Hydrodynamic Stability of Marangoni Films

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The presence of thin films above the normal electrolyte meniscus on model gas diffusion electrodes and their importance in the operation of fuel cells has been demonstrated [*1*, *2*, *3*, *4*]. A probable explanation for the formation and maintenance of these films, often against the pull of gravity, has been recently suggested [*5*]. The suggestion was that upward directed surface tension gradients, induced either by concentration or temperature gradients, cause the films to rise spontaneously up vertical walls. This will in general cause convection patterns which result in net upward or downward motion of fluid, depending on the magnitude of the surface tension gradient. In analyzing the hydrodynamic problem the flow was postulated to be laminar and nonrippling, and was described by a simple extension of the classic Nusselt development.

It is possible that flowing films with concentration or temperature gradients in the direction of flow may be hydrodynamically unstable and that instability may arise either within the film or at its edges. We will consider here one possible type of instability arising within the film.

We postulate that random perturbations may cause local thickening of an initially flat flowing film. When the gravitational contribution to the flow is predominant such a local thickening will cause the surface elements to move downward in relation to those on either side. The surface tension in the thickened regions will then be relatively high and tend to cause flow into the thickened area, reinforcing the effect of the original disturbance. The high surface velocities in these thickened regions would in turn lead to rivulets of relatively cold liquid.

Qualitatively such rivulets can be obtained by dipping a clean, cold, polished metal plate into a beaker with warm water, withdrawing it quickly but allowing the lower edge to contact the warm water in the beaker. The rivulets may also be obtained by performing the classical experiments [Slattery and Stuckey (*6*)] of draining a liquid film instead of an isothermal liquid from a flat plate, but using a mixture of warm and cold fluid which has not yet come to thermal equilibrium. Irregularities in film thickness may easily be made visible by interferometry. The results of such an experiment are shown in Figure 1, and a sketch of the simple interferometer used is given in Figure 2.

Pronounced rippling of the type shown can have a profound effect on flow distribution in the film. This in turn can affect the heat and mass transfer characteristics of such varied apparatus as partial condensers, film coolers, wetted wall columns and gas diffusion electrodes.

The purpose of this paper is to formulate a hydrodynamic stability analysis for the above problem, that is, a thin film flowing over (up or down) a vertical solid plate of high heat capacity and thermal conductivity, with a constant downward directed temperature gradient (cold top, warm bottom).

The analysis will assume infinitesimal disturbances of the film thickness in the form of waves, whose amplitudes vary in the horizontal ($x - y$) plane. They can also be thought of as vertical, cylindrical roll cells, in analogy with the roll cells used by Sternling and Scriven in their treatment of interfacial turbulence due to the Marangoni effect (*7*). We shall seek conditions under which such disturbances cause increasing perturbations in the three fluid velocity components and temperature. We shall assume the perturbed surface to be nearly flat so that we may describe the effect of curvature by means of the approxima-

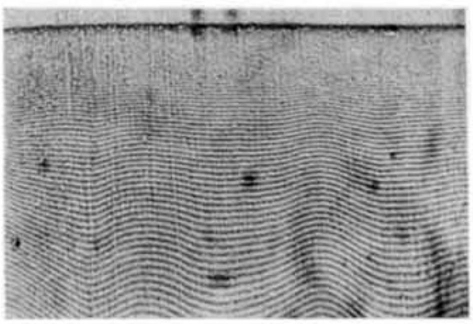

Fig. 1. Initiation of Marangoni instability in a draining liquid film.

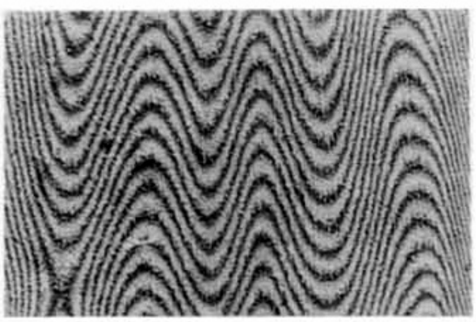

Fig. 1a. Fully developed Marangoni instability.

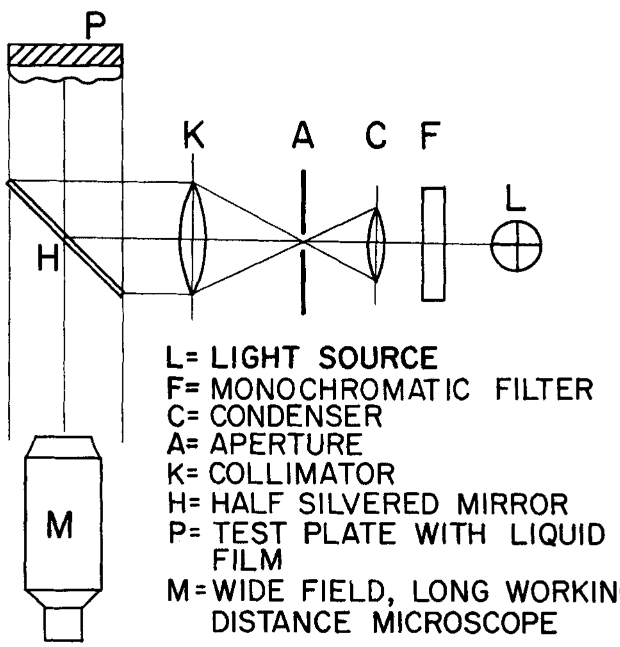

Fig. 2. Interference apparatus for observing thin films.

tions, introduced by Scriven and Sternling (8) in their analysis of Bénard cells, and we shall assume a clean surface with no adsorbed surfactants.

