Stability of Falling Liquid Films. Effect of Interface and Interfacial Mass Transport

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Previous studies of the effect of surface active agents on the stability of falling liquid films indicated that surface elasticity was primarily responsible for the observed stabilizing action. Since the elastic nature of a surface is thought to be controlled by interface and interfacial mass transport, it is of interest to understand how these transport rates affect the stability of the liquid film. The analysis for both soluble and insoluble surface active agents is presented in terms of a perturbation solution of the Orr-Sommerfeld equation.

DISCUSSION

It is an established fact that the presence of surface active agents may alter the stability of an interface. Levich (*7*, p. 608) has pointed out that the striking effect of surface active agents on wave motion was known to the ancient Greeks; nearly a century ago Reynolds (*12*) commented on the phenomenon and correctly deduced the cause; and in the last decade this phenomenon has been observed during the course of gas absorption studies in falling liquid films (*4, 8, 11*). Recent papers (*1, 13*) have confirmed Reynolds' early deduction that the stabilizing action results from surface tension variations. Since these surface tension variations are presumably caused by variations in surface concentration, the interface (diffusive and convective transport on the surface) and interfacial (transport between the surface and bulk fluids) mass transport rates play an important role in the stability problem. The opinion taken in this paper is that the surface elasticity is compositional as opposed to structural in nature; however, structural elasticity may be an important factor if the surface cannot be treated as a two-dimensional Newtonian fluid.

The physics of the problem under investigation may be clarified by examining the equations governing the transport of mass and momentum for the bulk and surface fluids shown in Figure 1. These are *illustrative* equations, presented only to clarify the problem under investigation. The analysis of the mass and momentum equations for the bulk fluid is straightforward; however, the mass and momentum equations for a wavy surface have not yet been treated in a precise fashion. Earlier intuitive studies of these equations for the case of small disturbances (*1, 13*) are correct, but it seems reasonable that an exact formulation of the surface conditions should be available in the literature. This formulation is presented in the Appendix.

PRIMARY FLOW

The configuration under investigation is illustrated in Figures 2 and 3. The primary flow (the stability of which we wish to analyze) is given by*

$$\bar{u}(y) = u_o\,(1 - y^2/h^2) \tag{1}$$

where the surface velocity u_o is

$$u_o = h^2\, g \sin\theta/2\nu \tag{2}$$

The Reynolds number N_{Re} will be defined as

$$N_{Re} = u_o h/\nu \tag{3}$$

The surface and bulk phase densities of the surface active agent, γ_s and ρ_s, are assumed to be constant in the primary flow, thus

$$\bar{\gamma}_s = \gamma_s{}^o \tag{4a}$$

$$\bar{\rho}_s = \rho_s{}^o \tag{4b}$$

and the densities in the two phases are related by an equilibrium constant.

$$\gamma_s{}^o = K\rho_s{}^o \tag{5}$$

Bulk Fluid | Surface Fluid

$$\begin{tikzcd}
\rho\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right) = -\frac{\partial p}{\partial x} + \mu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \arrow[r, leftrightarrow, dashed, "\substack{\text{Momentum Balance}\\ \text{connected by stress}}", "\text{and velocity}"'] & \gamma\left(\frac{\partial u_s}{\partial t} + u_s\frac{\partial u_s}{\partial x}\right) = \tau_{yx} + \frac{\partial \sigma}{\partial x} + (k+\epsilon)\left(\frac{\partial^2 u_s}{\partial x^2}\right) \arrow[d, leftrightarrow, dashed, "\substack{\text{connected by surface tension --}\\ \text{surface concentration relationship}}"] \\
\frac{\partial c_s}{\partial t} + u\frac{\partial c_s}{\partial x} + v\frac{\partial c_s}{\partial y} = \mathfrak{D}\left(\frac{\partial^2 c_s}{\partial x^2} + \frac{\partial^2 c_s}{\partial y^2}\right) \arrow[r, leftrightarrow, dashed, "\substack{\text{Mass Balance}\\ \text{connected by some}}", "\text{kinetic expression}"'] & \frac{\partial \gamma}{\partial t} + u_s\frac{\partial \gamma}{\partial x} = \mathfrak{D}_s\left(\frac{\partial^2 \gamma}{\partial x^2}\right) + \mathfrak{D}\left(\frac{\partial c_s}{\partial y}\right)
\end{tikzcd}$$

Fig. 1. Governing equations.

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* Throughout this paper the bar (—) and the tilde (~) will be used to denote primary and disturbance quantities, respectively.

DISTURBED FLOW

The position of the wavy interface shown in Figure 3 is given by

$$l = \delta h \exp\left[2\pi i\,(x - ct)/\lambda\right] \quad (6)$$

The real part of the growth rate constant c_r is the wave velocity, and the complex part c_i determines the exponential growth rate of the disturbance. The disturbance stream function may be written as

$$\tilde{\psi} = \delta f(y)\exp\left[2\pi i\,(x - ct)/\lambda\right] \quad (7)$$

and the disturbance velocities are given by

$$\tilde{u} = \delta f'(y)\exp\left[2\pi i\,(x - ct)/\lambda\right] \quad (8a)$$

$$\tilde{v} = -\frac{2\pi i}{\lambda}\,\delta f(y)\exp\left[2\pi i\,(x - ct)/\lambda\right] \quad (8b)$$

Here the prime (′) denotes differentiation with respect to y. When $u = \bar{u} + \tilde{u}$ and $v = \tilde{v}$ are substituted into the Navier-Stokes equations the well-known Orr-Sommerfeld equation results (*6*). In dimensionless form it may be written as

$$F'''' - 2\alpha^2 F'' + \alpha^4 F = i\alpha N_{Re}\left[(\bar{U} - C)(F'' - \alpha^2 F) - \bar{U}'' F\right] \quad (9)$$

where the prime (′) now denotes differentiation with respect to Y. The dimensionless position of the interface is given by

$$\eta = \delta\exp\left[i\alpha\,(X - C\Theta)\right] \quad (10)$$

The kinematic surface condition (*10*, p. 389) requires that

$$v = \frac{\partial l}{\partial t} + u\frac{\partial l}{\partial x}, \quad y = l \quad (11)$$

or in terms of the dimensionless stream function

$$F = C - 1, \quad Y = 0 \quad (12)$$

Here the first term of a Taylor series has been used to transform the kinematic condition from $y = l$ to $y = 0$. The procedure is outlined in detail in Section A.2 of the Appendix. Equations (9) and (12), when subjected to the boundary conditions at the solid wall and at the surface, will yield a solution for the growth rate constant C.

Continuity of velocity at the solid wall gives the two boundary conditions

$$F = F' = 0, \quad Y = 1 \quad (13)$$

The normal and tangential components of the surface equation of motion give the two surface conditions [Equations (A.3-19) and (A.3-25)]

$$-\rho g l\cos\theta - \tilde{p} + 2\mu\left(\frac{\partial\tilde{v}}{\partial y}\right) + \sigma\left(\frac{\partial^2 l}{\partial x^2}\right) = 0, \quad y = 0 \quad (14)$$

$$\mu l\left(\frac{\partial^2\bar{u}}{\partial y^2}\right) + \mu\left(\frac{\partial\tilde{u}}{\partial y} + \frac{\partial\tilde{v}}{\partial x}\right) + \frac{\partial\sigma}{\partial x} + (\kappa + \epsilon)\frac{\partial^2\tilde{u}}{\partial x^2} = 0, \quad y = 0 \quad (15)$$

These equations result from treating the surface as a two-dimensional Newtonian fluid with κ and ϵ representing the dilational and shear surface viscosity coefficients, respectively. Substitution of the pressure from Equation (14) into the x direction bulk fluid equation of motion yields a suitable form of the normal stress condition.

