Flow of a Thin Liquid Layer Due to Ambient Disturbances

A closed-form solution for the transient deformation of a thin liquid layer caused by ambient pressure disturbances predicts the level of disturbances that will produce significant flow in the time available. The effects of viscosity, gravity, surface tension, and a soluble surface-active agent are included in the analysis. The major simplification is the use of the lubrication approximation to the equations of flow. Nearly stationary pressure disturbances are found to be more dangerous than moving disturbances. Surface tension gradients arising from convection of surfactant in the surface oppose flow and reduce the film deformation. The thermodynamic properties of the surfactant, as well as its diffusion coefficient, are important in determining whether significant surface tension gradients develop. However, the effectiveness of a surfactant at minimizing film deformation also depends upon flow parameters such as the natural time scale for flow.

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Introduction

Considerable attention has been focused on thin film flows driven by moving boundaries or by gravity. An example of a flow driven by a moving boundary is dip coating (Landau and Levich, 1942), where a thin film is formed as an immersed surface is withdrawn from a reservoir of liquid. Examples of flow driven by gravity include a bubble rising in a tube, leaving behind a thin liquid film (Bretherton, 1961), and the flow of a layer down an inclined plane (Fulford, 1964).

The flow instabilities that cause the layer thickness to become nonuniform have also been extensively studied. These include the ribbing-line instability encountered in coating flows (Pitts and Greiller, 1961), the formation of waves on a layer flowing down an inclined plane (Benjamin, 1957), surface-tension-driven convection (Pearson, 1958; Scriven and Sternling, 1964), and the damping of capillary waves (Lucassen-Reynders, 1969). Whether or not the basic flow remains stable and the layer uniform has important consequences for many heat and mass transfer operations in general, and for coating (i.e., thin film formation) processes in particular (Ruschak, 1985).

The flow of a thin, viscous, horizontal layer resulting from incessant ambient pressure disturbances is considered here. Although such a layer is stable according to linear stability theory, ambient pressure disturbances will cause the layer to deform. A common assumption in the analysis of film flows is that the surrounding air has a negligible effect upon flow. Whether this is in fact the case will depend upon what deformations are considered to be negligible; upon the intensity, motion, and spectral composition of the disturbances; upon the resistance to flow of the layer due to gravitational, viscous, and surface tension effects; and upon the length of time that the layer is subjected to these disturbances. In the precision coating industry, deformations of just a few percent can be highly undesirable.

In the present analysis, small deformations of a thin liquid layer from an initial state of rest, due to ambient pressure disturbances, are modeled using the lubrication approximation to the flow equations. Viscous, gravitational, and surface tension effects are retained, as well as surface tension gradients due to the presence of a soluble, surface-active agent. A closed-form solution to the problem, including transients, is found. The model can be useful in estimating the level of disturbances that will produce significant deformation of the layer in the time available, in determining the wavelength of the most dangerous disturbance, in selecting surfactants that are effective at retarding flow, and in assessing the relative importance of the several effects that oppose flow.

The present problem is related to that of the damping of capillary waves (Lucassen-Reynders, 1969; van den Tempel and van de Riet, 1965). The usual approach is a linear stability analysis to determine whether small, but otherwise arbitrary disturbances of the liquid layer will decay, and the main result is a temporal or spatial damping factor that arises from an eigenvalue problem. In the approach taken here, an initially uniform liquid layer is subjected to incessant ambient disturbances, and the development with time of the resulting flow is calculated. In other words, particular disturbances presumed to be quantitatively known are directly incorporated in the analysis. This approach relates more directly to practical applications whenever the nature of the dominant disturbance is known. Pramanik and Majumdar (1985) analyzed the generation of capillary-gravity waves by a surface pressure distribution. As usual in analyses of capillary waves, they retained inertial effects and regarded the layer as infinitely deep. Additionally, they included viscosity only as a perturbation from inviscid flow, and they did not include the effects of surface-active agents. In the present analysis viscous effects are dominant and the layer has a finite thickness. In these respects, the present work resembles Orchard's (1963) treatment of the leveling of a viscous layer.

Governing Equations

Up to time $t = 0$, a film of Newtonian liquid is motionless, horizontal, and of uniform thickness d. A Cartesian coordinate system is employed with x measured horizontally and y measured vertically upward from the substrate. The liquid has viscosity μ, density ρ, and surface tension σ. The film contains a surface-active agent of uniform bulk concentration $\bar{C}$ and an equilibrium surface concentration $\bar{\Gamma}$. For $t > 0$, the film is subject to a small ambient disturbance considered to be a sinusoidal pressure wave of amplitude P_e, wave speed c, and wavelength λ. For convenience the wave number $\alpha = 2\pi/\lambda$ will appear in the equations instead of the wavelength.