DESCRIPTION OF THE UNPERTURBED SYSTEM

The unperturbed system is indicated schematically in Figure 3. Here a liquid is in steady nonrippling flow down a long, wide, flat, vertical plate. The surface temperature of the plate varies linearly with z, and the free liquid surface is adiabatic. That is:

At

$$y = 0 \quad \overline{T} = \overline{G}_o z + \overline{T}_o \tag{1}$$

and

$$y = \overline{\delta} \quad \frac{\partial \overline{T}}{\partial y} = 0 \tag{2}$$

All properties of the liquid except surface tension are assumed temperature independent.

For these conditions the temperature gradient $\partial \overline{T}/\partial z$ is independent of y as well as z. It then follows that:

$$y = \overline{\delta}, \quad \frac{\partial \overline{T}}{\partial z} = \overline{G}_o \tag{3}$$

and

$$\frac{\partial \sigma}{\partial z} = \Gamma \overline{G}_o = \gamma \tag{4}$$

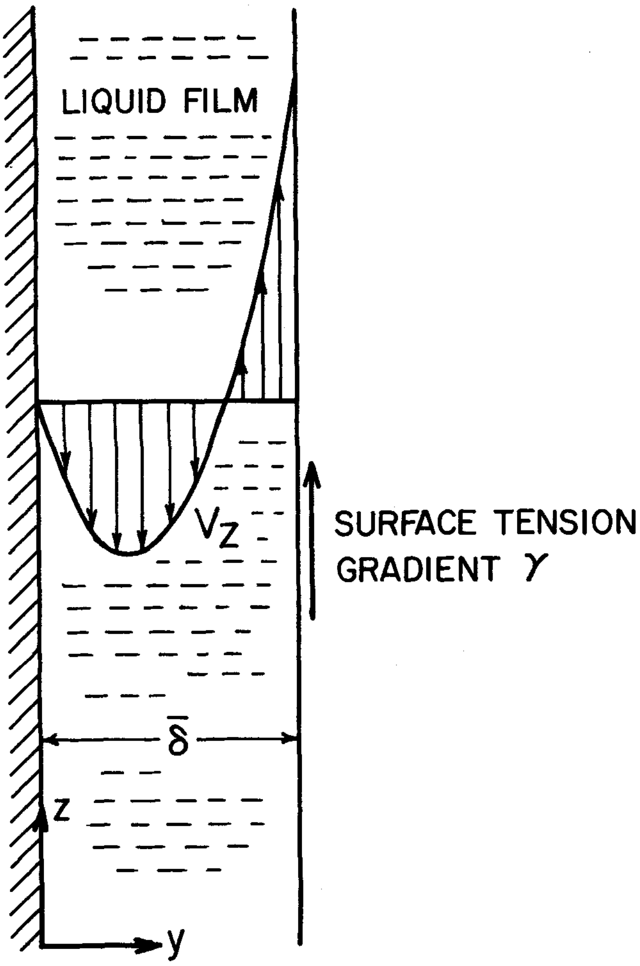

Fig. 3. Liquid film on a vertical solid surface. Gravity flow opposed by upward directed surface tension gradient.

where Γ is the rate of change of surface tension with temperature. The surface tension gradient results in a surface shear stress; written as

$$\overline{\tau}_{yz}\Big|_{y=\overline{\delta}} = -\mu \frac{\partial \overline{V}_z}{\partial y}\Big|_{y=\overline{\delta}} = -\gamma \tag{5}$$

It then follows that the velocity and temperature profiles have the form:

$$\overline{V}_x = \overline{V}_y = 0 \tag{6}$$

$$V_z = \left(\frac{\gamma\overline{\delta}}{\mu}\right)\eta - \left(\frac{\rho g \overline{\delta}^2}{\mu}\right)\left(\eta - \frac{1}{2}\eta^2\right) \tag{7}$$

$$\overline{T} = \overline{G}_o z + \overline{T}_o + \frac{\overline{G}_o \overline{\delta}^3}{\mu D_T}\left[\left(\frac{1}{3}\rho g \overline{\delta} - \frac{1}{2}\gamma\right)\eta + (\gamma - \rho g \overline{\delta})\frac{\eta^3}{6} + \rho g \overline{\delta}\frac{\eta^4}{24}\right] \tag{8†}$$

FORMAL DESCRIPTION OF THE PERTURBED SYSTEM

We now define perturbed variables by

$$\underline{V} = \underline{\mathbf{V}} + \underline{V}' \qquad \underline{V}^* = \underline{V}/\overline{V}_o \tag{9}$$

$$T = \overline{T} + T' \qquad T^* = T/\overline{T}_o \tag{10}$$

$$P = \overline{P} + P' \qquad P^* = P/\overline{P} \tag{11}$$

$$\delta = \overline{\delta} + \delta' \qquad \delta^* = \delta/\overline{\delta} \tag{12}$$

$$\nabla^* = \overline{\delta}\nabla$$

where the bold face quantities refer to the previously described unperturbed state and the primed quantities represent perturbations. Asterisks denote dimensionless quantities.

For small perturbations the equations of change describing this system may be written in the form (9):

$$(\nabla^* \cdot \underline{V}^{*\prime}) = 0 \tag{13}$$

$$\left[\frac{\overline{\delta}^2}{D_T t_o}\frac{\partial}{\partial \tau} - \nabla^{*2}\right]T^{*\prime} = -\frac{\overline{\delta}\overline{V}_o}{D_T}\left[\frac{\partial \overline{T}^*}{\partial \eta}V_y^{*\prime} + \frac{\partial T^{*\prime}}{\partial \zeta}\overline{V}_z^* + \frac{\partial \overline{T}^*}{\partial \zeta}V_z^{*\prime}\right] \tag{14}$$

$$\left[\frac{\overline{\delta}^2}{\nu t_o}\frac{\partial}{\partial \tau} - \nabla^{*2}\right]\nabla^{*2}\underline{V}^{*\prime} = 0 \tag{15}$$

$$\nabla^{*2}P^{*\prime} = 0 \tag{16}$$

Here we have used the dimensionless independent variables $\eta = y/\overline{\delta}$, $\zeta = z/\overline{\delta}$, and $\tau = t/t_o$. The method of obtaining above equations is discussed elsewhere (9).