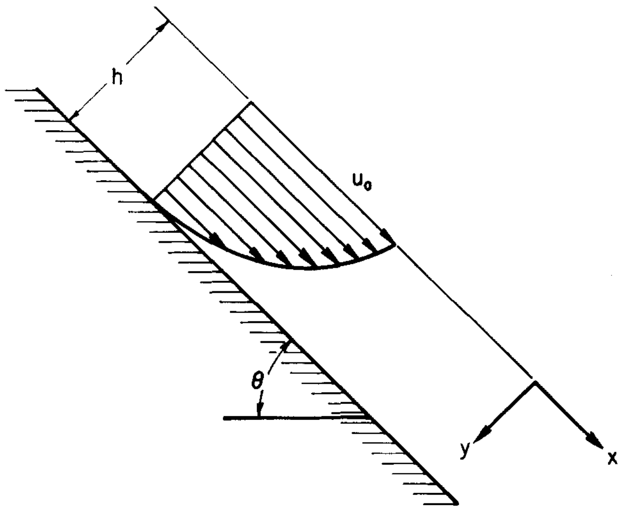

Fig. 2. Primary flow.

$$F''' - \left[i\alpha N_{Re}(1 - C) + 3\alpha^2\right]F' + i\alpha^3 N_{Re}N_{We} + 2i\cot\theta = 0, \quad Y = 0 \quad (16)$$

The tangential stress condition may also be put in dimensionless form to yield

$$F'' - \alpha^2 N_{Vi}F' + \alpha^2 F = 2 + N_{Re}N_{El}\left(\frac{\partial\Gamma}{\partial X}\right), \quad Y = 0 \quad (17)$$

The remaining problem is to determine the spatial variations of Γ which requires solving the bulk and surface phase mass transport equations. This problem has been discussed in some detail elsewhere (*13*), and it should suffice at this point to give only a brief description of the problem. If the mass transport process is confined to a region close to the surface, the disturbance equation takes the form

$$\left(\frac{\partial\tilde{\rho}_s}{\partial t}\right) + u_0\left(\frac{\partial\tilde{\rho}_s}{\partial x}\right) = \mathcal{D}\left(\frac{\partial^2\tilde{\rho}_s}{\partial x^2} + \frac{\partial^2\tilde{\rho}_s}{\partial y^2}\right) \quad (18)$$

The solution in dimensionless form is

$$\tilde{C}_s = \{A\exp(mY) + B\exp(-mY)\}\exp\left[i\alpha(X - C\Theta)\right] \quad (19)$$

where

$$m = \sqrt{i\alpha\,(1 - C)\,N_{Re}N_{Sc}} \quad (20)$$

Since the process is confined to a region close to the surface, we may consider the film to be semi-infinite with respect to mass transfer. Under these conditions Equation (19) reduces to

$$\tilde{C}_s = \{A\exp(mY)\}\exp\left[i\alpha\,(X - C\Theta)\right] \quad (21)$$

since the real part of m is negative provided the dimensionless wave velocity is greater than one.

The surface mass transport equation [Equation (A.2-23)] in dimensionless form is

$$\frac{\partial\tilde{\Gamma}}{\partial\Theta} + \frac{\partial\tilde{\Gamma}}{\partial X} + \frac{\partial\tilde{U}}{\partial X} = \left(\frac{\mathcal{D}_s}{u_0 h}\right)\left(\frac{\partial^2\tilde{\Gamma}}{\partial X^2}\right) + \left(\frac{\mathcal{D}}{u_0 K}\right)\left(\frac{\partial\tilde{C}_s}{\partial Y}\right), \quad Y = 0 \quad (22)$$

Equation (22), along with a kinetic expression describing the mass transport between the surface and the bulk phase, will provide a solution for $\tilde{\Gamma}$. Not a great deal is known about the kinetics of adsorption and desorption for

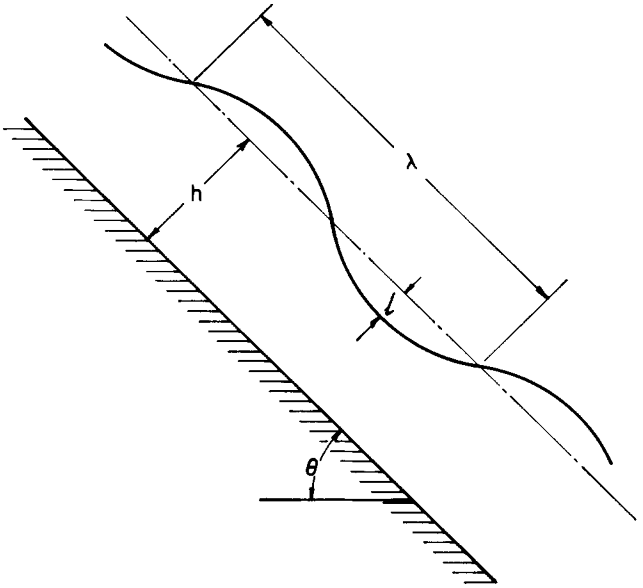

Fig. 3. Disturbed flow.

surface active agents (2, 3, 5); however, the net rate of exchange can certainly be written as

$$-\mathcal{D}\left(\frac{\partial \rho_s}{\partial y}\right) = f\,(\gamma_s - \gamma_s^{eq}), \quad y = l \tag{23}$$

Equation (23) indicates that the net rate of exchange of mass between the surface and the substrate is given by some unknown function f of the deviation from equilibrium, $\gamma_s - \gamma_s^{eq}$. Since we are dealing with small disturbances the unknown function f may be expanded in a Taylor series about the point $\gamma_s - \gamma_s^{eq} = 0$ to yield

$$-\mathcal{D}\left(\frac{\partial \rho_s}{\partial y}\right) = f(0) + \left.\frac{\partial f}{\partial(\gamma_s - \gamma_s^{eq})}\right|_{\gamma_s - \gamma_s^{eq} = 0} (\gamma_s - \gamma_s^{eq}), \quad y = l \tag{24}$$

where the higher order terms have been dropped in accordance with the usual order of magnitude analysis. Expressing the equilibrium surface mass density in terms of the substrate mass density

$$\gamma_s^{eq} = K\rho_s \tag{25}$$

where the equilibrium constant is defined by*

$$K = \gamma_s^o/\rho_s^o \tag{26}$$

allows us to write Equation (24) as

$$-\mathcal{D}\left(\frac{\partial \rho_s}{\partial y}\right) = k_1\,(\gamma_s - K\rho_s), \quad y = l \tag{27}$$

Here we have noted that $f(0) = 0$ and defined a rate constant k_1 by

$$k_1 = \left.\frac{\partial f}{\partial(\gamma_s - \gamma_s^{eq})}\right|_{\gamma_s - \gamma_s^{eq} = 0} \tag{28}$$

The dimensionless form of the disturbance equation which results from Equation (27) is

$$-N_{IR}\left(\frac{\partial \widetilde{C}_s}{\partial Y}\right) = \mathcal{K}\,(\widetilde{\Gamma} - \widetilde{C}_s), \quad Y = 0 \tag{29}$$

This result allows us to express $\widetilde{\Gamma}$ in terms of $\widetilde{C}_s$, and then Equation (22) may be used to determine the constant A in Equation (21). The derivative of Γ in Equation (17) is then

$$\frac{\partial \Gamma}{\partial X} = \alpha^2 F'(0) \Bigg/ \left\{ i\alpha\,(1 - C) + \frac{\alpha^2}{N_{Re}N_{Sc}{}^s} - \frac{\sqrt{i\alpha(1-C)N_{Re}N_{Sc}}}{N_{Re}N_{Sc}(\mathcal{K} - N_{IR}\sqrt{i\alpha(1-C)N_{Re}N_{Sc}})} \right\} \tag{30}$$

In the previous study of this problem (13), this result was simplified by the assumption $C_i << (C_r - 1)$ in order to eliminate the time-consuming use of trigonometric subroutines in the computer solution. No such difficulties are encountered in the perturbation solution presented here, and the more complete description of the mass transfer process will be used.

SOLUTION OF THE STABILITY PROBLEM

Previous studies of this problem have indicated that the critical wave number α_c tends toward zero as the surface tension variations become large. Under such conditions it is suitable to use the wave number α as a perturbation parameter; however, we encounter some difficulty in this process because of the square root dependence of α in the denominator of $\partial\Gamma/\partial X$. In order to obtain a perturbation solution, we must expand this term in a Taylor series in β where

$$\beta = \alpha^{1/2} \tag{31}$$

Unfortunately, this provides us with a slowly converging perturbation solution, and in addition there is a singularity in the expansion of $\partial\Gamma/\partial X$ for $\mathcal{K} \to \infty$. Since the insoluble surface active agent is a case of some interest, we must attack the stability problem in two ways: for $\mathcal{K} \to \infty$ we obtain a solution in powers of α, and for finite values of $\mathcal{K}$ we obtain a solution in powers of β.

Case I, $\mathcal{K} \to \infty$

We assume that the stream function and growth rate constant may be expanded in a Taylor series and write

$$F = \sum_{n=0}^{\infty} \alpha^n F_n \tag{32a}$$

$$C = \sum_{n=0}^{\infty} \alpha^n C_n \tag{32b}$$

For $\mathcal{K} \to \infty$, Equation (30) may be written as

$$\frac{\partial \Gamma}{\partial X} = \frac{\alpha F'(0)}{i(1-C) + \dfrac{\alpha}{N_{Re}N_{Sc}{}^s}} \tag{33}$$

The expansion of the denominator of Equation (33) is expressed as

$$\left(i(1-C) + \frac{\alpha}{N_{Re}N_{Sc}{}^s}\right)^{-1} = \sum_{n=0}^{\infty} \alpha^n \phi_n \tag{34}$$

where

$$\phi_0 = -\frac{i}{(1 - C_0)}$$

$$\phi_1 = -\frac{(iC_1 - 1/N_{Re}N_{Sc}{}^s)}{(1 - C_0)^2}$$

$$\phi_2 = \frac{i(iC_1 - 1/N_{Re}N_{Sc}{}^s)^2}{(1 - C_0)^3} - \frac{iC_2}{(1 - C_0)^2}$$

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* Here the standard small disturbance order of magnitude analysis is again invoked.