The governing equations will be nondimensionalized for the following special case of flow. Several of the restrictions imposed here for the purpose of scaling the variables are later relaxed. Consider the case in which surface tension depends weakly on the concentration of surfactant in the surface. In this situation, the response of the liquid to the ambient pressure disturbance is not affected by the presence of the surfactant. The concentration of surfactant will, however, vary along the surface as a result of convection, resulting in diffusion to and from the bulk phase. Furthermore, it will be supposed that the pressure disturbance is stationary ($c = 0$), that inertial effects are negligible compared with viscous effects, and that the wavelength of the disturbance is much larger than the thickness of the film. On the time scale of the fluid flow, diffusion to and from the interface is considered to have a negligible effect on the concentration of the surfactant at the interface, and the bulk concentration is considered to be affected only near the interface, where there is a diffusion boundary layer. Thus, the bulk concentration near the substrate does not change and the film can be regarded as infinitely thick for the diffusion process. Under these special circumstances, the film will deform until an equilibrium state is reached in which the stationary ambient pressure variation is balanced by surface tension and the hydrostatic pressure field in the liquid.

Only small disturbances are considered, and the governing equations are linearized about the rest state. The wavelike nature of the solution is anticipated, and the explicit appearance of x in the equations is eliminated, by introducing the complex exponential function when defining dimensionless dependent variables.

$$U = (\alpha d^2 P_e/\mu)\hat{U}(y,t)\exp[i\alpha(x-ct)] \qquad (1a)$$

$$V = (\alpha^2 d^3 P_e/\mu)\hat{V}(y,t)\exp[i\alpha(x-ct)] \qquad (1b)$$

$$P = \rho g(d-y) + P_e\hat{P}(y,t)\exp[i\alpha(x-ct)] \qquad (1c)$$

$$C = \bar{C} + [k\bar{\Gamma}P_e/d(\rho g + \sigma\alpha^2)]\hat{C}(y,t)\exp[i\alpha(x-ct)] \qquad (1d)$$

$$H = d + [P_e/(\rho g + \sigma\alpha^2)]\hat{H}(t)\exp[i\alpha(x-ct)] \qquad (1e)$$

$$\Gamma = \bar{\Gamma} + [\bar{\Gamma}P_e/d(\rho g + \sigma\alpha^2)]\hat{\Gamma}(t)\exp[i\alpha(x-ct)] \qquad (1f)$$

$$y = d\hat{y} \qquad (1g)$$

$$\eta = (d-y)/\sqrt{D\tau} \qquad (1h)$$

$$t = \tau\hat{t} \qquad (1i)$$

Here U is the horizontal or x component of velocity, V the vertical or y component of velocity, P the pressure, C the surfactant concentration in the bulk, H the thickness of the film, Γ the concentration of surfactant at the interface, g the gravitational acceleration, D the bulk diffusion coefficient of the surfactant, and k the derivative of the bulk concentration of surfactant with respect to surface concentration under conditions of equilibrium. The overbar indicates the constant and uniform value of a variable for $t < 0$. The expression for the pressure contains the linear hydrostatic pressure field of the rest state. The variables capped ˆ are nondimensional, complex numbers that determine the amplitude and phase of the departure from the initial state. The scale factors preceding the capped variables correspond to the special case of flow described previously and considered in more detail later. The scale factor for time, τ, is given by $\mu/[\alpha^2 d^3(\rho g + \sigma\alpha^2)]$, and is the characteristic time for the deformation of the layer to take place. Note that $\hat{y}$ is a nondimensional y coordinate in which distance is measured vertically upward from the substrate in units of the film thickness, and it will appear in the equations directly related to the flow of the liquid. On the other hand, η is a nondimensional y coordinate in which distance from the liquid/air interface is measured vertically downward from the interface in units of the characteristic thickness of the diffusion boundary layer, $\sqrt{D\tau}$, and it will appear in the diffusion equation.