The behavior of the liquid-gas interface is described by the following equations (8):

$$(\underline{\delta}_y \cdot \underline{V}^*) = V_y^* \quad \frac{\overline{\delta}}{\overline{V}_o t_o}\frac{\partial \delta^*}{\partial \tau} + (\underline{V}_{II}^* \cdot \nabla_{II}^* \delta^*) \tag{17}$$

$$\frac{1}{\mu \overline{V}_o}\nabla_{II}^* \sigma + \frac{\sigma}{\mu \overline{V}_o}\nabla_{II}^{*2}\delta^* \underline{\delta}_y = -\left(\frac{P\overline{\delta}}{\overline{V}_o \mu}\right)P^* \underline{\delta}_y + \underline{\delta}_y \cdot [\nabla^* \underline{V}^* + (\nabla^* \underline{V}^*)^\dagger] \tag{18}$$

where $\underline{II}$ denotes two dimensional vectors, in surface co-

† Equation (8) is the solution to the differential equation

$$\overline{V}_z \frac{\partial \overline{T}}{\partial z} = D_T \frac{\partial^2 \overline{T}}{\partial y^2}$$

with Equations (1) and (2) as boundary conditions.

ordinates (x, z) only.

Equation (17) is the kinematic condition, and Equation (18) is an interfacial equation of motion for a clean interface between immiscible fluids. It will be convenient to consider separately the normal component of Equation (18) on one hand, and its surface divergence on the other.

$$\frac{\sigma}{\mu \overline{V}_o} \nabla_{II}^{*2} \delta^* = -\left(\frac{\overline{P}\overline{\delta}}{\overline{V}_o \mu}\right) P^* + 2\frac{\partial V_y^*}{\partial \eta} \quad (19)$$

$$\frac{1}{\mu \overline{V}_o} \nabla_{II}^{*2} \sigma = \frac{\partial^2 V_y^*}{\partial \xi^2} + \frac{\partial^2 V_y^*}{\partial \zeta^2} - \frac{\partial^2 V_y^*}{\partial \eta^2} \quad (20)$$

Here we have defined $\xi = x/\overline{\delta}$.

These equations togther with the requirement of no slip at the wall and the assumption of zero shear stress in the gas are needed for integration of the equation of motion. The boundary conditions on temperature have already been specified.

ASSUMED FORM OF THE PERTURBATIONS

In accordance with the principles of linearized stability theory and analysis in terms of normal modes (9) we now assume the form of the primary disturbance, as a periodic variation on the film thickness along the horizontal x direction, with wave number α, a complex growth constant β, and an infinitesimal (and unspecified) amplitude b_o. Thus:

$$\delta^{*\prime} = \frac{b_o}{\overline{\delta}} e^{i\alpha\xi} e^{\beta\tau} \quad (21)$$

Note that α is a dimensionless wave number defined in terms of wavelength as $\alpha = 2\pi\overline{\delta}/\lambda$. This form of the film disturbance is consistent with the arguments presented in the introduction, and its form can be schematically shown in Figure 4 and compared with the photographs of Figure 1. The linearized stability theory requires that other dependent variables are of the same functional form in ξ and τ.

$$P^{*\prime} = P(\eta)\, e^{i\alpha\xi} e^{\beta\tau} \quad (22)$$

$$T^{*\prime} = T(\eta)\, e^{i\alpha\xi} e^{\beta\tau} \quad (23)$$

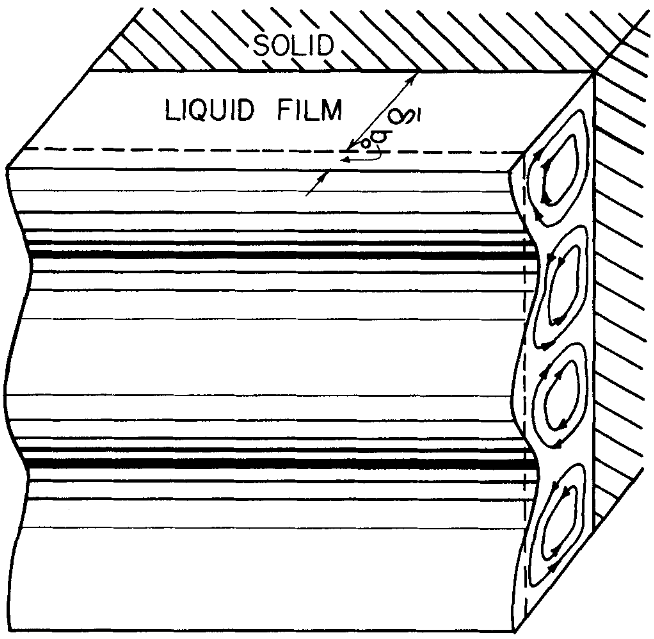

Fig. 4. Qualitative picture of vertical roll cell disturbances.

$$V_z^{*\prime} = V_z(\eta)\, e^{i\alpha\xi} e^{\beta\tau} \quad (24)$$

$$V_y^{*\prime} = V_y(\eta)\, e^{i\alpha\xi} e^{\beta\tau} \quad (25)$$

$$V_x^{*\prime} = V_x(\eta)\, i e^{i\alpha\xi} e^{\beta\tau} \quad (26)$$

No variations in the ζ-direction are considered. We only ask whether a variation in the $\xi - \eta$ $(x - y)$ plane will grow in place.

We are primarily concerned here with determining whether or not infinitesimal disturbances of the specified type will grow or decay. Hence, we shall seek conditions of marginal stability, that is conditions for which the real part of β is zero. For simplicity we will ignore the possibility of overstability (oscillatory behavior) and set the imaginary part of β to zero also. It is our belief that oscillatory disturbances should not be important in the very thin films, which we are primarily interested in, since they would require a very large rate of viscous dissipation of mechanical energy.