Equation (33) becomes

$$\frac{\partial \Gamma}{\partial X} = \alpha \sum_{n=0}^{\infty} \alpha^n F_n'(0) \sum_{n=0}^{\infty} \alpha^n \phi_n \tag{35}$$

Substitution of Equations (32*a*), (32*b*), and (35) into Equations (9), (12), (13), (16), and (17), and the equating of coefficients of the powers of α yield an infinite set of differential equations and boundary conditions which will not be listed here. Only the zeroeth, first, and second perturbations were solved, and the first three terms of the series representing the complex growth rate constant are

$$C_0 = 2$$

$$C_1 = iN_{Re}\left(\frac{8}{15} - N_{El} - \frac{2}{3}\frac{\cot\theta}{N_{Re}}\right)$$

$$C_2 = -\left\{2 + N_{Vi} + \frac{N_{El}}{N_{Sc}^{s}} - N_{Re}^2 \left[\left(\frac{5}{6} + \frac{1}{6}\frac{\cot\theta}{N_{Re}}\right) N_{El} - 0.51 + 0.64\frac{\cot\theta}{N_{Re}}\right]\right\}$$

Substitution of these values into Equation (32*b*), and extraction of the real part of C gives the wave velocity

$$C_r = 2 - \alpha^2 \left\{2 + N_{Vi} + \frac{N_{El}}{N^{s}_{Sc}} - N_{Re}^2 \left[\left(\frac{5}{6} + \frac{1}{6}\frac{\cot\theta}{N_{Re}}\right) N_{El} - 0.51 + 0.64\frac{\cot\theta}{N_{Re}}\right]\right\} \tag{36}$$

For very long waves, $\alpha \to 0$ and the wave velocity is twice the free surface velocity. This is in agreement with the theory of kinematic waves given by Lighthill and Whitham (*9*). Equation (36) indicates that the wave velocity should decrease with increasing Reynolds number, and increase with an increasing elasticity number. Both these trends are in agreement with previous calculations. No direct comparison can be made since the wave number having the maximum growth rate cannot be determined without the third perturbation. However, we can use previously calculated values of α_m to indicate the range of validity of Equation (36). For a *clean* interface having zero surface tension* and $\theta = \pi/2$, Equation (36) reduces to

$$C_r = 2 - \alpha^2 (2 + 0.51\, N_{Re}^2) \tag{37}$$

The calculated value of α_m (13) is nearly independent of Reynolds number for this condition and is given as

$$\alpha_m = 0.56 \tag{38}$$

The wave velocity for the wave having the maximum growth rate is now given by

$$C_r = 1.37 - 0.16\, N_{Re}^2 \tag{39}$$

Previously calculated values of C_r range from 1.58 at $N_{Re} = 1$ to 1.07 at $N_{Re} = 40$, and we conclude that this perturbation solution cannot satisfactorily predict wave velocities.

The imaginary part of C is given by

$$C_i = \alpha N_{Re}\left(\frac{8}{15} - N_{El} - \frac{2}{3}\frac{\cot\theta}{N_{Re}}\right) \tag{40}$$

indicating that the axis $\alpha = 0$ is part of the neutral stability curve, and there is a bifurcation point at

$$N_{El} + \frac{2}{3}\frac{\cot\theta}{N_{Re}} = \frac{8}{15} \tag{41}$$

Thus the film is stable with respect to all small disturbances when

$$N_{El} \geqq \frac{8}{15} - \frac{2}{3}\frac{\cot\theta}{N_{Re}} \tag{42}$$

Previous numerical calculations (13) for $\theta = \pi/2$ indicated a stable film for

$$N_{El} \geqq 0.46 \tag{43}$$

which is reasonably good agreement for the two different methods of solution. The elasticity number and the Reynolds number are related by

$$N_{Re} = \left\{\frac{2\rho\left(-\frac{\partial\sigma}{\partial\Gamma}\right)^3}{N_{El}^3\, g\mu^4 \sin\theta}\right\}^{1/5} \tag{44}$$

thus the critical Reynolds number $N_{Re,c}$ for a vertical film is

$$N_{Re,c} = 1.68 \left\{\frac{\rho\left(-\frac{\partial\sigma}{\partial\Gamma}\right)^3}{g\,\mu^4}\right\}^{1/5} \tag{45}$$

If $\partial\sigma/\partial\Gamma$ is taken to be —20 dynes/cm. this expression indicates that the critical Reynolds number may be on the order of 100 for water, provided, of course, interfacial mass transfer can be neglected.

The most important aspect of this analysis is that the result is identical to that obtained by Benjamin (*1*), who treated the surface as a linear viscoelastic two-dimensional fluid.

Case II, Finite $\mathcal{K}$

For this case we must expand $\partial\Gamma/\partial X$ in terms of β, thus the differential equation and the boundary conditions are written as

$$F'''' - 2\beta^4 F'' + \beta^8 F = i\beta^2 N_{Re} [(\bar{U} - C)(F'' - \beta^4 F) - \bar{U}''F] \tag{46}$$

$$F = F' = 0, \quad Y = 1 \tag{47}$$

$$F''' - [i\beta^2 N_{Re}(1 - C) + 3\beta^4] F' + i\beta^6 N_{Re} N_{We} + 2i\beta^2 \cot\theta = 0, \quad Y = 0 \tag{48}$$

$$F'' - \beta^4 N_{Vi} F' + \beta^4 F = 2 + N_{Re} N_{El}\left(\frac{\partial\Gamma}{\partial X}\right), \quad Y = 0 \tag{49}$$

The term $\partial\Gamma/\partial X$ is arranged in the form

$$\frac{\partial\Gamma}{\partial X} = \beta^3 F'(0) \Bigg/ \left\{ i\beta(1 - C) + \frac{\beta^3}{N_{Re} N_{Sc}^{s}} - \frac{\sqrt{1-C}}{A - B\beta\sqrt{1-C}} \right\} \tag{50}$$

where

$$A = \sqrt{N_{Re} N_{Sc} \mathcal{K}^2 / i}$$

$$B = N_{Re} N_{Sc} N_{IR}$$

Following the procedure outlined in Case I, F, C, and $\partial\Gamma/\partial X$ are expanded in powers of β to yield an infinite set of differential equations and boundary conditions which may be solved to obtain the complex growth rate constant C. The results are

$$C_0 = 2$$

$$C_1 = 0$$

$$C_2 = iN_{Re}\left(\frac{8}{15} - \frac{2}{3}\frac{\cot\theta}{N_{Re}}\right)$$

$$C_3 = -\Omega\,(1 + i)$$

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* This is a necessary restriction in order to make a comparison, since surface tension does not enter this analysis until the third pertubation.

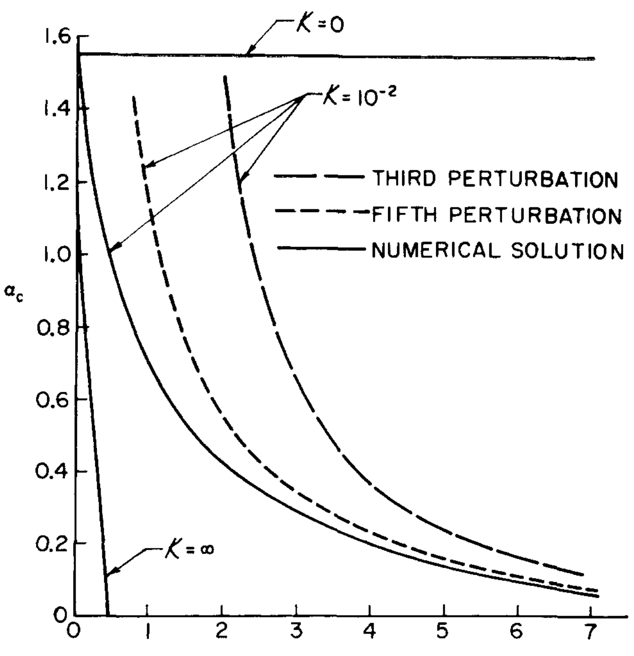

Fig. 4. Critical wave number as a function of N_{El} for $N_{Re} = 1$, $N_{Sc} = 10^3$, and $N_{IR} = 0$.

