$\mathbf{V}$, V, V_x, V_y = velocity vector, absolute magnitude value and component value, respectively
V_0 = average superficial velocity
x, y = rectangular coordinates
$X = x/D$ = dimensionless coordinate
$Y = y/D$ = dimensionless coordinate

Greek Letters

ϵ = porosity (void fraction)
∇ = gradient
μ = dynamic viscosity
$\psi,(\psi^* = \psi/V_0D)$ = dimensionless and dimensionless stream function, respectively
ρ = density

Subscripts

0 = average quantity

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Instability of Film Coating of Wires and Tubes

The stability problem of the free coating of wires and tubes by withdrawal is formulated and solved. The necessary condition for the stability of the film coating is given explicitly in terms of the Reynolds number, wave number, the Weber number, and implicitly in terms of the withdrawal velocity. The outcome of the competition between the destabilizing capillary pinching and the stabilizing capillary restoring force associated with the film thickness variation is shown to dictate the stability of the film. The comparisons between the present theoretical results and the known experimental results for falling films and creeping annular threads of viscous liquids are good. A possible application of the present results to some aspects of the qualitative design of a coating process is given.

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SCOPE

The film flows down a solid surface under the simultaneous actions of the gravity, the surface tension, and the viscous drag are frequently encountered in many important industrial processes. Such processes include: film coating of photographic paper or plates, cleaning, draining, coating of insulation on a wire, and the protection coating of tube walls, etc. A smooth and uniform film coating is usually difficult to attain because of the flow instability. The instability frequently either sets a limit on the production rate or dictates the selection of the material in precision coatings. A predictive theory of film instability is therefore of considerable practical significance. The purpose of this paper is to offer such a stability theory for the particular film flows encountered in the free coatings of circular wires or tubes.

The film flow down the surface of a circular wire withdrawn vertically from a bath of a viscous liquid has been investigated by Goucher and Ward (1922), Derayagin and Titiyevskava (1945), and recently by Tallmadge et al. (1965). References to more recent works in this area can be found in the works of Tallmadge (1969). References to works in the closely related area of meniscus mechanics can be found in Huh and Scriven (1969, 1971). The main concern of the existing works is the prediction of the shape of the liquid-air interface created by the vertical withdrawal of a wire, in a direction opposite to the gravitational acceleration, from a large liquid pool. A particular emphasis is placed, in practice, on the prediction of the uniform film thickness which is reached in the region far away from the liquid bath. The predicted uniform film thickness can be attained, however, only if the flow is stable. The instability of an annular thread of fluid creeping on the wall of a thin wire or tube has been studied both theoretically and experimentally by Goren (1962). His results are relevant to an annular thread of fluid with the viscosity and the surface tension so high and the radius of the wire or tube so small that the gravitational force can be neglected in comparison with the viscous and surface forces. In the present study we consider the cases in which the effects of gravity, viscosity, and surface tension are of equal importance as is the situation in falling films and films formed by withdrawal. Thus, the present work includes Goren's creeping annular thread and Benjamin-Yih's falling film as special cases when the gravity and the wall curvature are respectively put to zero. The present theoretical predictions are compared with the numerical results of Goren and the experimental results for falling films obtained by Binnie (1957), Kapitza and Kapitza (1949), and with the measurements for creeping annular thread obtained by Goren (1962). The instability in a film formed by withdrawal has been observed by Tallmadge and White (1968). Unfortunately no data on wavelengths are given, which makes a comparison between the present theory and their observation impossible. The present theoretical results on the instability of a film flow depend crucially on the wavelength of the disturbance.

CONCLUSIONS AND SIGNIFICANCE

A nonlinear partial differential equation which describes the motion of the free surface of an axisymmetric film flow, under the action of gravity in the axial direction, down the outer or inner wall of a circular cylinder is derived. Based on this equation, a linear stability analysis is carried out for the film flows encountered in the free coating of wires or tubes by withdrawal. An explicit condition under which a film of a constant thickness can be attained is given in terms of relevant physical parameters. A cut-off wave number is found. The film coating is unstable due to capillary pinching, under all conditions, to disturbances of wave numbers smaller than this cut-off value. If the wave number of the disturbance is larger than the cut-off wave number, then the capillary restoring force associated with the variation of the surface curvature in the axial direction may dominate over the capillary pinching if the Reynolds number of the flow is sufficiently small. Thus, there exists a critical Reynolds number above which a film of a given fluid is unstable with respect to a disturbance of a given wavelength. The onset of instability leads to the surface wave formation. The predicted wavelength and speed corresponding to the most amplified disturbances compare well with some observations. A possible application of the present results to the design of a wire or tube coating process is demonstrated.

FORMULATION

Consider the flows of a viscous incompressible fluid down the outer and inner walls of a circular cylinder as shown respectively in Figures 1 and 2. With respect to the reference frame moving with the constant velocity V of the wire (tube) withdrawn from the coating bath in a direction opposite to the gravitational acceleration g, the governing equations of the fluid motion are

$$\nabla \bullet \mathbf{V} = 0$$
$$\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \bullet \nabla)\mathbf{V} = -\frac{1}{\rho}\nabla P + \mathbf{g} + \nu\nabla^2\mathbf{V} \tag{1}$$

where ∇ is the gradient operator and ∇^2 is the Laplacian. Far away from the bath, the film attains a constant thickness h_0 under stable conditions, the flow being parallel in the axial direction. For this primary flow the above equations are reduced to

$$g + \frac{\nu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial V_z}{\partial r}\right) = 0$$

where V_z is the axial velocity component in the direction of g and r is the radial distance measured from the axis of the wire (tube). The solutions of the above equation which satisfy the no slip condition at the solid-fluid interface $r = r_0$ and the condition of vanishing net force at each element of the fluid-air interface $r = r_0 \pm h_0$ give the following velocity and pressure distributions in the primary flows:

$$\overline{V}_z = \frac{g}{4\nu}(r_0^2 - r^2) + \frac{g}{2\nu}(r_0 \pm h_0)^2 \ln\left(\frac{r}{r_0}\right)$$
$$\overline{P} = P_0 = \text{atmospheric pressure,} \tag{2}$$

where h_0 the uniform film thickness, and the upper or lower sign that is, + or − in the above equation, as well as in the equations to follow, refers to the case of wire or tube.