With the above assumed functional forms we see that the equations of change simplify greatly. The various operators can now be written as

$$\frac{\partial}{\partial \tau} = \beta = 0, \ \nabla_{II}^{*2} = -\alpha^2, \text{ and } \nabla^{*2} = D^2 - \alpha^2$$

$$\text{where } D = \frac{\partial}{\partial \eta}$$

Thus the equations of change become

$$-\alpha V_x(\eta) + DV_y(\eta) = 0 \quad (27)$$

$$[D^2 - \alpha^2]^2 V_x(\eta) = 0 \quad (28)$$

$$[D^2 - \alpha^2]^2 V_y(\eta) = 0 \quad (29)$$

$$[D^2 - \alpha^2]^2 V_z(\eta) = 0 \quad (30)$$

$$[D^2 - \alpha^2]\, T(\eta) = \frac{\overline{\delta}\overline{V}_o}{D_T}\left[\frac{\partial \overline{T}^*}{\partial \eta} V_y(\eta) + \frac{\partial \overline{T}^*}{\partial \zeta} V_z(\eta)\right] \quad (31)$$

$$[D^2 - \alpha^2]\, P(\eta) = 0 \quad (32)$$

We shall see later that Equation (30) can be further simplified.

We note that if Equations (29) and (30) are first solved for the velocity components $V_y(\eta)$ and $V_z(\eta)$, we can then solve the energy equation as an nonhomogeneous differential equation in $T(\eta)$ and η. The velocity component $V_x(\eta)$ can be determined by Equation (27).

THE NORMAL VELOCITY PROFILE $V_y(\eta)$

To solve Equation (29) we use the following four boundary conditions:

Boundary Condition 1 at

$$\eta = 0, V_y(\eta) = 0 \quad (33)$$

Boundary Condition 2 at

$$\eta = 0, \frac{\partial V_y(\eta)}{\partial \eta} = 0 \quad (34)$$

Boundary Condition 3 at

$$\eta = 1, V_y(\eta) = 0 \quad (35)$$

Boundary Condition 4 at

$$\eta = 1, D(D^2 - \alpha^2)V_y(\eta) = \frac{\sigma}{2\mu\overline{V}_o}\frac{b_o}{\overline{\delta}}\alpha^4 \quad (36)$$

The third and fourth boundary conditions come from the kinematic condition, Equation (17), and the normal component of the surface equation of motion, Equation

(19), respectively by Taylor expansion about $\eta = 1$. Equation (29) may now be integrated to give

$$V_y(\eta) = \frac{\sigma}{4\mu\overline{V}_o}\frac{b_o}{\overline{\delta}}\frac{\alpha^2}{\sinh\alpha}\left[\alpha\eta\cosh\alpha\eta - \sinh\alpha\eta - \left(\frac{\alpha}{\tanh\alpha} - 1\right)\eta\sinh\alpha\eta\right] \quad (37)$$

The x component of velocity may now be obtained from Equation (37) with the aid of the equation of continuity, Equation (27). Thus

$$V_x(\eta) = \frac{\sigma}{4\mu\overline{V}_o}\frac{b_o}{\overline{\delta}}\frac{\alpha}{\sinh\alpha}\left[\alpha^2\eta\sinh\alpha\eta - \left(\frac{\alpha}{\tanh\alpha} - 1\right)(\eta\alpha\cosh\alpha\eta + \sinh\alpha\eta)\right] \quad (38)$$

THE AXIAL VELOCITY PERTURBATION

If we write the z component of the equation of motion as

$$-\left(\frac{\overline{P}\overline{\delta}}{\mu\overline{V}_o}\right)\frac{\partial P^{*\prime}}{\partial\zeta} + \nabla^{*2}V_z^{*\prime} = 0 \quad (39)$$

instead of Equation (30), considerable simplification occurs. Since the perturbations are considered to vary only in the horizontal plane $\partial P^{*\prime}/\partial\zeta = 0$ then actually we only have to solve the equation:

$$[D^2 - \alpha^2]\,V_z(\eta) = 0 \quad (40)$$

having substituted the assumed form of $V_z^{*\prime}$. We note that this differential equation allows for z momentum transfer in the x direction as do Equations (28) to (30).

The first of the two boundary conditions needed to solve this equation is obtained directly from the requirement of no slip at the solid surface:

Boundary Condition 1 at

$$y = o, V_z(\eta) = 0 \quad (41)$$

The vertical shear on the free surface is the same as for the unperturbed state (no perturbation in the z direction). Defining the free surface by Taylor expansion about $\eta = 1$ as before, we get the second boundary condition:

Boundary Condition 2

$$\eta = 1, \frac{\partial V_z(\eta)}{\partial\eta} = -\frac{\overline{\delta}b_o\rho g}{\mu\overline{V}_o} \quad (42)$$

With these boundary conditions the solution of Equation (40) is:

$$V_z(\eta) = -\frac{\overline{\delta}b_o\rho g}{\mu\overline{V}_o\alpha\cosh\alpha}\sinh\alpha\eta \quad (43)$$

THE TEMPERATURE PROFILE

We are now in a position to solve the differential equation for the temperature profile:

$$[D^2 - \alpha^2]T(\eta) = \frac{\overline{\delta}V_o}{D_T}\left[\frac{\partial\overline{T}^*}{\partial\eta}V_y(\eta) + \frac{\overline{\delta}\overline{G}_o}{\overline{T}_o}V_z(\eta)\right] = F(\eta) \quad (44)$$