$$C_4 = -\left\{2 + N_{Vi} - N_{Re}^2\left[N_{El}N_{Sc}(\mathcal{K}^2 - N_{IR}) - 0.51 + 0.64\frac{\cot\theta}{N_{Re}}\right]\right\}$$

$$C_5 = \Omega\, N_{Re}\left[\frac{37}{30} - N_{Sc}\,(\mathcal{K}^2 - 2N_{IR}) - \frac{1}{6}\frac{\cot\theta}{N_{Re}}\right](1 - i)$$

where

$$\Omega = N_{Re}^{3/2}N_{El}N_{Sc}^{1/2}\mathcal{K}/\sqrt{2}$$

The complex growth rate constant is given by

$$C = \sum_{n=0}^{\infty} \beta^n C_n \tag{51}$$

The wave velocity for this case is given by

$$\begin{aligned} C_r = 2 - \alpha^{3/2}\,\Omega &- \alpha^2\left\{2 + N_{Vi} - N_{Re}^2\left[N_{El}N_{Sc}(\mathcal{K}^2 - N_{IR}) - 0.51 + 0.64\frac{\cot\theta}{N_{Re}}\right]\right\} \\ &+ \alpha^{5/2}\Omega N_{Re}\left[\frac{37}{30} - N_{Sc}(\mathcal{K}^2 - 2N_{IR}) - \frac{1}{6}\frac{\cot\theta}{N_{Re}}\right] \end{aligned} \tag{52}$$

Note that for a clean interface

$$N_{El} = N_{Vi} = 0 \tag{53}$$

and Equation (52) reduces to Equation (37). Therefore we cannot expect Equation (52) to predict accurately wave velocities, although it should satisfactorily predict the effect of the various parameters.

The imaginary part of C is given by

$$C_i = \alpha N_{Re}\left(\frac{8}{15} - \frac{2}{3}\frac{\cot\theta}{N_{Re}}\right) - \alpha^{3/2}\,\Omega - \alpha^{5/2}\,\Omega\, N_{Re}\left[\frac{37}{30} - N_{Sc}(\mathcal{K}^2 - 2N_{IR}) - \frac{1}{6}\frac{\cot\theta}{N_{Re}}\right] \tag{54}$$

indicating once again that the $\alpha = 0$ axis is a part of the neutral stability curve, and for a clean interface there is a bifurcation point at

$$\frac{2}{3}\frac{\cot\theta}{N_{Re}} = \frac{8}{15} \tag{55}$$

Expressions for the critical wave number and the wave number giving a maximum growth rate can be extracted from Equation (54); however, these expressions are cubics in $\alpha^{1/2}$ and are of little value in themselves.

It will be of some interest in comparing these results with previous calculations to examine the results in terms of both the third and fifth perturbations. The critical wave number for the third perturbation is given by

$$\alpha_c^{(3)} = \frac{2\left(\frac{8}{15} - \frac{2}{3}\frac{\cot\theta}{N_{Re}}\right)^2}{N_{Re}\,N_{El}^2\,N_{Sc}\,\mathcal{K}^2} \tag{56}$$

Both $\alpha_c^{(3)}$ and $\alpha_c^{(5)}$ are compared with previous numerical calculations in Figure 4 for $\mathcal{K} = 10^{-2}$, $N_{Re} = 1$, $N_{Sc} = 10^3$, and $N_{IR} = 0$. The agreement is seen to be quite good with the fifth perturbation being a significant improvement over the third perturbation. However, if the equilibrium constant is decreased to 10^{-1} there is a drastic change in the agreement between the two solutions. In Figure 5 we see that the third perturbation is in excellent agreement with the numerical solution, while the fifth perturbation does not allow a positive value of α below values of $N_{El} = 1.8$.

Examination of Equation (54) shows that C_i appears to be expressed in increasing powers of N_{Re}, N_{Sc}, and $\mathcal{K}$. While the infinite series may converge, any finite number of terms can diverge for values of the coefficients tending toward infinity. The present results can only be considered useful for small values of these coefficients.

In order to survey the topology of the neutral stability curves and the maximum growth rates in a manner that

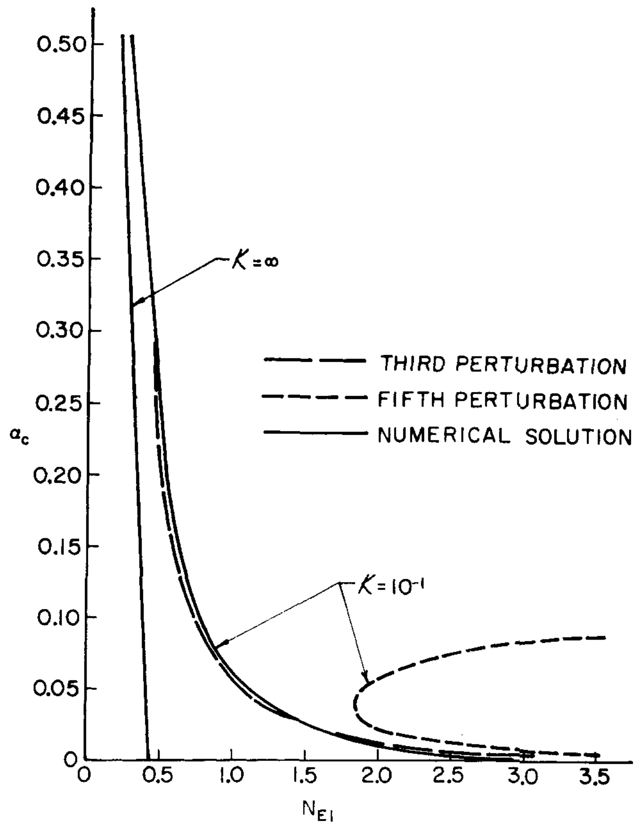

Fig. 5. Critical wave number as a function of N_{El} for $N_{Re} = 1$, $N_{Sc} = 10^3$, and $N_{IR} = 0$.

might apply to real systems, we express the elasticity number in terms of N_σ and N_{Re} according to the relation

$$N_{El} = N_\sigma^{1/3} N_{Re}^{-5/3} \qquad (57)$$

where

$$N_\sigma = \frac{-2\rho\left(\dfrac{\partial\sigma}{\partial\Gamma}\right)}{g\mu^4}$$

Expressing the growth rate constant in terms of N_σ and restricting ourselves to vertical films yields

$$C_i = \frac{8}{15}\alpha N_{Re} - \alpha^{3/2}\left(\frac{N_{Re}^{-1/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) - \alpha^{5/2}\left(\frac{N_{Re}^{5/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) \left[\frac{37}{30} - N_{Sc}(\mathcal{K}^2 - 2N_{IR})\right] \qquad (58)$$

The critical wave number is determined by solving the cubic equation in $\alpha^{1/2}$ given by

$$0 = \frac{8}{15}N_{Re} - \alpha_c^{1/2}\left(\frac{N_{Re}^{-1/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) - \alpha_c^{3/2}\left(\frac{N_{Re}^{5/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) \left[\frac{37}{30} - N_{Sc}(\mathcal{K}^2 - 2N_{IR})\right] \qquad (59)$$

and the wave number giving the maximum growth rate is given by

$$0 = 2\left(\frac{8}{15}\right)N_{Re} - \frac{5}{2}\alpha_m^{1/2}\left(\frac{N_{Re}^{-1/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) - \frac{7}{2}\alpha_m^{3/2}\left(\frac{N_{Re}^{5/6}}{\sqrt{2}}\right)(N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}) \left[\frac{37}{30} N_{Sc}(\mathcal{K}^2 - 2N_{IR})\right] \qquad (60)$$

The results are easiest to express in terms of the following three parameters: N_{Re}, $N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}$, and $N_{Sc}(\mathcal{K}^2 - 2N_{IR})$. If water is the bulk fluid and sodium lauryl sulfate is the surface active agent, representative values of the physical parameters might be taken as*

$$\left.\begin{array}{l}\mu = 10^{-2}\text{ poise}\\ \rho = 1\text{ g./cc.}\\ \mathcal{D} = 10^{-5}\text{ sq. cm./sec.}\end{array}\right\} N_{Sc} = 10^3$$

$$\left.\begin{array}{l}K = 10^{-4}\text{ cm.}\\ h = 10^{-2}\text{ cm.}\end{array}\right\} \quad \mathcal{K} = 10^{-2}$$

$$-\frac{\partial\sigma}{\partial\Gamma} = 20\text{ dynes/cm.} \quad N_\sigma = 4 \times 10^6$$

$$k_1 = 0\ (10\text{ sec.}^{-1}) \qquad N_{IR} = 10^{-2}$$

This leads to approximate values of the parameters in Equations (58), (59), and (60) of

$$N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K} = 0\ (10)$$
$$N_{Sc}(\mathcal{K}^2 - 2N_{IR}) = 0\ (-10)$$

Note that negative values of $N_{Sc}(\mathcal{K}^2 - 2N_{IR})$ will lead to well-behaved roots for α_c and α_m unlike the curve presented in Figure 5.