In terms of the nondimensional variables, the governing equations are:

$$O = -i\hat{P} + \hat{U}_{\hat{y}\hat{y}} \qquad (2a)$$

$$O = -\hat{P}_{\hat{y}} \qquad (2b)$$

$$\hat{V}_{\hat{y}} + i\hat{U} = 0 \qquad (2c)$$

$$\hat{C}_{\hat{t}} - i\gamma\hat{C} = \hat{C}_{\eta\eta} \qquad (2d)$$

$$\left.\begin{aligned}
&\hat{V} = \hat{H}_{\hat{t}} - i\gamma\hat{H} && (2e)\\
&\hat{P} - \hat{H} = 1 && (2f)\\
&\hat{U}_{\hat{y}} = i\chi\hat{\Gamma} && (2g)\\
&\hat{\Gamma}_{\hat{t}} - i\gamma\hat{\Gamma} = -i\hat{U} + \delta\hat{C}_{\eta} && (2h)\\
&\hat{C} = \hat{\Gamma} && (2i)
\end{aligned}\right\}\ (\hat{y} = 1)$$

$$\hat{U} = \hat{V} = 0 \quad (\hat{y} = 0) \qquad (2j, 2k)$$

$$\hat{C} \to 0 \quad (\eta \to \infty) \tag{2l}$$

$$\hat{C} = \hat{H} = \hat{\Gamma} = 0 \quad (\hat{t} = 0) \qquad \text{(2m, 2n, 2o)}$$

Equations 2a and 2b are the x and y components, respectively, of the Navier-Stokes equation, simplified by the lubrication approximation. The inertial terms have been neglected, and this is justified when both $\rho d^2/\mu\tau \ll 1$ and $\rho c d^2 \alpha/\mu \ll 1$. The viscous terms have been simplified by restricting the analysis to nearly rectilinear flow; this is the case when the film thickness is sufficiently small compared to the wavelength of the ambient pressure disturbance that $\alpha^2 d^2 \ll 1$. Equation 2c is from the continuity equation. The diffusion equation leads to Eq. 2d, provided that $\alpha^2 d^2 \ll 1$. Of the boundary conditions applicable at the free surface (Scriven, 1960), Eq. 2e is from the kinematic boundary condition, which relates the velocity of the liquid to the motion of the interface. The traction of the liquid on the free surface is balanced by the action of surface tension in the curved interface. The normal and tangential components of this boundary condition lead to Eqs. 2f and 2g, respectively, under the restriction of nearly rectilinear flow. In the tangential component, a surface tension gradient due to a nonuniform distribution of surfactant is balanced by a shear stress in the liquid. Equation 2h follows from the conservation equation for surfactant at the liquid/air interface (Levich, 1962). The first term on the right-hand side represents the convection of surfactant along the interface, and the second term is the rate of diffusion of surfactant to the interface. The diffusion of surfactant is presumed to be the rate-limiting step in the transfer of surfactant between the surface and the bulk; no adsorption barriers or orientation effects are considered. Indeed, the equilibrium relationship between the bulk and surface concentrations is presumed to hold even under dynamic conditions. This relationship, when linearized, leads to Eq. 2i. At the substrate the velocity is zero, leading to Eqs. 2j and 2k. If $\sqrt{D\tau}/d \ll 1$ so that the thickness of the diffusion boundary layer is small compared with the film thickness, the bulk concentration away from the interface will remain unchanged, as expressed by Eq. 2l. Finally, the rest state of the system up to time $t = 0$ gives rise to initial conditions, Eqs. 2m–2o.

The dimensionless groups of parameters appearing in these equations are defined as follows:

$$\gamma = \alpha c \tau \tag{3a}$$

$$\chi = E/[d^2(\rho g + \sigma \alpha^2)] \tag{3b}$$

$$\delta = k\sqrt{D\tau} \tag{3c}$$

But for the factor of 2π in the definition of the wave number, γ is the ratio of the distance traveled by the ambient pressure wave in the characteristic time τ to its wavelength, and is thus a dimensionless wave speed. In the expression for χ, which will be referred to as the elasticity group, $E = \beta\overline{\Gamma}$ is the surface or Gibbs elasticity and β is the (normally negative) derivative of surface tension with respect to surface surfactant concentration under conditions of equilibrium. As defined here, the surface elasticity is strictly an equilibrium property of the surfactant. The dimensionless group δ is a measure of the importance of diffusion to changes in surfactant concentration at the interface, and it will be called the diffusion group. Both the elasticity group and the diffusion group are important in determining whether significant surface tension gradients will exist. The elasticity group depends upon the derivative of surface tension with respect to surface surfactant concentration. A large derivative will favor significant surface tension gradients in the surface. Also important in determining whether significant surface tension gradients will exist, however, is the gradient of surfactant concentration along the surface. This will be less the larger the diffusion group. Thus, important surface tension gradients are favored by χ being large in magnitude and δ being small.

