\,(1 + bc)^2 h / 2H \tag{8.1}$$

there follows from (3.5) and (3.3) under the conditions of a predominating effect of the van der Waals forces

$$-\frac{A}{2\pi}\left(\frac{D\,(1+bc)^2}{4H^2 cRT} + \frac{1}{12\mu}\right)\operatorname{div}\left(\frac{1}{h}\,\mathbf{grad}\,h\right) = \frac{\partial h}{\partial t} \tag{8.2}$$

Although this equation is nonevolutionary and the Cauchy problem is incorrect for it, its solution is of interest because the films are sometimes thinned only under the effect of van der Waals forces [17] prior to breaking down.

Equation (8.2) admits of the solution

$$h = (h_0 - \alpha t)\, Y(x) \tag{8.3}$$

In the axisymmetric case the function Y(x) satisfies the equation

$$\frac{d^2Y}{dx^2} - \frac{1}{Y}\left(\frac{dY}{dx}\right)^2 + \frac{1}{x}\frac{dY}{dx} = Y^2\frac{\alpha}{G}, \quad G = \frac{A}{2\pi}\left(\frac{D\,(1+bc)^2}{4H^2 cRT} + \frac{1}{12\mu}\right) \tag{8.4}$$
$$Y = 1,\ Y' = 0 \quad \text{for } x = 0 \tag{8.4}$$

For numerical integration it is convenient to select the variable

$$\xi = x\sqrt{\alpha / G}$$

The result of a numerical computation is represented by the curve 1 (Fig. 5). At the point $\xi_0 = 2.828$ there is a vertical asymptote; the film thickness becomes infinite as $(\xi_0 - \xi)^{-2}$.

In (8.3) $\alpha = G\xi_r^2/r^2$. Here ξ_r is a point on the curve $y(\xi)$ to which the film radius r corresponds. The value of ξ_r can correspond to both the distance to the asymptote and to the distance $\xi_r = 1.53$, say, at which the film thickness doubles.

In this latter case the thinning law differs slightly for D = 0 from that which follows from the Reynolds equation [17]. The linear dependence (8.3) agrees with experiment [17].

In the plane case, an equation analogous to (8.4) which follows from (8.2)

$$Y d^2Y / d\xi^2 - (dY / d\xi)^2 = Y^3$$

is integrated explicity:

$$Y = 1 / \cos^2(\xi\sqrt{2}) \tag{8.5}$$

Evidently $Y \to \infty$ as $\xi \to \pi / \sqrt{2} = 2.221$. Curve 2 (Fig. 5) corresponds to (8.5).

When just surface diffusion is important, i.e., in the limit case opposite to (8.1), Eq. (3.5) is

$$\frac{AD_s}{4\pi cHRT}\operatorname{div}\left(\frac{1}{h^2}\,\mathbf{grad}\,h\right) = -\frac{\partial h}{\partial t} \tag{8.6}$$

if $6D_s \gg cHRT\,\mu$ is satisfied. There is the particular solution

$$h = h_0(1 - t/\tau)^{1/2} Y(x),\ Y(0) = 1$$

In the plane case Y (ξ) is determined by the quadrature

$$\sqrt{2} \int_0^{\sqrt{\ln Y}} e^{-t^2} dt = \xi, \quad \xi = x\sqrt{\frac{h_0}{\tau M}}, \quad M = \frac{AD_s}{2\pi c HRT}$$

The solution (Fig. 5, curve 3) becomes infinite at $\xi = \sqrt{\pi/2}$. The quantity ξ_r is determined in terms of the value of τ corresponding to the film radius r as

$$\tau = h_0 r^2 / (\xi_r^2 M)$$

As is seen from (8.6), in the axisymmetric case, Y (ξ) satisfies the equation

$$YY'' - 2Y'^2 + YY'x^{-1} - Y^4 = 0$$

The solution with the initial data Y = 1, Y' = 0 at $\xi = 0$ becomes infinite for $\xi = 1.68$ (Fig. 5, curve 4). The thickness h is twice the thickness at the center for $\xi = 1.325$.

The presence of a vertical asymptote in the solution is common to all four problems considered. The solutions obtained can be meaningful only when the capillary pressure in the meniscus is $p_\sigma \ll p_m = -\Pi(h_0)$, and, therefore, the film dimension is of the order of the distance to the vertical asymptote.

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