The critical wave number for a zero value of $N_{Sc}(\mathcal{K}^2 - 2N_{IR})$ is plotted in Figure 6 for the expected range of values of $N_\sigma^{1/3} N_{Sc}^{1/2} \mathcal{K}$. The location of the curves indicates that increasing values of N_σ, N_{Sc}, and $\mathcal{K}$ increases the stability of the film. Physically this occurs because an increase in any of these parameters tends to increase the value of the tangential surface stresses either by increasing $-(\partial\sigma/\partial\Gamma)$ or by decreasing the *rate* at which mass is exchanged between the surface and the substrate. A decrease in the rate of mass transfer allows larger surface density gradients to be maintained, and there lead to larger tangential stresses. The growth rates for the wave having the maximum growth rate are shown in Figure 7. As is to be expected, increasing values of N_σ, N_{Sc}, and $\mathcal{K}$ lead to decreasing growth rates. In addition there is an abrupt increase in αC_i with increasing Reynolds numbers which might encourage one to establish a pseudo critical Reynolds number. However, the appropriate choice of a growth rate constant for which the growth rate is neglig-

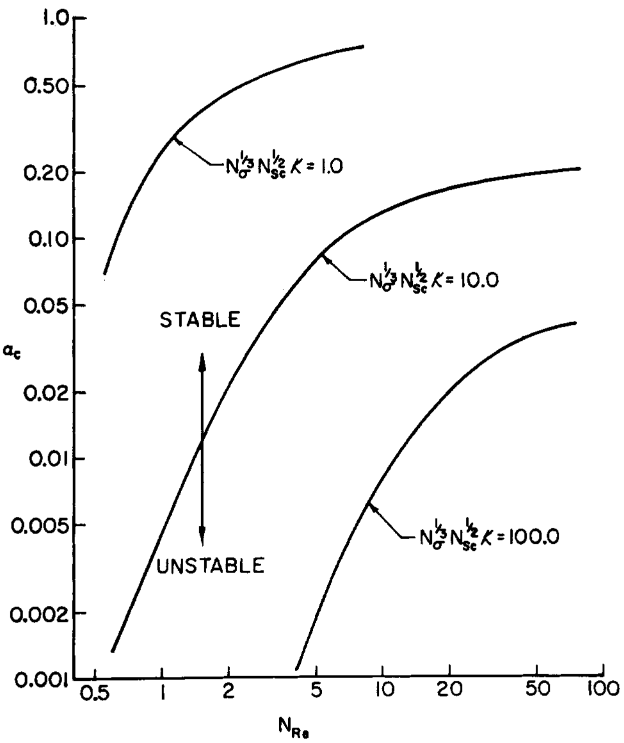

Fig. 6. Critical wave number for $N_{Sc}(\mathcal{K}^2 - 2N_{IR}) = 0$.

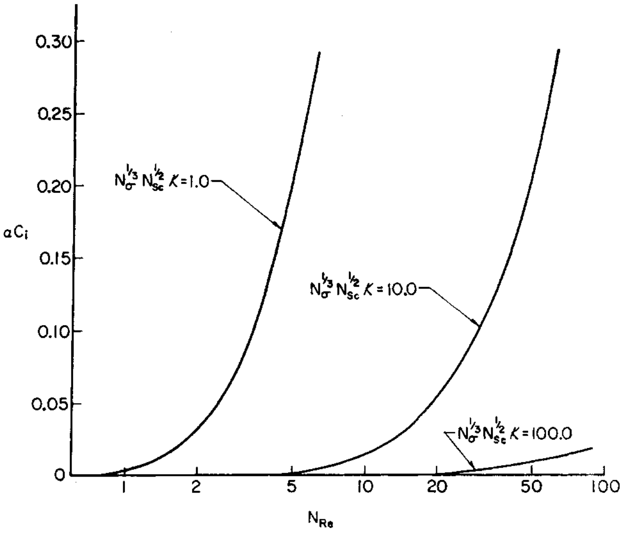

Fig. 7. Maximum growth rate for $N_{Sc}(\mathcal{K}^2 - 2N_{IR}) = 0$.

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* Very little is known about the rate constants for adsorption and the value taken for k_1 is speculation. However, we do know that adsorption must be reasonably fast if any stabilizing effects are to be obtained.

ible is rather arbitrary, and we will refrain from making a choice here. It is to be noted though, that a phenomenon somewhat like a critical flow rate can be expected for films contaminated with a surface active agent.

In examining the second key parameter in Equations (58), (59), and (60) we might first conclude that *increasing* values of N_{Sc} $(\mathcal{K}^2 - 2N_{IR})$ would lead to *increasing* stability of the film. Certainly larger values of the Schmidt number should lead to reduced mass transfer rates and higher tangential stresses which in turn increase the stability of the film. However, the sign of this term may be either + or −, depending on the relative magnitudes of $\mathcal{K}$ and N_{IR}, and the results shown in Figure 8 for $N_\sigma^{1/3}\, N_{Sc}^{1/2}\, \mathcal{K} = 10.0$ show that increased values of N_{Sc} *decrease* the stability if $\mathcal{K}^2 > 2N_{IR}$ and *increase* the stability if $\mathcal{K}^2 < 2N_{IR}$. This is a curious situation and needs to be discussed further. The dimensionless number N_{IR} would tend to infinity if the interfacial transfer process were rate controlled (by the kinetics of adsorption), and it would tend to zero if the interfacial transfer process were diffusion controlled. Thus we may look upon N_{IR} as a measure of the relative magnitudes of the two mass transfer processes, but independent of the overall transfer rate. Our results then indicate a decrease in the diffusion rate (increasing N_{Sc}) is *stabilizing* when the adsorption-desorption process is rate controlled, and *destabilizing* when the process is diffusion controlled. It should be pointed out here that values of N_{Sc} $(\mathcal{K}^2 - 2N_{IR})$ less than + 1.0 are within the region where good agreement is obtained between the perturbation solution and the numerical solution, so the validity of the perturbation solution does not seem to be open to question. Still, the results lack a physical explanation, and the following is offered: The fluctuations in the surface density γ are *in phase* with the surface rate of deformation $\partial u/\partial x$ only for an insoluble monolayer at the neutral stability condition. When diffusion and adsorption are taking place at nonzero values of C_i the situation is no longer so simple, and there is a phase lag between the rate of surface deformation and the surface density fluctuations. This phase lag will be different for diffusion-controlled and rate-controlled mass transfer. If the phase lag between the maximum surface stress and the surface rate of deformation influences the stability of the film, then it is possible that the *mechanism* of mass transfer (in addition to the *rate* of mass transfer) plays a key role in the stability analysis. This then may be an explanation of the results shown in Figure 8.

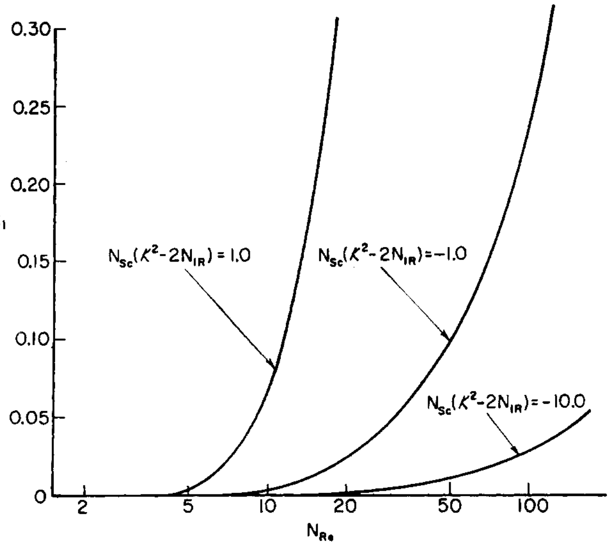

Fig. 8. Maximum growth rate for $N\sigma^{1/3}\, N_{Sc}^{1/2}\, \mathcal{K} = 10.0$.