Equations 2a–2c, 2f, 2g, 2j, and 2k can be solved to obtain expressions for $\hat{P}$, $\hat{U}$, and $\hat{V}$ in terms of $\hat{H}$:

$$\hat{U} = i(1 + \hat{H})(\hat{y}^2/2 - \hat{y}) + i\chi\hat{\Gamma}\hat{y} \tag{4a}$$

$$\hat{V} = (1 + \hat{H})(\hat{y}^3/6 - \hat{y}^2/2) + \chi\hat{\Gamma}\hat{y}^2/2 \tag{4b}$$

$$\hat{P} = 1 + \hat{H} \tag{4c}$$

Note that the velocity profile is parabolic. The remaining equations then reduce to:

$$\hat{C}_{\hat{t}} - i\gamma\hat{C} = \hat{C}_{\eta\eta} \tag{5a}$$

$$\hat{H}_{\hat{t}} + (1/3 - i\gamma)\hat{H} - \chi\hat{\Gamma}/2 = -1/3 \tag{5b}$$

$$\left.\begin{array}{ll} \hat{\Gamma}_{\hat{t}} - (\chi + i\gamma)\hat{\Gamma} + \hat{H}/2 = -1/2 + \delta\hat{C}_{\eta} & \text{(5c)} \\ \hat{C} = \hat{\Gamma} & \text{(5d)} \end{array}\right\} (\hat{y} = 1)$$

$$\hat{C} \to 0 \quad (\eta \to \infty) \tag{5e}$$

$$\hat{C} = \hat{H} = \hat{\Gamma} = 0 \quad (\hat{t} = 0) \qquad \text{(5f, 5g, 5h)}$$

Solution When Diffusion Effects Are Negligible

The solution of Eqs. 5a–5h for the special case where diffusion effects are negligible will be presented first, followed by the general solution. When $\delta \ll 1$, Eqs. 5b and 5c uncouple from Eq. 5a, the diffusion equation. Equations 5b and 5c can then be solved, subject to the initial conditions given by Eqs. 5g and 5h, to obtain the following results:

$$\hat{H} = -\left[A + \frac{(1 + Aa_2)}{(a_1 - a_2)}\exp(a_1\hat{t}/3) - \frac{(1 + Aa_1)}{(a_1 - a_2)}\exp(a_2\hat{t}/3)\right] \tag{6a}$$

$$\hat{\Gamma} = -\frac{3}{2}\left[B + \frac{(1 + Ba_2)}{(a_1 - a_2)}\exp(a_1\hat{t}/3) - \frac{(1 + Ba_1)}{(a_1 - a_2)}\exp(a_2\hat{t}/3)\right] \tag{6b}$$

$$a_1 = 3i\gamma - (1 - 3\chi)/2 + \sqrt{(1 - 3\chi)^2 + 3\chi}/2 \tag{6c}$$

$$a_2 = 3i\gamma - (1 - 3\chi)/2 - \sqrt{(1 - 3\chi)^2 + 3\chi}/2 \tag{6d}$$

$$A = \frac{i\gamma + \chi/4}{i\gamma + \chi/4 + 3\gamma^2 - 3i\gamma\chi} \tag{6e}$$

$$B = \frac{i\gamma}{i\gamma + \chi/4 + 3\gamma^2 - 3i\gamma\chi} \tag{6f}$$

Both a_1 and a_2 are negative, and so the exponential terms vanish at long times.

Two informative limits of these results are for extreme values of the elasticity group. In the limit where $\chi \to 0$, $\hat{H}$ and $\hat{\Gamma}$ are given by

$$\hat{H} \to -\frac{1 - \exp[-(1 - 3i\gamma)\hat{t}/3]}{1 - 3i\gamma} \tag{7a}$$

$$\hat{\Gamma}/\hat{H} \to 3/2 \quad (\chi \to 0) \tag{7b}$$

If the disturbance is furthermore required to be stationary ($\gamma \to 0$), the special case of flow on which the nondimensionalization was based is recovered, and the dependent variables are seen to be of order unity as anticipated. On the other hand, in the limit where $\chi \to -\infty$ the following results are obtained:

$$\hat{H} \to -\frac{1 - \exp[-(1/4 - 3i\gamma)\hat{t}/3]}{1 - 12i\gamma} \tag{8a}$$

$$\hat{\Gamma} \to 0 \quad (\chi \to -\infty) \tag{8b}$$

In this case, the presence of the surfactant immobilizes the interface. These results can, in fact, be obtained by specifying a zero x component of velocity at the interface instead of the tangential stress boundary condition given by Eq. 2g. It should be noted that the exponential term in Eq. 8a decays more slowly than that in Eq. 7a. It is also apparent that for a stationary disturbance ($\gamma \to 0$), $\hat{H}$ approaches unity at long times in both cases. In other words, the ultimate deformation of the film when surface tension gradients are dominant is identical with that when surface tension gradients are negligible. In the case of a stationary disturbance the surfactant slows down the rate at which the deformation takes place. If the disturbance is not stationary, then the ultimate amplitude of the film deformation is less than unity in both cases.