The stability of the above primary flows is again governed by Equations (1). The perturbed velocity and pressure fields can be written as

$$\mathbf{V} = \mathbf{i}_z\overline{V}_z + \mathbf{v}, \quad P = \overline{P} + p \tag{3}$$

where $\mathbf{i}_z$ is the unit vector in the direction of g, and v and p are respectively the velocity and the pressure perturbations. Substituting the above equations into Equation (1) and writing out the resulting equations in the cylindrical coordinates (r, θ, z), we have

$$u_r + u/r + w_z = 0$$

$$u_t + uu_r + (\overline{W} + w)u_z = -p_r/\rho$$

$$+ \nu (u_{rr} - u/r^2 + u_r/r + u_{zz}) \quad (4)$$

$$w_t + (\overline{W} + w)w_z + u(\overline{W} + w)_r = - p_z/\rho + \nu[(rw_r)_r/r + W_{zz}]$$

where (u, v, w) are the (r, θ, z) components of v, $\overline{W} = \overline{V}_z$, and the subscripts denote partial differentiations. In arriving at the above equations, we assume the disturbance to be axisymmetric, that is, v is taken to be zero.

The boundary conditions which must be satisfied by the velocity perturbations are:

1. The no-slip conditions at the solid-liquid interface, that is,

$$u = w = 0 \quad \text{at} \quad r = r_0 \quad (5)$$

2. The vanishing of the total tangential and the normal force per unit area of the liquid-air interface, that is,

$$p_s = 0 \quad (6)$$

$$P_0 + p_n - T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 0 \quad \text{at} \quad r = r_0 \pm h \quad (7)$$

where h is the distance from the solid wall to the free surface,

$$\frac{1}{R_2} = \frac{h_{zz}}{(1 + h_z^2)^{3/2}} \quad \text{and} \quad \frac{1}{R_1} = \frac{\mp 1}{r(1 + h_z^2)^{3/2}}$$

are the two principal curvatures of the free surface, and p_s and p_n are, respectively, the tangential and the normal force exerted by the fluid on each unit area of the free surface. p_s and p_n are related to the components of the stress tensor in the cylindrical coordinate system by the relations

$$p_s = p_{12}\cos 2\phi + (1/2)(p_{22} - p_{11})\sin 2\phi$$
$$p_n = p_{22}\cos^2\phi + p_{11}\sin^2\phi - p_{12}\sin 2\phi$$
$$p_{11} = - P + 2\rho\nu(\partial V_z/\partial z)$$
$$p_{22} = - P + 2\rho\nu(\partial V_r/\partial r)$$
$$p_{12} = \rho\nu(\partial V_z/\partial r + \partial V_r/\partial z)$$
$$\tan\phi = h_z$$

where V_r and V_z are, respectively, the velocity components in the r and z directions. In addition, the following kinematic condition at the free surfaces $r = r_0 \pm h$ must be satisfied:

$$u = h_t + (\overline{W} + w)h_z \quad (8)$$

By use of the following dimensionless variables:

$$z = l\xi, \quad r = h_0\eta, \quad h = h_0 d, \quad t = l\tau/W_0$$
$$u = u'(h_0 W_0/l), \quad (\overline{W} + w) = W_0(W + w')$$
$$(\overline{P} + p) = \rho g h_0(\overline{P}' + p')$$

where l is the characteristic length in the axial direction $W_0 = \overline{W}_{\max}$ and introducing the stream function ψ related to the velocity perturbations by

$$w' = \psi_\eta/\eta, \quad u' = - \psi_\xi/\eta,$$

we can combine the equations in (1) to give

$$\eta^{-1}\psi_{\eta\eta\eta\eta} - 2\eta^{-2}\psi_{\eta\eta\eta} + 3\eta^{-3}\psi_{\eta\eta} - 3\eta^{-4}\psi_\eta$$
$$= \mu Re\,[\eta^{-1}\psi_{\tau\eta\eta} - \eta^{-2}\psi_{\tau\eta} - W\eta^{-2}\psi_{\eta\xi} - \eta^{-3}\psi_\eta\psi_{\eta\xi}$$
$$+ W\eta^{-1}\psi_{\eta\eta\xi} + \eta^{-2}\psi_\eta\psi_{\eta\eta\xi} + \eta^{-1}\psi_\xi(\eta^{-1}W_\eta - W_{\eta\eta}$$
$$- 3\eta^{-3}\psi_\eta + 3\eta^{-2}\psi_{\eta\eta} - \eta^{-1}\psi_{\eta\eta\eta})]$$
$$+ 2\mu^2[\eta^{-2}\psi_{\eta\xi\xi} - \eta^{-1}\psi_{\eta\eta\xi\xi}] + \mu^3 Re\,[\psi_{\tau\xi\xi}$$
$$+ (W + \eta^{-1}\psi_\eta)\psi_{\xi\xi\xi} + 2\eta^{-2}\psi_\xi\psi_{\xi\xi} - \eta^{-1}\psi_{\eta\xi\xi}\psi_\xi]$$
$$- \mu^4\psi_{\xi\xi\xi\xi} \quad (9)$$