CONCLUSIONS

The results presented here corroborate the previously established fact that an insoluble monolayer gives rise to a critical Reynolds number. The tangential surface stresses may be interpreted as compositional (this work) or structural (*1*), both approaches giving the same result. When there is interfacial mass transfer and the elasticity is treated as compositional, the existence of a critical Reynolds number is prohibited. The results indicate that both the mechanism and the magnitude of the mass transfer affect the stability of the liquid film. Further theoretical and experimental work is in order if the precise role of surface active agents in stabilizing falling liquid films is to be understood.

ACKNOWLEDGMENT

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NOTATION

c = complex growth rate constant, cm./sec.
C = c/u_o, dimensionless complex growth rate constant
$\mathfrak{D}$ = bulk phase diffusion coefficient, sq. cm./sec.
$\mathfrak{D}_s$ = surface phase diffusion coefficient, sq. cm./sec.
f = stream function, sq. cm./sec.
F = $f/u_o h$, dimensionless stream function
g = gravitational acceleration, cm./sec.^{2}
h = film thickness, cm.
k_1 = interfacial rate transport coefficient, sec.$^{-1}$
K = equilibrium coefficient, cm.
l = position of interface, cm.
p = fluid pressure, dynes/sq. cm.
t = time, sec.
u,v = fluid velocities in the x and y directions, respectively, cm./sec.
u_o = surface velocity, cm./sec.
U = u/u_o, dimensionless velocity
x,y = spatial coordinates, cm.
X,Y = x/h, y/h, dimensionless spatial coordinates

Greek Letters

α = $2\pi h/\lambda$, dimensionless wave number
β = $\sqrt{\alpha}$
γ = surface density, g./sq. cm.
Γ = γ/γ^o, dimensionless surface density
δ = dimensionless number << 1
ϵ = surface shear viscosity coefficient, (dyne) (sec.)/cm.
κ = surface dilational viscosity coefficient, (dyne) (sec.)/cm.
λ = wavelength, cm.
μ = bulk fluid viscosity coefficient, (dyne) (sec.)/sq. cm.
ρ = bulk fluid density, g./cc.
σ = surface tension, dyne/cm.
ν = μ/ρ, bulk fluid kinematic viscosity coefficient, sq. cm./sec.
θ = angle of inclination
Θ = tu_o/h, dimensionless time
ψ = stream function, sq. cm./sec.

Subscripts

c = critical value
r = real part of a complex function
i = imaginary part of a complex function
s = surface property or surface active agent

Dimensionless Groups

$\mathcal{K}$ = K/h, dimensionless equilibrium constant

N_{Re} = $u_o h/\nu$, Reynolds number
$N_{Re,c}$ = critical Reynolds number
N_{We} = $\sigma/\rho u_o^2 h$, Weber number
N_{Sc} = $\nu/\mathfrak{D}$, bulk fluid Schmidt number
$N_{Sc}{}^{s}$ = $\nu/\mathfrak{D}_s$, surface fluid Schmidt number
N_{El} = $(\partial\sigma/\partial\Gamma)/u_o^2 h$, elasticity number
N_{Vi} = $(\kappa + \epsilon)/uh$, surface viscosity number
N_σ = $2\rho\ (\partial\sigma/\partial\Gamma)/g\mu^4$, modified elasticity number
N_{IR} = $\mathfrak{D}/k_1 h^2$, interfacial rate transport number

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APPENDIX

The purpose of this appendix is to present a precise analysis of the surface mass and momentum equations for the wavy surface illustrated in Figure 3. The results are in agreement with previous intuitive studies for the case of small disturbances (*4, 9*); however, it seems reasonable that one exact formulation of the problem be available in the literature. The tensor notation to be used follows that of Aris (*1*) and McConnell (*5*), and the equations to be considered are those presented by Scriven (*6*) and more recently Slattery (*7*), who included the case of multicomponent surfaces.

A.1 The Surface Mass Balance

In this section we examine the continuity equation for some species A which may exist in both phases and on the interface separating the phases. For a moving surface, Slattery has derived the continuity equation*

$$\frac{\partial \gamma_{(A)}}{\partial t} + \Big[\gamma_{(A)}\, v^{a}{}_{(A)}\Big]_{,\alpha} + \frac{\gamma_{(A)}}{2a}\left(\frac{\partial a}{\partial t}\right) = -\,\rho_{(A1)}\,[v^{i}{}_{(A1)} - w^{i}]\,n_{(1)i} - \rho_{(A2)}\,[v^{i}{}_{(A2)} - w^{i}]\,n_{(2)i} \qquad \text{(A. 1-1)}$$

where

$$A = 1, 2, 3, \ldots, K$$

The subscripts in parenthesis indicate the species and phase, thus

$\gamma_{(A)}$ = surface density of component A
$v^{i}{}_{(A2)}$ = velocity of species A in phase 2 at the surface
$n_{(1)i}$ = unit normal directed from the surface into phase 1
w^{i} = velocity of the surface

The total surface and bulk phase densities are defined by

$$\gamma = \sum_{A=1}^{K} \gamma_{(A)} \qquad \text{(A. 1-2}a\text{)}$$

$$\rho_{(1)} = \sum_{A=1}^{K} \rho_{(A1)} \qquad \text{(A. 1-2}b\text{)}$$

$$\rho_{(2)} = \sum_{A=1}^{K} \rho_{(A2)} \qquad \text{(A. 1-2}c\text{)}$$

and the mass average velocities are given by

$$\gamma v^{\alpha} = \sum_{A=1}^{K} \gamma_{(A)}\, v^{\alpha}{}_{(A)} \qquad \text{(A. 1-3}a\text{)}$$

$$\rho v^{i} = \sum_{A=1}^{K} \rho_{(A)}\, v^{i}{}_{(A)} \qquad \text{(A. 1-3}b\text{)}$$

We define the diffusion velocities for the surface and bulk fluid as

$u^{\alpha}{}_{(A)} = v^{\alpha}{}_{(A)} - v^{\alpha}$, diffusion velocity of A on the surface (A. 1-4a)

$u^{i}{}_{(A1)} = v^{i}{}_{(A1)} - v^{i}{}_{(1)}$, diffusion velocity of A in phase 1 (A. 1-4b)

$u^{i}{}_{(A2)} = v^{i}{}_{(A2)} - v^{i}{}_{(2)}$, diffusion velocity of A in phase 2 (A. 1-4c)

This allows us to write Equation (A. 1-1) as

$$\overbrace{\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\gamma_{(A)}}{2a}\left(\frac{\partial a}{\partial t}\right)}^{\text{local rate of change of density}} + \overbrace{[\gamma_{(A)}\, v^{\alpha}]_{,\alpha}}^{\text{convective surface transport}}$$

$$+ \overbrace{[\rho_{(A1)}\,(v^{i}{}_{(1)} - w^{i})n_{(1)i} + \rho_{(A2)}\,(v^{i}{}_{(2)} - w^{i})n_{(2)i}]}^{\text{convective transport between the surface and the bulk fluid}} \qquad \text{(A. 1-5)}$$

$$= -\underbrace{[\gamma_{(A)}\, u^{\alpha}{}_{(A)}]_{,\alpha}}_{\text{surface diffusion}} - \underbrace{[\rho_{(A2)}\, u^{i}{}_{(A1)}\, n_{(1)i} + \rho_{(A2)}\, u^{i}{}_{(A2)}\, n_{(2)i}]}_{\text{diffusive transport between the surface and the bulk fluid}}$$

In order that the interface not be diffuse, that is, may represent it by a mathematical surface, we require that the normal component of the species velocity at the interface be equal to the normal component of the surface velocity.

$$v^{i}{}_{(A)}\, n_{(1)i} = w^{i} n_{(1)i} \qquad \text{(A. 1-6)}$$

However, we will not require that the species velocity $v^{i}{}_{(A)}$ be a continuous function, for if this were so, the net transfer of mass between the surface and the bulk fluids would be zero. The surface is then a singular surface with respect to the species velocity. If the bulk fluids 1 and 2 are incompressible, the velocity fields $v^{i}{}_{(1)}$ and $v^{i}{}_{(2)}$ are solenoidal and only the tangential components can exhibit a jump at the singular surface (*8*, p. 495). The assumption of incompressible flow seems reasonable, provided "small causes produce small effects" (*3*, p. 4). This assumption leads to

$$v^{i}{}_{(1)}\, n_{(1)i} = w^{i} n_{(1)i} = v^{i}{}_{(2)}\, n_{(1)i} \qquad \text{(A. 1-7)}$$

and Equation (A. 1-5) becomes

$$\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\gamma_{(A)}}{2a}\left(\frac{\partial a}{\partial t}\right) + [\gamma_{(A)}\, v^{\alpha}]_{,\alpha} \qquad \text{(A. 1-8)}$$
$$= -\,[\gamma_{(A)}\, u^{\alpha}{}_{(A)}]_{,\alpha} - [\rho_{(A1)}\, u^{i}{}_{(A1)}\, n_{(1)i} + \rho_{(A2)}\, u^{i}{}_{(A2)}\, n_{(2)i}]$$