Knowing the unperturbed temperature profile and the perturbation velocities $V_y(\eta)$ and $V_z(\eta)$ we can show that $F(\eta)$ can be written as

$$F(\eta) = \frac{\overline{G}_o b_o}{\overline{T}_o}\frac{\alpha^2}{4N_{cr}\sinh\alpha}\left[\left\{\left(\frac{1}{3}N_d - \frac{1}{2}N_{Ma}\right) + (N_{Ma} - N_a)\frac{\eta^2}{2} + N_d\frac{\eta^3}{6}\right\}\cdot\left\{\alpha\eta\cosh\alpha\eta - \sinh\alpha\eta - \left(\frac{\alpha}{\tanh\alpha} - 1\right)\eta\sinh\alpha\eta\right\} - 4N_d N_{cr}\frac{1}{\alpha^3}\tanh\alpha\cdot\sinh\alpha\eta\right] \quad (45)$$

where N_{Ma} and N_{cr} are the Marangoni and crispation number defined by Scriven and Sterling [8] as $N_{Ma} = \frac{\gamma\overline{\delta}^2}{\mu D_T} = \frac{\Gamma\overline{G}_o\overline{\delta}^2}{\mu D_T}$ and $N_{cr} = \frac{\mu D_T}{\sigma\overline{\delta}}$. The dimensionless number N_d is defined as $N_d = \frac{\rho g\overline{\delta}^3}{\mu D_T}$ which can be expressed as a product of film Froude number, Reynolds number and Prandtl number $N_d = N_{Fr}N_{Re}^2N_{Pr}$. These three numbers are defined as $N_{Fr} = \frac{g\overline{\delta}}{\overline{V}_o^2}$; $N_{Re} = \frac{\rho\overline{\delta}\overline{V}_o}{\mu}$ and $N_{Pr} = \frac{\mu}{D_T\rho}$.

This combination can be considered to give the effect of laminar gravity flow on heat transfer in the thin film. The crispation number gives an inverse measure of the rigidity of the surface, and the Marangoni number gives the effect of surface tension gradients on the velocity profile and the heat transfer in the film.

The two boundary conditions needed for solution of the above differential equation are:

Boundary Condition 1 at

$$\eta = 0, T(\eta) = 0 \quad (46)$$

Boundary Condition 2 at

$$\eta = 1, DT(\eta) = 0 \quad (47)$$

The first assumes no perturbations at the solid, that is, it assumes high heat capacity and thermal conductivity in the solid. The second boundary condition is based on the assumption of an effectively insulated free surface.

A homogeneous solution to Equation (44) can easily be found and a particular solution can be obtained by the method of undetermined coefficients, since it can only involve products of the forms $\eta^5\cosh\eta$ and $n^5\sinh\alpha\eta$ and lower powers of η. The complete solution is of the form:

$$T(\eta) = \frac{\overline{G}_o b_o}{\overline{T}_o}\frac{\alpha^2}{4\sinh\alpha\, N_{cr}}[A\cosh\alpha\eta + B\sinh\alpha\eta + C\eta^5\sinh\alpha\eta + D\eta^5\cosh\alpha\eta + E\eta^4\sinh\alpha\eta + F\eta^4\cosh\alpha\eta + G\eta^3\sinh\alpha\eta + H\eta^3\cosh\alpha\eta + I\eta^2\sinh\alpha\eta + J\eta^2\cosh\alpha\eta + K\eta\sinh\alpha\eta + L\eta\cosh\alpha\eta] \quad (48)$$

where

$$A = 0$$

$$B = -\left[(C + E + G + I + K) + (D + F + H + J + L)\tanh\alpha + (5D + 4F + 3H + 2J + L)\frac{1}{\alpha}\right.$$

$$+ (5C + 4E + 3G + 2I + K)\frac{\tanh\alpha}{\alpha}\Big]$$

$$C = \frac{1}{60}N_d$$

$$D = -\frac{S}{60\alpha}N_d$$

$$E = \left(\frac{S}{24\alpha^2} - \frac{1}{16}\right)N_d + \frac{1}{16}N_{Ma}$$

$$F = \frac{1}{16\alpha}(S-1)N_d - \frac{S}{16\alpha}N_{Ma}$$

$$G = \frac{1}{8\alpha^2}(1-S)N_d + \frac{S}{8\alpha^2}N_{Ma}$$

$$H = \left(\frac{5}{24\alpha} - \frac{S}{12\alpha^3}\right)N_d - \frac{5}{24\alpha}N_{Ma}$$

$$I = \left(\frac{1}{12} - \frac{5}{16\alpha^2} + \frac{S}{8\alpha^4}\right)N_d + \left(\frac{5}{16\alpha^2} - \frac{1}{8}\right)N_{Ma}$$

$$J = \left(\frac{3S}{16\alpha^3} - \frac{S}{12\alpha} - \frac{3}{16\alpha^3}\right)N_d + \left(\frac{S}{8\alpha} - \frac{3S}{16\alpha^3}\right)N_{Ma}$$

$$K = \left(\frac{3}{16\alpha^4} + \frac{S}{12\alpha^2} - \frac{3S}{16\alpha^4}\right)N_d + \left(\frac{3S}{16\alpha^4} - \frac{S}{8\alpha^2}\right)N_{Ma}$$

$$L = \left(\frac{5}{16\alpha^3} - \frac{1}{4\alpha} - \frac{S}{8\alpha^5}\right)N_d + \left(\frac{3}{8\alpha} - \frac{5}{16\alpha^3}\right)N_{Ma} - \frac{2}{\alpha^4}\tanh\alpha\, N_d N_{cr}$$

Here we have defined $S = \dfrac{\alpha}{\tanh\alpha} - 1$. Thus all the coefficients are determined as functions of dimensionless numbers and wave number α.

THE CHARACTERISTIC EQUATION

Expressions have now been obtained for the temperature and velocity profiles in terms of *wave numbers and dimensionless groups for the condition of neutral stability.* It remains to complete the characteristic value problem by determining α of neutral stability for any system and operating conditions. This can be done by substituting the temperature and velocity expressions into Equation (20), the surface divergence of the surface equation of motion that we have not used so far.