General Solution

The general solution to Eqs. 5a–5h was obtained through LaPlace transforms.

$$\hat{H} = -\exp(i\gamma\hat{t}) \sum_{j=1}^{6} K_j z_j w(-iz_j\sqrt{\hat{t}}) \tag{9a}$$

$$\hat{\Gamma} = -\exp(i\gamma\hat{t}) \sum_{j=1}^{6} L_j z_j w(-iz_j\sqrt{\hat{t}}) \tag{9b}$$

$$\hat{C} = -\exp(i\gamma\hat{t}) \exp(-\eta^2/4\hat{t}) \sum_{j=1}^{6} \cdot L_j z_j w(-iz_j\sqrt{\hat{t}} + i\eta/2\sqrt{\hat{t}}) \tag{9c}$$

The function $w(z)$ is related to the complex complementary error function by (Abramowitz and Stegun, 1964):

$$w(z) = \exp(-z^2) \operatorname{erfc}(-iz) \tag{9d}$$

The z_j ($j = 1,4$) are the roots of the polynomial $p(z)$ defined by

$$p(z) = z^4 + \delta z^3 + (1/3 - \chi)z^2 + \delta z/3 - \chi/12 \tag{9e}$$

and z_5 and z_6 are given by

$$z_5 = m, \quad z_6 = -m; \quad m = (1 - i)\sqrt{\gamma/2} \qquad (9f, 9g, 9h)$$

The constants K_j and L_j are determined from the z_j as follows:

$$K_j = (z_j^2/3 + \delta z_j/3 - \chi/12)/q_z(z_j) \tag{9i}$$

$$L_j = (z_j^2/2)/q_z(z_j) \tag{9j}$$

$$q(z) = (z - z_5)(z - z_6)p(z) \tag{9k}$$

The solution to Eqs. 5a–5h at times sufficiently long for all transients to have disappeared is also of interest. This can be found by setting the time derivatives of $\hat{C}$, $\hat{H}$, and $\hat{\Gamma}$ to zero and ignoring the initial conditions. The resulting equations are straightforward to solve, and the results are:

$$\hat{H} \to -(i\gamma + \chi/4 - \delta m)/J \tag{10a}$$

$$\hat{\Gamma} \to -1.5i\gamma/J \tag{10b}$$

$$\hat{C} \to -(1.5i\gamma/J)\exp(-m\eta) \tag{10c}$$

where J is defined by

$$J = i\gamma + \chi/4 + 3\gamma^2 - 3i\gamma\chi - \delta m + 3i\gamma\delta m \tag{10d}$$

Discussion

Since the amplitude of the surface deformation of the film is of particular interest, attention will be focused on the modulus of $\hat{H}$. According to Eq. 10a, when the disturbance is stationary ($\gamma = 0$), the amplitude of the surface deformation approaches unity at long times for any values of χ and δ. The diffusion and the elasticity groups affect only the time it takes for the ultimate film deformation to be reached. The situation is more complicated when γ is not zero, and the effect of increasing wave speed is to decrease the ultimate deformation of the film.

This is illustrated in Figure 1, where the ultimate amplitude

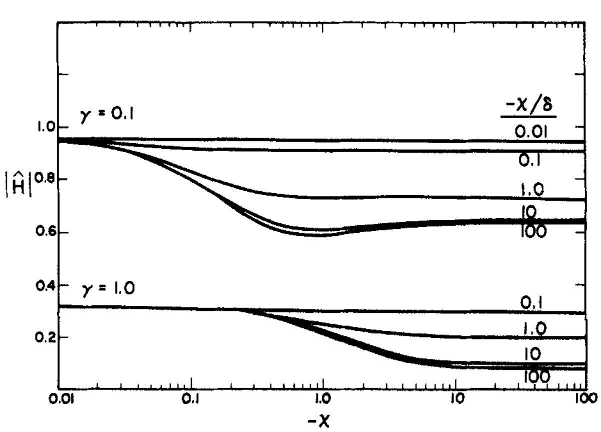

Figure 1. Amplitude of surface deformation at long times as a function of elasticity group.