At this point we restrict the analysis to a two-component system (a surface active agent and water for instance), and take phase 1 to be the liquid and phase 2 to be the surrounding air. At present there is no experimental information available regarding surface diffusion; however, we will assume that the

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* Latin indices indicate tensors with respect to coordinate transformations in three-space, and Greek indices indicate tensors with respect to surface coordinate transformations. Comma notation stands for covariant differentiation and the summation convention is employed throughout.

diffusional transport on the surface and in the bulk fluid follows Fick's law (2, p. 502).*

$$\gamma_{(A)}\, u^{\alpha}{}_{(A)} = -\gamma\, \mathcal{D}_s \left(\frac{\gamma_{(A)}}{\gamma} \right)^{,\alpha} \qquad (A.\ 1\text{-}9)$$

$$\rho_{(A1)}\, u^{i}{}_{(A1)} = -\rho \mathcal{D} \left(\frac{\rho_{(A1)}}{\rho} \right)^{,i} \qquad (A.\ 1\text{-}10)$$

The use of Fick's law may lead to considerable error in the general case; however, the linearization of any general constitutive equation would lead to a form similar to Equations (A. 1-9) and (A. 1-10). While the general validity of these equations is open to question, they will certainly be satisfactory for a small disturbance analysis.

By assuming constant diffusivities and constant bulk and surface densities, we may substitute Equations (A. 1-9) and (A. 1-10) into Equation (A. 1-8) to obtain

$$\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\gamma_{(A)}}{2a}\left(\frac{\partial a}{\partial t}\right) + (\gamma_{(A)}\, v^{\alpha})_{,\alpha}$$
$$= \mathcal{D}_s\, (\gamma_{(A)})^{,\alpha}{}_{,\alpha} + \mathcal{D} \rho^{,i}{}_{(A1)}\, n_{(1)i} \qquad (A.\ 1\text{-}11)$$

We now wish to investigate the special form this equation takes for the wavy surface illustrated in Figure 3.

A.2 The Wavy Surface

Let y^i ($i = 1, 2, 3$) represent the fixed rectangular Cartesian coordinates, and take the surface coordinates u^{α} ($\alpha = 1, 2$) as

$$u^1 = y^1 \text{ (where } y^1 = x \text{ in Figure 2)} \qquad (A.\ 2\text{-}1a)$$

$$u^2 = y^3 \text{ (where } y^3 = z \text{ in Figure 2)} \qquad (A.\ 2\text{-}1b)$$

The position of the interface is given by

$$y^2 = l = \delta h \exp\left[2\pi i\, (y^1 - ct)/\lambda\right] \qquad (A.\ 2\text{-}2)$$

and to make the following equations somewhat more compact we will define Ψ as

$$\Psi = \exp\left[2\pi i\, (y^1 - ct)/\lambda\right] \qquad (A.\ 2\text{-}3)$$

The surface metric tensor $a_{\alpha\beta}$ is defined by (5, p. 167)

$$a_{\alpha\beta} = g_{ij} \frac{\partial y^i}{\partial u^{\alpha}} \frac{\partial y^i}{\partial u^{\beta}} \qquad (A.\ 2\text{-}4)$$

which leads us to

$$a_{11} = 1 - \delta^2 \alpha^2 \Psi^2$$
$$a_{22} = 1$$
$$a_{12} = a_{21} = 0$$

where α is equal to the dimensionless wave number $2\pi h/\lambda$ when it is not used as a subscript or superscript. The important point to be noted here is that a_{11} differs from unity by a term of $0(\delta^2)$, and in a small disturbance analysis all terms of $0(\delta^2)$ are considered negligible compared to term of $0(\delta)$.

The determinant of the metric tensor is

$$a = a_{11}\, a_{22} - a_{12}\, a_{21} = 1 - \delta^2 \alpha^2 \Psi^2 \qquad (A.\ 2\text{-}5)$$

The second term on the left-hand side of Equation (A. 1-11) represents the time rate of change of surface density owing to dilation of the surface. For the wavy surface this term becomes

$$\frac{1}{2a}\left(\frac{\partial a}{\partial t}\right) = \frac{1}{2}\left\{\frac{\delta^2 \alpha^2 \left(\frac{4\pi i c}{\lambda}\right) \Psi^2}{1 - \delta^2 \alpha^2 \Psi^2}\right\} = 0(\delta^2) \qquad (A.\ 2\text{-}6)$$

and we see that it will not contribute to the small disturbance analysis of interface mass transport.

If A^{α} is some absolute surface vector, then (5, p. 155)

$$A^{\alpha}{}_{,\alpha} = \frac{1}{\sqrt{a}} \frac{\partial}{\partial u^{\alpha}} (\sqrt{a}\, A^{\alpha}) \qquad (A.\ 2\text{-}7)$$

Carrying out the differentiation yields

$$A^{\alpha}{}_{,\alpha} = \frac{\partial A^{\alpha}}{\partial u^{\alpha}} - \left\{\frac{\delta^2 \alpha^2 \left(\frac{2\pi i}{\lambda}\right) \Psi^2}{1 - \delta^2 \alpha^2 \Psi^2}\right\} A^1 = \frac{\partial A^{\alpha}}{\partial u^{\alpha}} + 0(\delta^2) \qquad (A.\ 2\text{-}8)$$

On the basis of Equations (A. 2-6) and (A. 2-8,) the left-hand side of Equation (A. 1-11) may be written as

$$\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\gamma_{(A)}}{2a}\left(\frac{\partial a}{\partial t}\right) + (\gamma_{(A)}\, v^{\alpha})_{,\alpha}$$
$$= \frac{\partial \gamma_A}{\partial t} + \frac{\partial}{\partial u^{\alpha}} (\gamma_{(A)}\, v^{\alpha}) + 0(\delta^2) \qquad (A.\ 2\text{-}9)$$

Expanding the surface diffusion term gives

$$(\gamma_{(A)})^{,\alpha}{}_{,\alpha} = a^{\alpha\beta}\left[\left(\frac{\partial^2 \gamma_{(A)}}{\partial u^{\alpha}\, \partial u^{\beta}}\right) - \left\{ {\omega \atop \alpha\,\beta} \right\} \frac{\partial \gamma_{(A)}}{\partial u^{\omega}}\right] \qquad (A.\ 2\text{-}10)$$

however, the second Christoffel symbol $\left\{ {\omega \atop \alpha\,\beta} \right\}$ is composed entirely of derivatives of the components of the surface metric tensor (5, p. 173) and Equation (A.2-10) becomes

$$(\gamma_{(A)})^{,\alpha}{}_{,\alpha} = a^{\alpha\beta}\left(\frac{\partial^2 \gamma_{(A)}}{\partial u^{\beta}\, \partial u^{\alpha}}\right) + 0(\delta^2) \qquad (A.\ 2\text{-}11)$$

In examining the last term on the right-hand side of Equation (A. 1-11), we note first that

$$\rho^{,i}{}_{(A1)} = g^{ij}\, \rho_{(A1),j} \qquad (A.\ 2\text{-}12)$$

The unit normal is given by (5, p. 197)

$$n_{(1)i} = \frac{1}{2} \epsilon^{\alpha\beta}\, \epsilon_{ijk} \left(\frac{\partial y^j}{\partial u^{\alpha}}\right)\left(\frac{\partial y^k}{\partial u^{\beta}}\right) \qquad (A.\ 2\text{-}13)$$

and the two nonzero components are

$$n_{(1)1} = \frac{i\alpha\delta\Psi}{[1 - \delta^2 \alpha^2 \Psi^2]^{1/2}} = i\alpha\delta\Psi + 0(\delta^2) \qquad (A.\ 2\text{-}14a)$$

$$n_{(1)2} = [1 - \delta^2 \alpha^2 \Psi^2]^{1/2} = 1 + 0(\delta^2) \qquad (A.\ 2\text{-}14b)$$

If we now substitute Equations (A.2-9), (A.2-11), and (A. 2-12) into Equation (A. 1-11) and drop all the terms of $0(\delta^2)$ we obtain

$$\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\partial}{\partial u^{\alpha}} (\gamma_{(A)}\, v^{\alpha}) = a^{\alpha\beta}\, \mathcal{D}_s \left(\frac{\partial^2 \gamma_{(A)}}{\partial u^{\alpha}\, \partial u^{\beta}}\right)$$
$$+ g^{ij}\, \mathcal{D}\, (\rho_{(A1)})_{,j}\, n_{(1)i} \qquad (A.\ 2\text{-}15)$$

We now need only relate the surface velocity vector v^{α} to the three-space vector v^i to obtain a useful form of the surface mass transport equation. This relationship is given by (5, p. 195)

$$v^{\alpha} = a^{\alpha\beta}\, g_{ij} \left(\frac{\partial y^j}{\partial u^{\beta}}\right) v^i \qquad (A.\ 2\text{-}16)$$

which may be written as

$$v^{(\alpha)} = v^{(i)} + 0(\delta^2),\ i = \alpha = 1, 2 \qquad (A.\ 2\text{-}17)$$

Here the superscripts are inclosed in parentheses to indicate lack of tensorial significance. Thus we see that the components of the surface velocity vector are equal to the two components of the spatial velocity vector to within an order of δ^2.