Assuming the surface tension to be a linear function of temperature:

$$\sigma = \Gamma(T - \overline{T}_o) + \sigma_o \qquad (49)$$

and using the assumed form of the disturbances Equation (20) becomes

$$T(\eta) = \frac{\mu \overline{V}_o}{\overline{T}_o \Gamma \alpha^2}(D^2 + \alpha^2)V_y(\eta) \qquad (50)$$

Substituting for $T(\eta)$ and $V_y(\eta)$ we obtain:

$$[(B + C + E + G + I + K)\tanh^2\alpha + (D + F + H + J + L)\tanh\alpha] = \frac{2}{N_{Ma}}\left[\frac{\tanh\alpha}{\alpha} - \frac{1}{\cosh^2\alpha}\right] \qquad (51)$$

Again substituting for coefficients and rearranging we can finally obtain the form:

$$\begin{aligned} &N_{Ma}^2[15\alpha^6 - 45\alpha^4 + \tanh\alpha\,(25\alpha^5 + 60\alpha^3) \\ &\quad + \tanh^2\alpha\,(-15\alpha^6 + 45\alpha^4 - 60\alpha^2) \\ &\quad + \tanh^3\alpha\,(-25\alpha^5 - 60\alpha^3 + 45\alpha)] \\ &\quad + N_{Ma}N_d\,[-9\alpha^6 + 25\alpha^4 - 30\alpha^2 \\ &\quad + \tanh\alpha\,(-16\alpha^5 + 25\alpha^3 + 60\alpha) \\ &\quad + \tanh^2\alpha\,(9\alpha^6 - 25\alpha^4 + 60\alpha^2 - 30) \\ &\quad + \tanh^3\alpha\,(16\alpha^5 + 25\alpha^3 - 60\alpha) \\ &\quad + 480\,N_{cr}\,(\alpha^2\tanh^4\alpha - \alpha\tanh^3\alpha - \alpha^2\tanh^2\alpha)] \\ &\quad - 480\left[\alpha^5\tanh\alpha - \frac{\alpha^6}{\cosh^2\alpha}\right] = 0 \end{aligned} \qquad (52)$$

This equation is the characteristic equation for marginal stability ($\beta = 0$). It implicitly relates the wave number α to the physical properties of the film and the operating conditions through the various dimensionless groups. It will give us the loci of Marangoni numbers or surface tension gradients vs. wave numbers, which separate regions of hydrodynamic stability from regions of instability.

As can be expected the stability criterion is independent of the amplitude of the disturbance b_o, and any other unspecified reference quantity like $\overline{V}_o$ or $\overline{T}_o$, as they have all dropped out of Equation (52). We also note that since $\tanh\alpha$ is an odd function in α and since all odd powers of α in the equation are multiplied by odd powers of $\tanh\alpha$, then the equation as a whole is even and independent of the sign of α and the origin of the x coordinate. All of these features, of course, can be expected on physical grounds.

LOCI OF NEUTRALLY STABLE DISTURBANCES

We now can map the loci of neutrally stable disturbances for any given fluid and film thickness by solving Equation (52) for γ in terms of assumed real values of α.

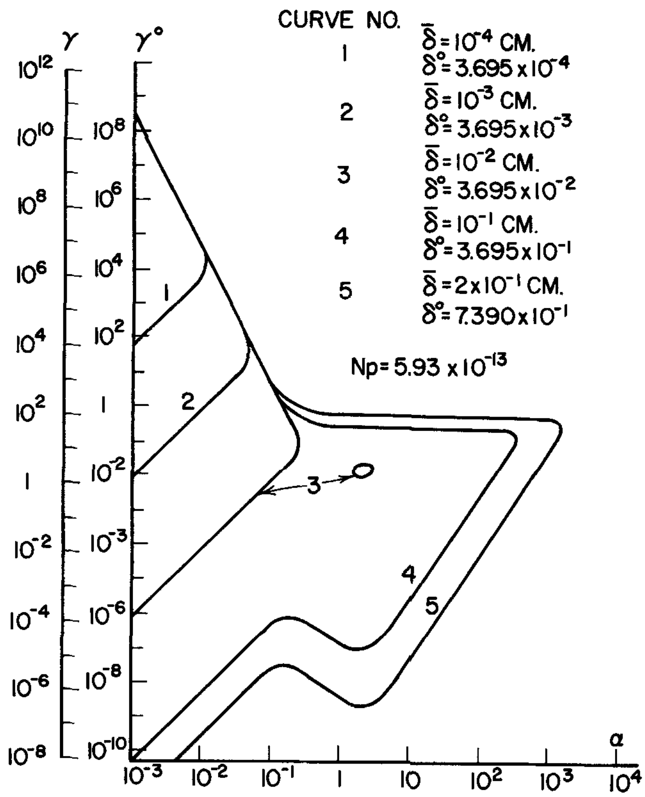

Fig. 5. Loci of neutral stability for water films of various thicknesses.

We choose here to work with a dimensionless surface tension gradient defined as $\gamma^o = \gamma/\sqrt{\rho g \sigma} = N_{Ma}\sqrt{N_{cr}/N_d}$. It is seen that Equation (52) has the form:

$$a\gamma^{o2} + b\gamma^o + c = o$$

where the coefficients a, b, and c, are functions of the dimensionless film thickness $\delta^o = \bar{\delta}\sqrt{\rho g/\sigma} = \sqrt{N_d N_{cr}}$ and a physical property ratio, $N_p = \mu^2 D^2_T \rho g/\sigma^3$, as well as the dimensionless wave number α. It is clear that real values of γ^o are possible for a limited range of α for which the discriminant $b^2 - 4ac$ is positive. We also see that γ^o is a double valued function of α for neutral stability.

The form of the relation between γ^o and α is shown in Figure 5 for several thicknesses of water films, and in Figure 6 for 2 mm. films of two different thermal diffusivities. The unstable region is the one enclosed by the neutral stability locus and is of finite extent. Stable operation is always predicted for sufficiently low or sufficiently high surface tension gradient at any α, and for sufficiently large α at any γ^o. We find for example in the case of 1μ water films, that only wave numbers of less than about 10^{-2} can be expected to give instability at any surface tension gradient, and for surface tension gradients smaller than 10^4 or larger than 10^{11} all α's larger than 10^{-3} give stable operation.