Top curves, dimensionless wavespeed $\gamma = 0.1$; bottom curves, $\gamma = 1.0$

of the surface deformation is plotted against the elasticity group for several values of the ratio χ/δ. When this ratio is large in magnitude (χ large and/or δ small), important surface tension gradients are favored. The top group of curves is for $\gamma = 0.1$, and the bottom set of curves for $\gamma = 1.0$. When the time scale for flow is small compared with the time scale for the movement of the pressure wave ($\gamma \ll 1$), the external pressure variation is balanced by surface tension and gravity alone, and so surface deformation occurs. On the other hand, when the time scale for flow is large compared with that for movement of the pressure wave, the external pressure variation is largely balanced by the viscous resistance to flow, and less surface deformation occurs. For either value of γ in Figure 1, the ultimate film deformation decreases with increasing elasticity group. However, the smaller the ratio χ/δ, the smaller the decrease. When diffusion is dominant, significant surface tension gradients do not exist.

In Figure 2, the amplitude of the surface deformation $\hat{H}$ is plotted as a function of time $\hat{t}$ for the limiting case where diffusion is negligible ($\delta \rightarrow 0$, see Eq. 6a). The curves correspond to different values of the elasticity group. The dimensionless wave speed γ is zero for all curves. The top and bottom curves are given by Eqs. 7a and 8a, respectively. It is evident that surface elasticity increases the time it takes for the full deformation of the layer to occur.

The effects of diffusion for the case of zero wave speed are illustrated in Figure 3, where the amplitude of the surface deformation is plotted against dimensionless time for several values of χ. The ratio χ/δ has the value -1.0 for all curves. In a comparison of the curves in Figures 2 and 3 corresponding to the same elasticity group, it is evident that when diffusion effects are important, the final film deformation is approached more rapidly. Again, diffusion diminishes the surface tension gradients that oppose flow. The curves in Figure 4 differ from those in Figure 3 in that the wave speed γ is 1.0 instead of zero. The modulus of the final deformation of the layer is reduced by the motion of the disturbance, Figure 1.

The effects of diffusion for the case of zero wave speed are further illustrated in Figure 5, where the amplitude of the surface deformation at the dimensionless time $\hat{t} = 6$ is plotted against the ratio χ/δ for several values of the elasticity group. When the elasticity group χ is small, the surfactant has no effect upon the flow (top curve) regardless of the value of the diffusion group. On the other hand, when the elasticity group is large the film deformation is reduced unless diffusion effects are even larger (bottom curve). When χ/δ is small so that diffusion effects are dominant, the elasticity group has no effect on the film deformation.

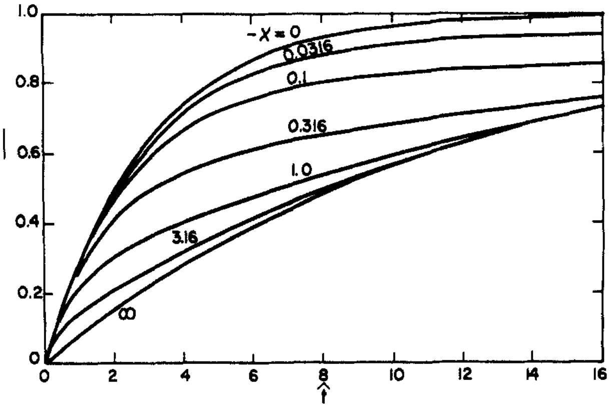

Figure 2. Amplitude of surface deformation as a function of dimensionless time $\hat{t}$ when δ and γ are small.

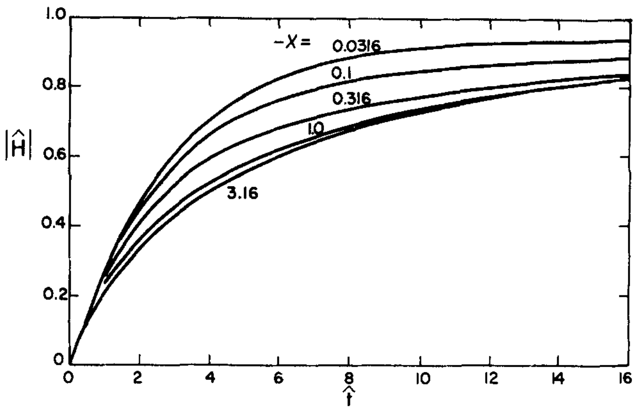

Figure 3. Amplitude of surface deformation as a function of dimensionless time $\hat{t}$ when $\chi/\delta = -1.0$ and γ is small.