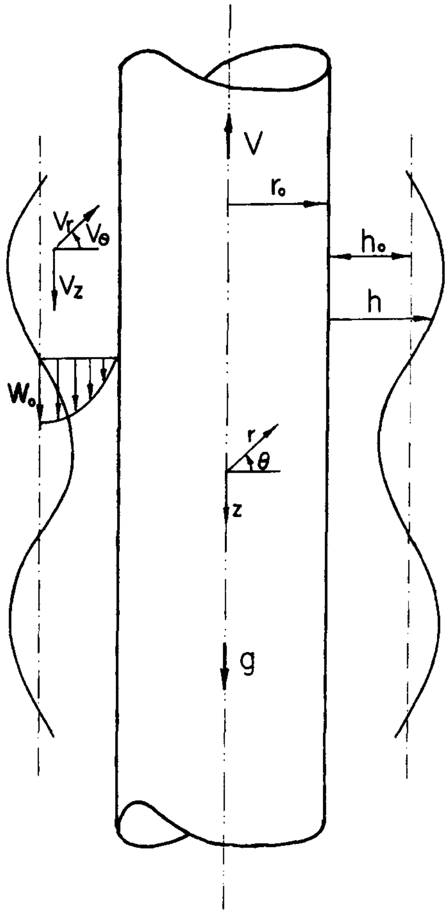

Fig. 1. Definition sketch.

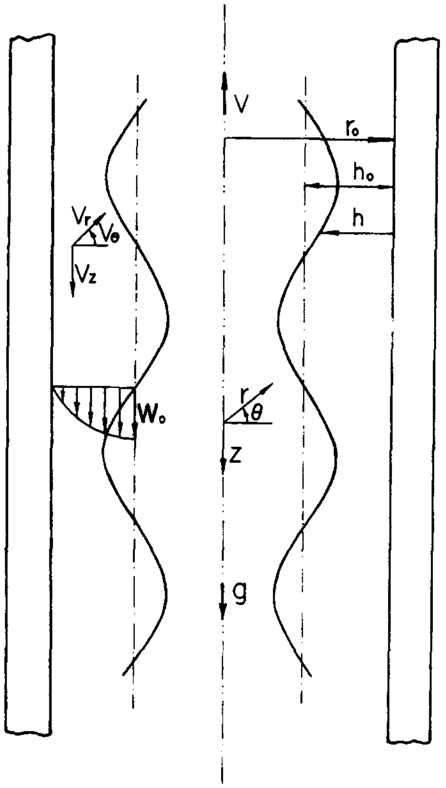

Fig. 2. Definition sketch.

where $\mu = h_0/l$ and $Re = W_0h_0/\nu$ is the Reynolds number.

Similarly the boundary conditions can be written in dimensionless forms in terms of the stream function. The no-slip condition demands

$$\psi_\eta = \psi_\xi = 0 \quad \text{at} \quad \eta = \eta_0 \qquad (10)$$

and Equations (6), (7), and (8) can be written, respectively, as

$$W_\eta - \eta^{-1}\psi_\eta + \eta^{-1}\psi_{\eta\eta} - \mu^2\eta^{-1}\psi_{\xi\xi} = -\mu^2 \frac{d_\xi}{1-\mu^2 d_\xi^2} \times (2\eta^{-2}\psi_\xi - 4\eta^{-1}\psi_{\xi\eta}) \qquad (11)$$

$$-p' + \mu \frac{\psi_{\eta\xi}}{\eta(1+\mu^2 d_\xi^2)} + \frac{W_e}{\eta(1+\mu^2 d_\xi^2)^{1/2}} - \frac{\mu^2 W_e d_{\xi\xi}}{(1+\mu^2 d_\xi^2)^{3/2}} + \mu^3 \frac{\psi_{\eta\xi} d_\xi^2}{\eta(1+\mu^2 d_\xi^2)} = 0 \qquad (12)$$

$$d_\tau + W d_\xi + \eta^{-1}\psi_\eta d_\xi + \eta^{-1}\psi_\xi = 0 \qquad (13)$$

at $\eta = \eta_0 \pm d$, where $\eta_0 = r_0/h_0$, $W_e = T/(\rho g h_0^2) \equiv$ Weber number and p' is related to ψ by the equation of motion

$$p_\xi' = 0.5_\mu^{-1}[\eta^{-1}\psi_{\eta\eta\eta} - \eta^{-2}\psi_{\eta\eta} + \eta^{-3}\psi_\eta] + 0.5\mu\eta^{-1}\psi_{\xi\xi\eta} - 0.5R_e[\eta^{-1}\psi_{\eta\tau} + (W + \eta^{-1}\psi_\eta)\eta^{-1}\psi_{\eta\xi} + \eta^{-1}\psi_\xi \times (W_\eta - \eta^{-2}\psi_\eta + \eta^{-1}\psi_{\eta\eta})] \qquad (14)$$

Note the dimensionless primary flow velocity W in the above equations is given by

$$W = 0.5(\eta_0^2 - \eta^2) + (\eta_0 \pm 1)^2 \ln(\eta/\eta_0)$$

SOLUTIONS, RESULTS, AND COMPARISONS WITH EXPERIMENTS

According to observations, the film instability exhibits itself as gravity capillary waves so long that $\mu = h_0/l << 1$, where l is taken here to be $\lambda/2\pi$, λ being the wavelength. Therefore, we expand the solution of Equation (9) in powers of the small parameter μ as

$$\psi = \sum_{n=0} \mu^n \psi^{(n)} \qquad (15)$$

The stream functions $\psi^{(n)}$ in the above expansion are determined by solving Equations (9) to (12) order by order with the method of regular perturbation. The substitution of the series solution thus obtained into the kinematic condition, Equation (13), gives a single nonlinear partial differential equation which governs the motion of the free surface. The derivation of this equation, that is, Equation (A2), is given in the Appendix.