This behavior can be explained qualitatively in rather simple arguments. If γ^o is very small (or zero) the driving force for instability is essentially absent or has dissipated fast enough so that the system is stable. For intermediate values, in which the surface velocity is affected both by gravitational and surface tension effects as shown in Figure 7*a*, any chance thickening leads to downward flow of high surface tension liquid, which is a potentially unstable situation as discussed before. At very large positive γ^o the flow will be relatively unaffected by gravitational forces and directed upward with a nearly constant velocity gradient $\partial V_z/\partial y \doteq \gamma/\mu$ as shown in Figure 7*b*. The result of chance

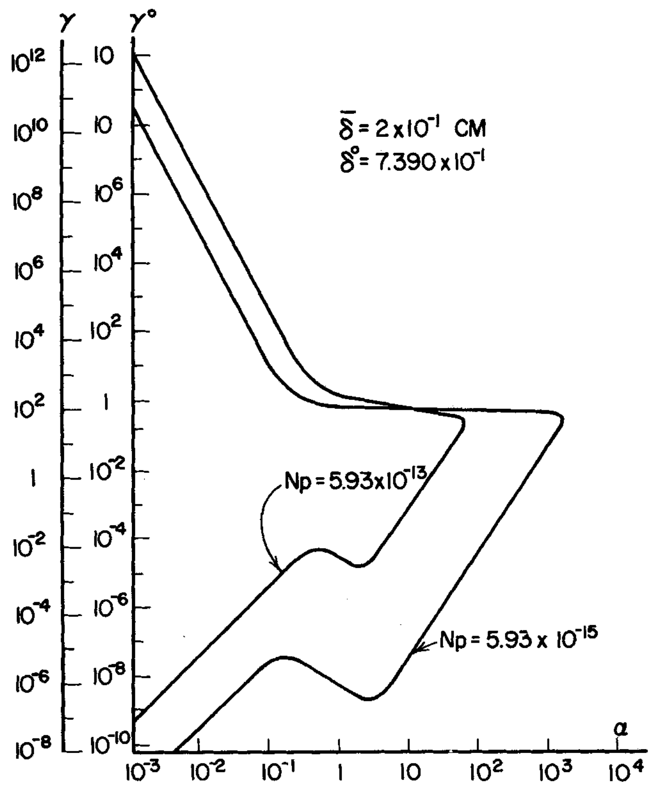

Fig. 6. Loci of neutral stability for 2mm. films of different thermal diffusivities.

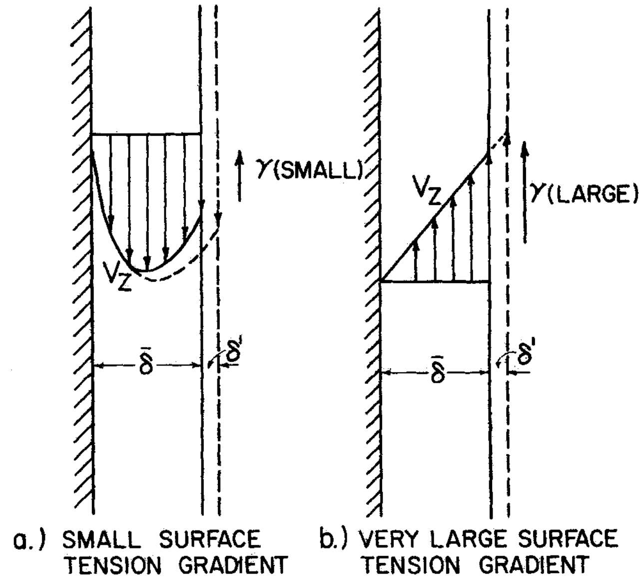

Fig. 7. Comparison of perturbed velocity profile for small and large surface tension gradient.

thickening now is to increase the upward surface velocity (since the velocity gradient must remain the same), which brings fluid of lower surface tension upwards and leads to a stable situation; that is, lateral surface tension gradients now tend to decrease the thickening. Finally, if the wave numbers of the disturbance are sufficiently large, lateral temperature gradients caused by any flow disturbance will also be large and lateral surface tension gradients will be rapidly dissipated by heat conduction. Hence the general form of the curves in Figure 5 seems reasonable. When the thermal conductivity is varied, the shift of the curves in Figure 6 is also reasonable since we expect to find higher values of neutrally stable γ^o when the temperature variations are dissipated faster by conduction.

The presence of further regions of instability for very high α cannot be ruled out. They appear unlikely, however, in view of the above physical arguments and also because the viscous dissipation of mechanical energy becomes large for short waves.

The possibility of oscillatory disturbances, not investigated here, also seems unlikely for thin films for reasons discussed before. It still remains to determine the importance of the long wave length (small α) disturbances which are predicted to cause instability even at modest positive γ^o. In principle these disturbances should become unimportant if they are sufficiently large, because they are slow growing due to inertial effects and because they may exceed the dimensions of the physical system.

As an example we consider a 1μ water film in which γ is just sufficient enough to cause the net flow to be zero. Here [5] $\bar{\delta} = 3/2\ \gamma/\rho g$ and it may be shown that $\gamma^o = 2.46 \cdot 10^{-4}$. The minimum unstable wavelength corresponding to $\alpha = 10^{-6}$ is then

$$\lambda_{\min} = \frac{2\pi\bar{\delta}}{\alpha} = \frac{2\pi \times 10^{-4}}{10^{-6}} = 2\pi \text{ meters}$$

This is much larger than any probable film width. For a 10μ film the corresponding γ^o is 2.46×10^{-3} and this system is marginally stable for $\alpha \doteq 6 \cdot 10^4$ or $\lambda = \dfrac{2\pi \times 10^{-3}}{6.10^{-4}} \doteq 10$ cm. which still is large in terms of most systems where such film can be expected. Thicker films as can be expected in film coolers, condensers, wetted wall columns and similar equipment would be unstable with respect to most values of α in the presence of even small surface tension gradients. Thus a millimeter thick water film disturbed with wavelength 1 cm. is unstable even if γ^o is as low as 10^{-5}.