The value of the dimensionless groups χ and δ will depend upon the bulk concentration of surfactant. To calculate this dependence, a surface equation of state is needed. The Szyszkowski-Langmuir equation of state (Rosen, 1978) is the simplest, and it will be used in this discussion. According to this model of surfactant adsorption, the surfactant concentration in the surface is related to the bulk concentration under conditions of equilibrium by

$$\Gamma = \Gamma_\infty (C/a)/(1 + C/a) \qquad (11)$$

where Γ_∞ is the saturated surface concentration at high bulk concentration, and a is the bulk concentration at which the surface concentration is half its fully saturated value. The surface tension is related to the bulk concentration by

$$\sigma = \sigma_0 - RT\Gamma_\infty \ln(1 + C/a) \qquad (12)$$

where σ_0 is the value of the surface tension when no surfactant is

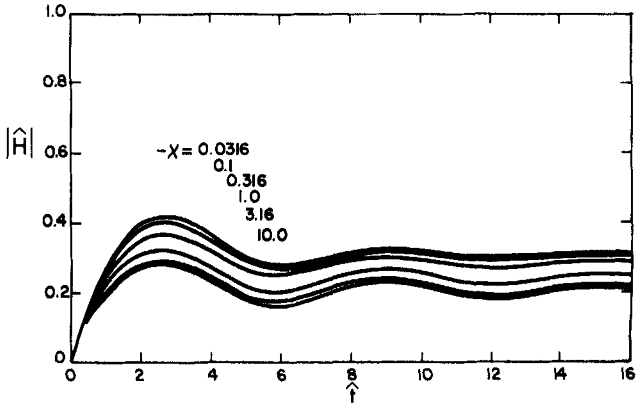

Figure 4. Amplitude of surface deformation as a function of dimensionless time $\hat{t}$ when $\chi/\delta = -1.0$ and $\gamma = 1.0$.

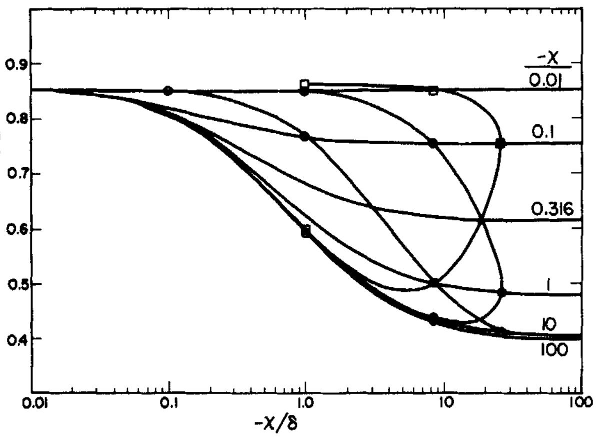

Figure 5. Amplitude of surface deformation for time $\hat{t} = 6$ as a function of χ/δ.

Curves drawn through points are for Szyszkowski-Langmuir equation of state, $N = 100$, $M = 0.1$, □; 1, ●; and 10, ○. Each successive point in clockwise direction represents a 10X increase in C/a; at farthest right point on each curve $C/a = 1.0$.

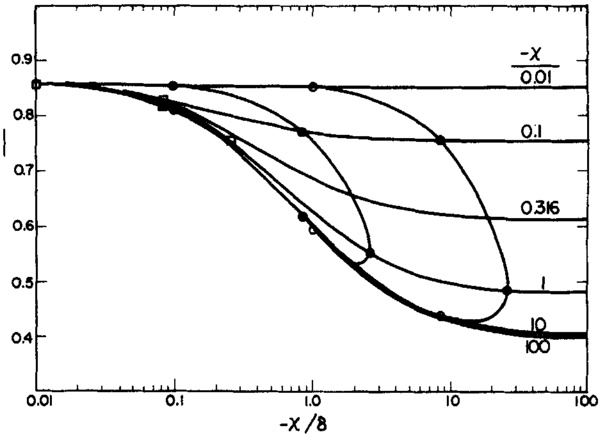

Figure 6. Amplitude of surface deformation for time $\hat{t} = 6$ as a function of χ/δ.

Curves drawn through points are for Szyszkowski-Langmuir equation of state, $M = 1$, $N = 1$, □; 10, ●; and 100, ○. Each successive point in clockwise direction represents a 10X increase in C/a; at farthest right point on each curve $C/a = 1.0$.

present and R is the gas constant. From these equations the surface elasticity can be calculated

$$E = -RT\Gamma_\infty (C/a) \qquad (13)$$

as well as k, the rate of change of bulk concentration with respect to surface concentration.

$$k = (a/\Gamma_\infty)(1 + C/a)^2 \qquad (14)$$

These expressions can, in turn, be used to evaluate the dimensionless groups χ and δ, and their ratio χ/δ.

$$\chi = -\left[\frac{RT\Gamma_\infty}{d^2(\rho g + \sigma\alpha^2)}\right] C/a \qquad (15)$$

For brevity the bracketed term in Eq. 15 will be denoted M.

$$\delta = \frac{a}{\Gamma_\infty}\sqrt{D\tau}(1 + C/a)^2 \qquad (16)$$

$$\frac{\chi}{\delta} = -\left[\frac{d\alpha^2\sqrt{\tau}}{\mu}\right]\left[\frac{RT\Gamma_\infty^2}{a\sqrt{D}}\right]\frac{C/a}{(1 + C/a)^2} \qquad (17)$$

The two bracketed terms together in Eq. 17 will be denoted as N. Note that the ratio $-\chi/\delta$ has a maximum value when the bulk concentration is equal to a.