During the initial stage of the instability, the wave amplitude is small, and thus we can write

$$d = 1 + \epsilon\zeta, \quad \epsilon << 1$$

Substituting the above equation into (A2) and neglecting terms smaller than $0(\epsilon)$, we have the following linearized equation of the free surfaces relative to the reference frame moving at the velocity $-\mathbf{i}_z V$:

$$\zeta_\tau + A_\pm(1)\zeta_\xi + \mu[\{R_e B_\pm(1) + W_e C_\pm(1)\}\zeta_{\xi\xi} + D_\pm(1)\zeta_{\xi\xi\xi\xi}] + 0(\mu^2) = 0,$$

where $A(1)$, $C(1)$, $E(1)$ and $F(1)$ are functions of η_0 defined in the Appendix. The equation of the free surfaces relative to the inertial frame can be obtained from the above equation with the Gallilei transformation $\xi = Z + V_0\tau$ and is given by

$$\zeta_\tau + [A_\pm(1) - V_0]\zeta_Z + \mu[\{R_e B_\pm(1) + W_e C_\pm(1)\}\zeta_{\xi\xi} + D(1)_\pm \xi_{ZZZZ}] = 0 \qquad (16)$$

where $V_0 = V/W_0$. The above equation admits the normal mode solution

$$\zeta = \delta \exp[i(Z - c\tau)]$$

where δ is the wave amplitude which is indeterminate in the framework of linear theory and $c = c_r + ic_i$ is the eigenvalue given by

$$c_r = A_\pm(1) - V \qquad (17)$$

$$c_i = \mu\{R_e B_\pm(1) + W_e[C_\pm(1) - 2M_\pm(1)\mu^2]\} \qquad (18)$$

where $M_\pm(1)$ is defined in the Appendix. In physical terms c_r is the absolute wave speed and c_i is the exponential growth rate or damping rate of the disturbance depending on if $c_i > 0$ or $c_i < 0$. The condition of neutral stability is therefore given by $c_i = 0$, that is

$$R_e = \frac{W_e}{B_\pm(1)}[2M_\pm(1)\mu^2 - C_\pm(1)] \qquad (19)$$

Equations (17) and (18) reduce to the known results of Benjamin (1957) and Yih (1963) in the limit of $V = 0$ and $\eta_0 \to \infty$ as they should. The neutral stability curves of a liquid film with $V = 0$, $W = 100$ are plotted in Figure 3 and Figure 4 for three different values of η_0. The film is stable in the region above each neutral curve since $c_i < 0$ there. For the rest of the region in the $\mu - R_e$ plane, $c_i > 0$ and the film is unstable. A few curves of constant damping and amplification rate are also given in the same figures. It is seen that each neutral curve intersects with the vertical axes $R_e = 0$ at a cut-off wave number μ_c. The cut-off wave number is easily obtained to the first-order approximation from Equation (19) to be

$$\mu_c = \frac{1}{\eta_0 \pm 1}$$

Any disturbance whose wave number is smaller than the cut-off wave number in a given film will make the flow unstable at all values of R_e. Moreover, it is seen from Figures 3 and 4 that the film becomes unstable with respect to the disturbance of a given wave number at a smaller R_e as η_0, the ratio of the wire or tube radius to the film thickness, decreases. To understand the physical reason for these predicted phenomena, we examine Equation (18) more closely. It can be shown from the definitions of $C_\pm(1)$ and $M_\pm(1)$ that $C_\pm(1) > 0$ and $M(1)_\pm > 0$. Thus, the terms $W_eC(1)$ and $-2M_\pm(1)W_e\mu^2$ in Equation (18) represent, respectively, destabilizing and

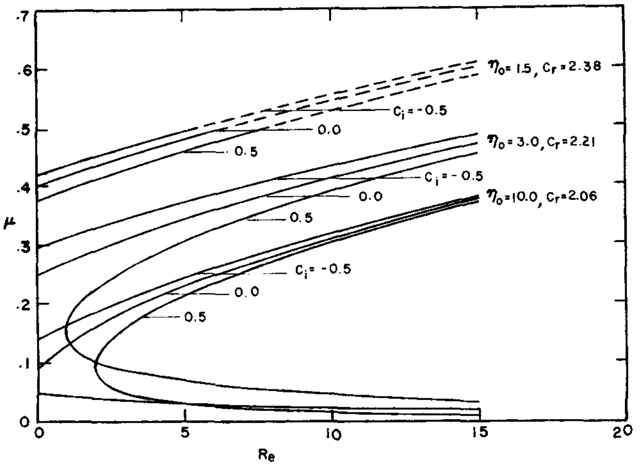

Fig. 3. Stability curves for $W_e = 100$, $V = 0$, and different values of wire radius.

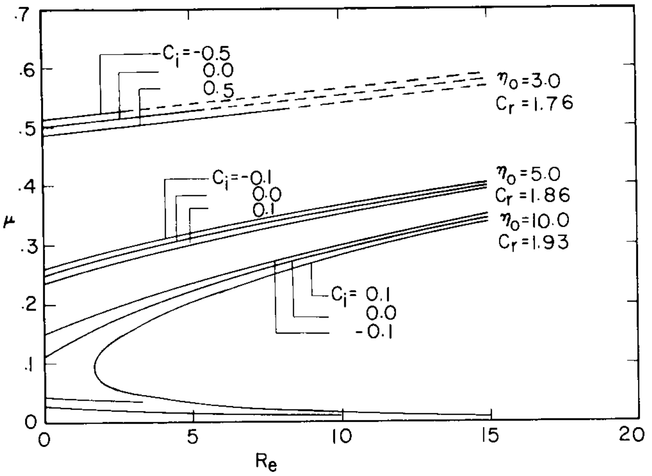

Fig. 4. Stability curves for W_e = 100, V = 0, and different values of tube radius.