No attempt has been made at determining the fastest growing α. This involves solving the system for real values of β not equal to zero and then maximizing with respect to α.

Finally we want to reemphasize that the preceding analysis is restricted to two dimensional disturbances of the particular kind described, and does not rule out the possibility that the system may be less stable with respect to three dimensional ones or, in general, other forms of disturbances. The chosen form is based on qualitative experimental observation and what looks to us the most reasonable type of unstable disturbance for the system.

CONCLUSIONS

In general we may conclude that unstable disturbances of the type postulated are possible over a restricted range of operating conditions. In particular the analysis has led to the following conclusions:

1. All thin films for which temperature induced surface tension gradient opposes gravitational flow are unstable with respect to disturbances of large enough wavelengths.
2. For any film thickness there is a minimum critical wave number above which the system is stable for all surface tension gradients.
3. The films tend to be stable for both low and very large surface tension gradients.
4. Films of higher thermal conductivity tend to be more stable.
5. Thicker films are much more sensitive to the type of instability considered than thin ones.
6. The very thin films believed to occur in gas diffusion electrodes are unlikely to be subject to this type of unstability.

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NOTATION

A–L = constants of integration
a, b, c = constants of the characteristic equation written as a quadratic in dimensionless surface tension gradients
b_o = unspecified infinitesimal disturbances on film thickness, (cm.)
D = $\partial/\partial\eta$ (cm.$^{-1}$)
D_T = thermal diffusivity (sq.cm./sec.)
$F(\eta)$ = functional form of the inhomogeneous part of the differential equation for temperature profile
$\underline{g}$ = gravitational acceleration (cm./sec.^{2})
$\overline{G}_o$ = unperturbed axial temperature gradient, (°C./cm.)
i = imaginary index
P = pressure (dyne/sq.cm.)
$\overline{P}$ = unperturbed pressure (dyne/sq.cm.)
P' = perturbation on pressure (dyne/sq.cm.)
P^*, $P^{*\prime}$ = dimensionless pressure and perturbation on pressure
S = $\alpha/\tanh\alpha - 1$
T = temperature (°C.)
$\overline{T}$ = unperturbed temperature (°C.)
T' = perturbation on temperature (°C.)
$\overline{T}_o$ = arbitrary reference temperature (°C.)
T^*, $T^{*\prime}$ = dimensionless temperature and unperturbed temperature
$T(\eta)$ = functional dependence of dimensionless perturbed temperature on η
t_o = arbitrary reference time (sec.)
V = velocity vector (cm./sec.)
$\overline{V}$ = unperturbed velocity vector (cm./sec.)
V' = perturbation velocity vector (cm./sec.)
$\overline{V}_o$ = arbitrary reference velocity (cm./sec.)
$V^*, \overline{V}^*, V^{*\prime}$ = dimensionless velocity vectors
$\overline{V}_x, \overline{V}_y, \overline{V}_z$ = unperturbed velocity components (cm./sec.)
V_x^*, V_y^*, V_z^* = dimensionless velocity components
$V_x^{*\prime}$, $V_y^{*\prime}$, $V_z^{*\prime}$ = dimensionless perturbed velocity components
$V_x(\eta)$, $V_y(\eta)$, $V_z(\eta)$ = functional dependence of dimensionless velocity components on η
V_{II}^* = dimensionless velocity vector in surface coordinates
x, y, z = cartesian coordinates (cm.)

Dimensionless Numbers

N_{cr} = $\mu D_T/\sigma\overline{\delta}$ = Crispation number
N_{Ma} = $\gamma\overline{\delta}^2/\mu D_T$ = Marangoni number
N_d = $\rho g\overline{\delta}^3/\mu D_T$ = $N_{Fr}N_{Re}{}^2N_{Pr}$ = dimensionless number
N_p = $\mu^2 D_T{}^2\rho g/\sigma^3$ = physical property group
N_{Fr} = $g\overline{\delta}/\overline{V}_o{}^2$ = Froude number
N_{Re} = $\rho\overline{\delta}\,\overline{V}_o/\mu$ = Reynolds number
N_{Pr} = $\mu/D_T\rho$ = Prandtl number

Greek Letters

α = $2\pi\overline{\delta}/\lambda$ = dimensionless wave number
β = complex growth constant (sec.$^{-1}$)
γ = surface tension gradient (dyne/sq.cm.)
γ^o = $\gamma/\sqrt{\rho g\sigma}$ = dimensionless surface tension gradient
δ = local film thickness (cm.)
$\overline{\delta}$ = unperturbed film thickness (cm.)
δ' = perturbed film thickness (cm.)
δ^*, $\delta^{*\prime}$ = dimensionless film thickness and perturbation on film thickness
δ^o = $\overline{\delta}\sqrt{\rho g/\sigma}$ = dimensionless film thickness
$\underline{\delta}_x, \underline{\delta}_y, \underline{\delta}_z$ = cartesian unit vectors
∇ = gradient vector (cm.$^{-1}$)
∇_{II} = surface gradient vector (cm.$^{-1}$)
∇^*, $\nabla_{II}{}^*$ = dimensionless gradient vectors
ρ = density (g./cc.)
μ = viscosity (poise)
σ = surface tension (dyne/cm.)
Γ = temperature coefficient of surface tension (dyne/cm. °C.)
ξ = x/δ = dimensionless cartesian coordinate
η = y/δ = dimensionless cartesian coordinate
ζ = z/δ = dimensionless cartesian coordinate
τ = dimensionless time
$\overline{\tau}_{yz}$ = unperturbed shear stress

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