The locus of points representing different surfactant concentrations is plotted in Figure 5, based upon these expressions for χ and χ/δ. In this figure, N is 100 and the values of M for the three curves are 0.1, 1, and 10. For any curve, note that there is a value of the surfactant concentration for which the deformation of the layer is minimized. Since N is the same for all three curves, they share the same, relatively large, maximum value of $-\chi/\delta$. Thus, it is possible in each case for the surfactant to reduce the film deformation to that corresponding to a flexible, but immobile, interface. However, the surfactant concentration at which this result is achieved, measured in units of a, varies substantially. In each case, the elasticity group must be of order unity to achieve most of the possible reduction in film deformation, and the elasticity group is the product of M and C/a.

In Figure 6, M is 1 and the values of N are 1, 10, and 100. When N is of order unity, it is not possible for the elasticity group to dominate the diffusion group, and the film deformation will be comparable to that for the case where no surfactant is present. Because M is unity, C/a need only be of order unity for the elasticity group to be of order unity, and for most of the possible reduction in film thickness to be realized.

From Eq. 15, the value of M depends upon more than just the properties of the surfactant. Elasticity effects are more prominent the thinner the liquid layer and the smaller the restoring effects of gravity and surface tension. Similarly, the diffusion group δ, as calculated from Eq. 16, depends upon the time scale of τ of the fluid motion in addition to the properties of the surfactant. The shorter the time scale of the fluid motion, the less important are diffusion effects. The time scale decreases as viscosity decreases, wave number increases, film thickness increases, and the opposing effects of gravity and surface tension increase. The effectiveness of the surfactant cannot be separated from the details of the fluid flow.

Notation

a = parameter in Szyszowski-Langmuir equation of state
A = parameter, Eq. 6e
B = parameter, Eq. 6f
C = bulk concentration of surfactant
$\bar{C}$ = uniform bulk concentration of surfactant for $t < 0$
d = average film thickness
D = diffusion coefficient
E = surface elasticity, $\beta\Gamma$
g = gravitational acceleration
H = film thickness
$\hat{H}$ = nondimensional film thickness, Eq. 1e
J = complex number, Eq. 10d
k = derivative of bulk surfactant concentration with respect to surface concentration at equilibrium
K_j = complex number, Eq. 9i for $j = 1,6$
L_j = complex number, Eq. 9j for $j = 1,6$
m = complex number equal to $(1 - i)\sqrt{\gamma/2}$

M – parameter, following Eq. 15
N – parameter, following Eq. 17
p – polynomial, Eq. 9e
P – pressure
q – polynomial, Eq. 9k
R – gas constant
t – time
$\hat{t}$ – dimensionless time, t/τ
T – absolute temperature
U – x component of velocity
$\hat{U}$ – nondimensional x component of velocity, Eq. 1a
V – y component of velocity
$\hat{V}$ – nondimensional y component of velocity, Eq. 1b
w – complex-valued function of z, Eq. 9d
x – horizontal coordinate
y – vertical coordinate
$\hat{y}$ – dimensionless y coordinate, y/d
z – complex number
z_j – root of polynomial $p(z)$ for $j = 1,4$
z_5 – complex number equal to m
z_6 – complex number equal to $-m$

Greek letters

α – wave number
β – derivative of surface tension with respect to surface surfactant concentration at equilibrium
γ – dimensionless wave speed, $\alpha c\tau$
Γ – surface surfactant concentration
$\hat{\Gamma}$ – nondimensional surface surfactant concentration, Eq. 1f
$\bar{\Gamma}$ – uniform surface surfactant concentration for $t < 0$
Γ_∞ – surface surfactant concentration at saturation
δ – diffusion group, $k\sqrt{D\tau}$
η – diffusion boundary layer coordinate, Eq. 1h
μ – viscosity
ρ – density
σ – surface tension
σ_0 – surface tension in absence of surfactant
τ – time scale of flow, $\mu/\alpha^2 d^3\ (\rho g + \sigma\alpha^2)$
χ – elasticity group $E/[d^2(\rho g + \sigma\alpha^2)]$

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