stabilizing effects. On the other hand, it is seen from the derivation given in the Appendix that the terms $W_eC(1)$ and $-2M_\pm(1)W_e\mu^2$ arise, respectively, from the curvatures terms T/R_1 and T/R_2 in the free surface boundary condition. Note that R_2^{-1} is the free surface curvature associated with the surface displacement variation in the axial direction and R_1^{-1} is the curvature measured along a surface curve orthogonal to the wave profile. Therefore, the term $W_eC_\pm(1)$ represents capillary pinching which destabilizes the film, and the term $-2M_\pm(1)W_e\mu^2$ represents the capillary elasticity which opposes the surface wave formation. We further note that the sum $W_e[C_\pm(1) - 2M_\pm(1)\mu^2]$ in Equation (18) is positive if $\mu < \mu_c$. This implies that when $\mu < \mu_c$ the wavelength is so long that the capillary elasticity is entirely dominated by the capillary pinching which is independent of the wavelength, and thus the film is unstable no matter how small the destabilizing inertial effect represented by R_e is. On the other hand, the same sum is negative if $\mu > \mu_c$. This implies that if the wavelength is sufficiently small, then the capillary elasticity dominates over the capillary pinching and the film may be stable if R_e is sufficiently small. Comparing the stability curves for the film coating over the wire and the tube with the same value of η_0, we find that capillary pinching is more effective on the tube coating than on the wire coating. The wave velocity calculated from Equation (17) for various values of η_0 are also given in Figures 3 and 4. It is interesting to see that while the disturbance propagates at a speed less than twice the speed of the fluid at the free surface of the primary flow for the case of tube coating, the opposite is true for the case of wire coating. Moreover, the wave speed decreases as η_0 increases for the case of wire coating, but the reverse is true for the case of tube coating. Nevertheless, in the limit of $\eta_0 \to \infty$, $c_r \to 2$ for both cases as it should.

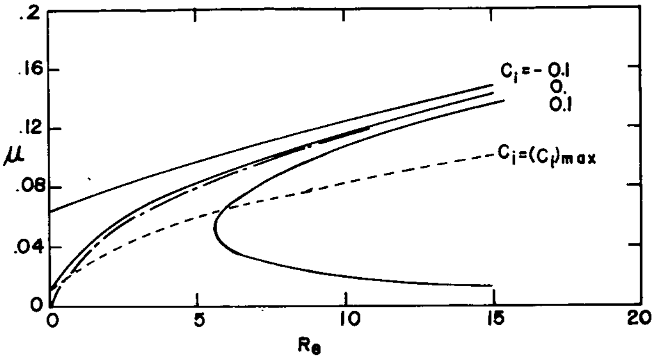

Fig. 5. Stability curves for the water film in Binnie's experiment; W_e = 594.96, η_0 = 118.75, ——·——, neutral curve obtained from Benjamin-Yih theory.

The comparisons between the present theoretical results and the experimental observation of Kapitza and Kapitza (1949) and Binnie (1957) for falling films are given in Table 1. In this table μ_0 is the wave number obtained from the neutral curve given by Equation (18) for each observed film of given W_e and R_e, μ_m the wave number of the most amplified disturbance in each experiment, and μ_e is the observed wave number. It appears that μ_e agrees more closely with $\mu_{\max}$ than μ_0. The predicted wave speed is smaller than the observed value in Binnie's experiment but larger than the measurements of Kapitza and Kapitza. However, the difference is less than 17%. The predicted stability curves for the film observed by Binnie are plotted in Figure 5. The neutral stability curve for the same film calculated from Benjamin's flat film theory is also included in Figure 5. The effect of the curvature is seen to be, for this particular case, indeed small as assumed by Benjamin since the radius of the wire is more than one-hundred times larger than the thickness of the film. However, if η_0 is of order one, then the curvature effect is no longer negligible and the present results must be used.

As was pointed out earlier, Goren's creeping thin annular thread is a special case of the present work. His numerical results for the case of $\mu = \mu_m$ are given together with his experimental points in Figures 6 and 7. For the case of negligibly small gravitational force, $R_e = 0$ and Equation (18) is reduced to

$$c_i = \mu W_e[C_\pm(1) - 2M_\pm(1)\mu^2]$$

The wave number of the most amplified disturbance is obtained from $\partial c_i/\partial\mu = 0$, that is,

$$C_\pm(1) - 6M_\pm(1)\mu_m^2 = 0$$

It follows that

$$\mu_m = \left[\frac{C(1)}{6M(1)}\right]^{1/2} = \frac{1}{\sqrt{3}(\eta_0 \pm 1)}$$

Table 1. Comparisons Between Theoretical and Experimental Results

Data	Authors	μ_e	μ_0	μ_m	c_r
Water at 15°C	Kapitza and Kapitza (1949)	0.092			1.76
$h_0 = 0.013$ cm, $r_0 = 1.25$ cm					
$R_e = 8.07$, $W_e = 463.3$	Present theory		0.1191	0.0842	2.009
Alcohol at 15°C	Kapitza and Kapitza (1949)	0.144			1.67
$h_0 = 0.0162$ cm, $r_0 = 1.25$ cm					
$R_e = 5.04$, $W_e = 107.2$	Present theory		0.1956	0.1384	2.009
Water at 19°C	Binnie (1957)	0.066			2.34
$h_0 = 0.0118$ cm, $r_0 = 1.40$ cm					
$R_e = 6.60$, $W_e = 594.96$	Present theory		0.0952	0.0672	2.006

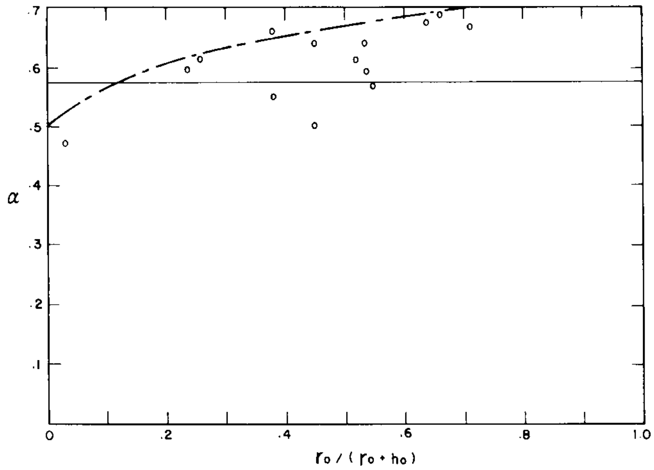

Fig. 6. Comparisons with Goren's results for wire coatings 0, Goren's experimental points; ——·——, Goren's numerical results; —— present results.

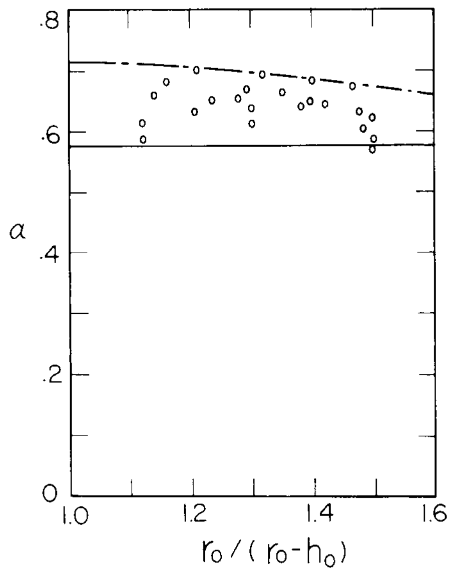

Fig. 7. Comparisons with Goren's results for tube coatings 0, Goren's experimental points; ——·——Goren's numerical results; ——— present results.

In order to make direct comparisons with Goren's results, we express the ratio $\alpha = 2\pi(r_0 \pm h_0)/\lambda$ in terms of μ,

$$\alpha = 2\pi(r_0 \pm h_0)/2\pi l_0$$
$$= \mu(\pi_0 \pm 1).$$

For the most amplified disturbance $\mu = \mu_m$ and the above ratio has the value

$$\alpha_m = 1/\sqrt{3}$$

in the first-order approximation for all values of η_0. It is seen from Figures 6 and 7 that the present results $\alpha_m = 1/\sqrt{3}$ bound Goren's experimental points from below and agree with Goren's theoretical results within the experimental scatter.

The instability in a film formed by withdrawal has been observed by Tallmadge and White (1968). Unfortunately, no data on the wavelengths of the drop formation have been reported. As a result, a comparison between the present theory and the experiment cannot be made for this case. However, an attempt will be made to explain a possible application of the present results to the qualitative design of a film coating process. As can be seen from Figures 3 and 4 and the accompanying discussion, the film coatings of a wire and a tube in the presence of disturbances of all possible wavelengths including an infinitely long one are unstable, no matter how small the R_e. However, the surface deformations corresponding to the extremely unstable long waves are usually not observed in practice since their amplification rate is smaller than that of the most amplified disturbance at the same R_e and their wavelengths are larger than the length of the tube or wire. Thus the maximum amplification rate $(c_i)_{\max}$ corresponding to the most amplified disturbance can be used as a useful reference in the process design. First the film thickness for given withdrawal velocity and coating liquid can be calculated from the known theories. Next, R_e and W_e for the film flow can be obtained from the calculated film thickness and the known fluid properties. The corresponding $(c_i)_{\max}$ can be determined from Equation (18). Within the time period τ, the most amplified disturbance multiplies its amplitude by a factor $\exp[(c_i)_{\max}\tau]$. Thus, the time τ_0 required for the disturbance to multiply by a tolerable factor $\exp[(c_i)_{\max}\tau_0]$ can be estimated. Within this time the coating process must be completed in order to keep the surface irregularities within the tolerable limit. This can be achieved either by limiting the length of the tube or wire to $c_r\tau_0$, where c_r is given by Equation (17), or by transferring them to a horizontal position before this limiting length is reached. The latter method is suggested by the observation that $R_eB \pm (1) > 0$ in Equation (18). This implies that the larger the relative velocity of the viscous fluid to the base the larger the amplification rate. Since the relative motion is caused by the gravity, a change of the film from the vertical to the horizontal direction will lead to a reduction in the relative velocity and thus to a reduction in the amplification rate. However, we have not proved this since our results are not applicable to the horizontal case except when $Re \to 0$. On the other hand, the coating length of the wire or tube can be lengthened by reducing the withdrawal velocity since then R_e and $(c_i)_{\max}$ are both reduced and τ_0 increased. The above estimates are bound to remain qualitative since the absolute wave amplitude remains unspecified in the linear theory. Only nonlinear theories can remove this arbitrariness in the value of the wave amplitude.

Finally, we should point out that the present analysis is relevant only to the stability of the Newtonian liquid film studied by the authors mentioned in the first section. In their experiments, the possible instabilities due to surface tension and temperature variations do not seem to be observed. These affects are most likely to be important in liquid films with very volatile solvent.

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NOTATION

$c = c_r + ic_i$ = complex wave speed
c_r = wave speed
c_i = temporal growth rate of disturbances
d = dimensionless film thickness, $d = h/h_0$
g = gravitational acceleration
h = dimensional variable film thickness
h_0 = dimensional constant film thickness of the primary flow
l = characteristic length in the axial direction
p_0 = atmospheric pressure
$P, \overline{P}, p$ = pressure, primary flow pressure, and nondimensional, $p = P/\rho g h_0$

r = radial distance from the wire (tube) axis
r_0 = radial distance from the axis to the solid wall
R = radius of curvature
R_e = Reynolds number = $W_0 h_0/\nu$
t = time
T = surface tension
u = velocity perturbation in the radial direction
V, V_0 = withdrawal speed, nondimensional, $V_0 = V/W_0$
$\mathbf{V}, \mathbf{v}$ = velocity, velocity perturbation
V_r, V_θ, V_z = velocity components in the r, θ and z directions
$\overline{W}, W$ = primary flow velocity, nondimensional, $\overline{W}/W_0$
W_0 = the speed of the fluid at the free surface in the primary flow
w = velocity perturbation in the axial direction
W_e = Weber number = $T/(\rho g h_0^2)$
z, Z = axial distance, nondimensional, z/l

Greek Letters

α = a ratio = $2(r_0 \pm h_0)/\lambda$
δ = wave amplitude
λ = wavelength
ϵ = maximum wave amplitude
θ = the angle defining the circumferential position in the cylindrical coordinates
ψ = stream function
η, η_0 = dimensionless radial distances: $\eta = r/h_0$, $\eta_0 = r_0/h_0$
ξ = dimensionless axial distance in a moving frame
ζ = dimensionless free surface perturbation, $\zeta = (d-1)/\epsilon$
μ = thin film parameter, $2\pi h_0/\lambda$
ρ = density
τ = dimensionless time, $t/(h_0/W_0)$
ν = kinematic viscosity

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APPENDIX—DERIVATION OF THE FREE SURFACE EQUATION

The equation of motion of a two-dimensional axisymmetric flow is given in Equation (9) in terms of the stream function. The boundary conditions for the liquid film flowing down the inner wall of a circular tube or the surface of a circular wire are given by Equations (10) to (13). The solution of this system for a wavy flow can be expanded as in Equation (15) in powers of the wave number.

Substituting Equation (15) in Equations (10) to (12) and retaining only the first-order terms, we have the following system:

$$\{\eta^{-1}[\eta(\eta^{-1}\psi_\eta{}^{(0)})_\eta]_\eta\}_\eta = 0$$
$$\psi_\eta{}^{(0)} = \psi_\xi{}^{(0)} = 0 \qquad \text{at} \quad \eta = \eta_0,$$
$$W_\eta - \eta^{-2}\psi_\eta{}^{(0)} + \eta^{-1}\psi_{\eta\eta}{}^{(0)} = 0$$
$$\eta^{-1}[\eta(\eta^{-1}\psi_\eta{}^{(0)})_\eta]_\eta + 2\mu d_\xi W_e/\eta^2 \quad \text{at} \quad \eta = \eta_0 \pm d,$$

where the subscripts denote partial differentiations.

The solution of the above system of equations is

$$\psi^{(0)} = 0.5\,[q^2 - (\eta_0 \pm 1)^2]\,[\eta^2 \ln(\eta/\eta_0) - 0.5(\eta^2 - \eta_0^2)] - [\eta^4 + \eta_0^4 + 2q^2(\eta^2 - \eta_0^2) - 2\eta_0^2\eta^2 - 4q^2\eta^2 \ln(\eta/\eta_0)] \cdot \{\mu W_e h_\xi/[8q^2]\}$$

where

$$q = \eta_0 \pm d$$

Substitution of the above solution into the kinematic condition, Equation (13), yields the first-order equation which describes the motion of the free surface.

$$d_\tau + A_\pm(d)d_\xi + N_\pm(d)\mu W_e d_\xi^2 + \mu W_e C(d) d_{\xi\xi} = 0 \tag{A1}$$

where

$$A_\pm(d) = \eta_0^2 - q^2 + 2q^2\ln(q/\eta_0)$$
$$N_\pm(d) = [(\eta_0/q)^4 + 4\ln(q/\eta_0) - 1]/4$$
$$C_\pm(d) = (q/8)\,[3 + (\eta_0/q)^4 - 4(\eta_0/q)^2 - 4\ln(q/\eta_0)]$$

The second-order solution can be obtained similarly. Substituting $\psi = \psi^{(0)} + \mu\psi^{(1)}$ into Equations (9) to (12) and neglecting terms smaller than $0(\mu)$, we have

$$\{\eta^{-1}[\eta(\eta^{-1}\psi_\eta{}^{(1)})_\eta]_\eta\}_\eta = R_e\,[\eta^{-1}\psi_{\tau\eta\eta}{}^{(0)} - \eta^{-1}\psi_{\eta\tau}{}^{(0)} - W\eta^{-2}\psi_{\eta\xi}{}^{(0)} - \eta^{-3}\psi_{\eta\xi}{}^{(0)} + W\psi_{\eta\eta\xi}{}^{(0)} + \eta^{-1}\psi_\eta{}^{(0)}\psi_{\eta\eta\xi}{}^{(0)} + \eta^{-1}\psi_\xi{}^{(0)}(\eta^{-1}W_\eta - W_{\eta\eta} - 3\eta^{-3}\psi_\eta{}^{(0)} + 3\eta^{-2}\psi_{\eta\eta}{}^{(0)} - \eta^{-1}\psi_{\eta\eta\eta}{}^{(0)})]$$

$$\psi_\eta{}^{(1)} = \psi_\xi{}^{(1)} = 0$$
$$[\eta^{-1}\psi_\eta{}^{(1)}]_\eta = 0$$
$$\eta^{-1}[\eta(\eta^{-1}\psi_\eta{}^{(1)})_\eta]_\eta = -2\mu^2 W_e d_{\xi\xi} + R_e d_\xi\,\{q^3\ln(q/\eta_0)\ \eta_0^2 q\ln(q/\eta_0) - 2q^3[\ln(q/\eta_0)]^2\}$$

The solution to the above differential system is

$$\psi^{(1)} = C_1\eta^4/16 + C_2\eta^2\,[0.5\ln(\eta/q) - 0.25 + C_3\eta^2/2 + C_4 + R_e d_\xi\{q^3\eta^2\,[n(\eta/q)]^2(\eta^2 - \eta_0^2)/8 - \eta_0^2\eta^4 q[\ln(\eta/q)]/16 + q^3\eta^2\,[\ln(\eta/q)](\eta_0^2/8 - \eta^2/4) + q^3\eta^2(3\eta^2 - \eta_0^2)/16 + 5\eta_0^2\eta^4 q/64 - q\eta^6/192\}$$

where

$$C_1 = R_e d_\xi\,\{q\ln Q(\eta_0^2 - q^2) - 2q^3(\ln Q)^2 + 0.5q(q^2 + \eta_0^2)\} - 2\mu^2 W_e d_{\xi\xi\xi}$$
$$C_2 = -R_e d_\xi q^3(q^2/8 + \eta_0^2/4) - 0.5\,q^2 C_1$$
$$C_3 = R_e d_\xi\,\eta_0^2[(\ln Q)^3(3 - \ln Q)/4 + (q\eta_0^2/4)\ln Q - 0.5\,q^3 - 7q\eta_0^2/32] - C_1\eta_0^2/4 - C_2\ln Q$$
$$C_4 = (R_e d_\xi \eta_0^4 q/8)\,[(q^2 + \eta_0^2/2)\ln Q - q^2 - 7\eta_0^2/12] + (\eta_0^2/2)(C_2/2 - C_3 - \eta_0^2 C_1/8 - C_2\ln Q)$$
$$Q = \eta_0/(\eta_0 \pm d).$$

Substituting $\psi = \psi^{(0)} + \mu\psi^{(1)}$ into the kinematic boundary condition gives the free surface equation

$$d_\tau + A_\pm(d)d_\xi + \mu\{W_e[N_\pm(d)d_\xi^2 + C_\pm(d)d_{\xi\xi}] + R_eB_\pm(d)d_{\xi\xi} + D_\pm d_{\xi\xi\xi\xi}\} + 0(\mu^2) = 0 \quad \text{(A2)}$$

where

$$B_\pm(d) = -0.5q^6(\ln Q)^3 + 5q^4(\eta_0^2 - q^2)(\ln Q)^2/8 + q^2\eta_0^2(17q^2 - 7\eta_0^2)(\ln Q)/16 + 59q^6/192 + 16\eta_0^6/192 - 15q^4\eta_0^2/64 - 9q^2\eta_0^4/64$$

$$D_\pm(d) = -2\mu^2W_eM_\pm(d)$$

$$M_\pm(d) = 3q^3/16 + \eta_0^3Q/16 - \eta_0^2q/4 + q^3\ln Q/4$$

In the limit of $\eta_0 \rightarrow \infty$, Equation (A2) reduces to the corresponding equation obtained by Benney (1965) for the film flow down an inclined plane. See also Lin (1974). Equation (A2) may be compared with (6.42) of Atherton & Homsy (1975).

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Enzyme Separation by Parametric Pumping

Affinity chromatography and parametric pumping were combined to reduce trypsin concentration in an aqueous solution. The trypsin inhibitor, chicken ovomucoid, was covalently bonded to Sepharose 4B beads. A solution was cycled over this packing in a column at a low *p*H in one direction followed by a high *p*H in the other direction. Trypsin retention was favored at the high *p*H and elution at the low *p*H. The decrease in trypsin concentration at one end of the column was fitted to an equation derived from the equilibrium parametric pumping model and was a function of the *p*H limits imposed on the column. Separation was much less than predicted by equilibrium data, but the equation based on trypsin reduction agreed with the α-chymotrypsin-trypsin separation.

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SCOPE

Parametric pumping is a separation technique based on the periodic movement of a fluid phase over a solid adsorbent bed and a coupled energy input into the system to effect the separation. The most common form of parametric pumping is one in which a packed bed of adsorbent, undergoing a cycling temperature change, is subjected to a synchronous, alternating, axial flow. The variation of adsorption selectivity with temperature and the synchronized relative motion of the fluid over the fixed phase makes possible the enrichment of a given component at one end of the column and its depletion at the other end. In the initial announcement, Wilhelm et al. (1966) described the separation of an aqueous NaCl solution into two fractions; one enriched and the other depleted in NaCl. The potentiality of the technique was demonstrated by Wilhelm and Sweed (1968) when they obtained a separation factor of 10^5 in a toluene-*n*-heptane-silica gel system under total reflux conditions. Using the same system, Chen et al. (1972, 1973) have obtained separations with both continuous and semi-continuous product withdrawal. Other separations accomplished by parametric pumping include argon-propane and ethane-propane (Jenczewski and Myers, 1970) boron isotopes (Schroeder and Hamrin, 1970), and Na^+ and K^+ in aqueous solution (Sabadell and Sweed, 1970). The latter separation was achieved by a recuperative-mode, *p*H pump in which *p*H control was maintained by acid addition at one of the end reservoirs.

Affinity chromatography is a new separation method for macromolecules such as enzymes of particular importance because of its great specificity. One example of this method employs an inhibitor attached to a solid support which will selectively and reversibly bind an enzyme

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