For two dimensional waves, we consider variations of concentration and velocity only in the y^1 and y^2 directions (x and y according to Figure 2). Under these conditions Equation (A. 2-15) reduces to

$$\frac{\partial \gamma_{(A)}}{\partial t} + \frac{\partial}{\partial x} (\gamma_{(A)}\, v_x) = \mathcal{D}_s \left(\frac{\partial^2 \gamma_{(A)}}{\partial x^2}\right) + \mathcal{D}\left(\frac{\partial \rho_{(A1)}}{\partial y}\right)$$
$$+ \mathcal{D}\left(\frac{\partial \rho_{(A1)}}{\partial x}\right)(i\delta\alpha\Psi) \qquad (A.\ 2\text{-}18)$$

---

* By $(\gamma_{(A)})^{,\alpha}$ we mean the associated tensor $a^{\alpha\beta}\ (\gamma_{(A)})_{,\beta}$, and $\rho^{,i}{}_{(A1)}$ denotes $g^{ij}\ (\rho_{(A1)})_{,j}$.

This equation has been derived previously (9) on an intuitive basis; however, the previous derivation contains an error in going from Equation (3A) to Equation (4A). Fortunately, the error did not affect the stability analysis presented in that work.

Equation (A. 2-18) applies at the surface, that is, at

$$y = l = \delta h \exp\,[2\pi i\,(x - ct)/\lambda] \qquad \text{(A. 2-19)}$$

However, in formulating the boundary conditions for the Orr-Sommerfeld equation, we require that they be specified at $y = 0$. Since the distance from the interface to $y = 0$ is small, the first term of a Taylor series expansion about $y = 0$ will be sufficient to relate the surface conditions to the conditions at $y = 0$.

As an example consider the arbitrary function $Z = Z\ (x, y)$ where

$$Z = \bar{Z} + \widetilde{Z}, \text{ and } \widetilde{Z}/\bar{Z} = 0(\delta)$$

The first term of a Taylor series gives

$$Z(x, l) = \bar{Z}(x, 0) + l\left(\frac{\partial \bar{Z}}{\partial y}\right)_{y=0} + \widetilde{Z}(x, 0) \qquad \text{(A. 2-20)}$$

where $l(\partial Z/\partial y)_{y=0}$ has been dropped since it is $0(\delta^2)$. For the primary flow under consideration the surface and bulk densities are independent of x and y. We therefore write

$$\gamma_{(A)} = \gamma^o{}_{(A)} + \widetilde{\gamma}_{(A)} \qquad \text{(A. 2-21}a\text{)}$$

$$\rho_{(A1)} = \rho^o{}_{(A1)} + \widetilde{\rho}_{(A1)} \qquad \text{(A. 2-1}b\text{)}$$

The velocity is expressed as

$$v_x = \bar{v}_x + \widetilde{v}_x \qquad \text{(A. 2-22)}$$

where

$$\bar{v}_x = u_o\,(1 - y^2/h^2)$$

Substitution of Equations (A. 2-21*a*), (A. 2-21*b*), and (A. 2-22) into Equation (A. 2-18), and the use of the idea expressed by Equation (A. 2-20) give

$$\frac{\partial \widetilde{\gamma}_{(A)}}{\partial t} + \gamma^o{}_{(A)}\left(\frac{\partial \widetilde{v}_x}{\partial x}\right) + u_o\left(\frac{\partial \widetilde{\gamma}_{(A)}}{\partial x}\right) = \mathcal{D}_s\left(\frac{\partial^2 \widetilde{\gamma}_{(A)}}{\partial x^2}\right) + \mathcal{D}\left(\frac{\partial \widetilde{\rho}_{(A1)}}{\partial y}\right) \qquad \text{(A. 2-23)}$$

where terms of $0(\delta^2)$ have been dropped. Equation (A. 2-23) is the final form of the surface mass balance for a wavy interface subject to the restriction that the disturbance be small and the initial surface and bulk densities of species A are uniform.

A.3 The Surface Momentum Equation

Referring to the work of Slattery (7), we consider the case of negligible momentum exchange with adjacent phase owing to mass transfer. The normal component of the surface momentum equation takes the form

$$\gamma n_{(1)i}\left(\frac{\partial w^i}{\partial t} + w^j w^i{}_{,j}\right) = F^i n_{(1)i} + b_{\alpha\beta}\,T^{\alpha\beta} \qquad \text{(A. 3-1)}$$

and the tangential component is

$$\gamma\left(\frac{\partial v^\alpha}{\partial t} + v^\beta v^\alpha{}_{,\beta}\right) = F^\alpha + T^{\alpha\beta}{}_{,\beta} + \gamma\,[2n_{(1)r}\,w^r b^{\alpha\beta}\,v_\beta + n_{(1)r}\,w^r\,a^{\alpha\beta}\,(n_{(1)j}\,w^j)_{,\beta}] \qquad \text{(A. 3-2)}$$

where

$F^i \;=\; f^i + T^{ij}{}_{(1)}\,n_{(1)j} + T^{ij}{}_{(2)}\,n_{(2)j}$
f^i = body force vector
$T^{ij}{}_{(k)}$ = stress tensor in the k^{th} phase
$b_{\alpha\beta}$ = second fundamental surface tensor (4, p. 200)

For purposes of an order of magnitude analysis the surface may be taken as that region where stress, density, etc., are changing rapidly. The thickness of this region is on the order of 10 Å.; thus the surface density is on the order of 10^{-7} g./sq.cm. and we may neglect all terms in Equations (A. 3-1) and (A. 3-2) which are multiplied by γ to obtain

Normal component:

$$T^{ij}{}_{(1)}\,n_{(1)j}\,n_{(1)i} + T^{ij}{}_{(2)}\,n_{(2)j}\,n_{(1)i} + b_{\alpha\beta}\,T^{\alpha\beta} = 0 \qquad \text{(A. 3-3)}$$

Tangential component:

$$a^{\alpha\beta}\,g_{ik}\left(\frac{\partial y^k}{\partial u^\beta}\right)[T^{ij}{}_{(1)}\,n_{(1)j} + T^{ij}{}_{(2)}\,n_{(2)j}] + T^{\alpha\beta}{}_{,\beta} = 0 \qquad \text{(A. 3-4)}$$

For a Newtonian surface fluid, the surface stress tensor is given by (6)

$$T^{\alpha\beta} = a^{\alpha\beta}\,[\sigma + (\kappa - \epsilon)\,S^\omega{}_\omega] + 2\epsilon S^{\alpha\beta} \qquad \text{(A. 3-5)}$$

where the rate of deformation tensor is

$$S_{\alpha\beta} = \frac{1}{2}\,[-\,2b_{\alpha\beta}\,n_{(1)i}\,w^i + v_{\alpha,\beta} + v_{\beta,\alpha}] \qquad \text{(A. 3-6)}$$

As was the case with the surface mass balance, our next step is to eliminate all terms of $0(\delta^2)$. We first note that the second fundamental surface tensor is given by

$$b_{\alpha\beta} = \left(\frac{\partial y^i}{\partial u^\alpha}\right)_{,\beta} n_{(1)i} = \left(\frac{\partial^2 y^i}{\partial u^\beta\,\partial u^\alpha}\right) n_{(1)i} + 0(\delta^2) \qquad \text{(A. 3-7)}$$

thus $b_{\alpha\beta}$ is $0(\delta)$. The normal component of the surface velocity may be written as[*]

$$n_{(1)i}\,w^i = \frac{\delta l}{\delta t} = 0(\delta) \qquad \text{(A. 3-8)}$$

On the basis of Equations (A. 3-7) and (A. 3-8), the surface rate of deformation tensor becomes

$$S_{\alpha\beta} = \frac{1}{2}\,(v_{\alpha,\beta} + v_{\beta,\alpha}) + 0(\delta^2) \qquad \text{(A. 3-9)}$$

By defining the mean curvature H by

$$2H = b_{\alpha\beta}\,a^{\alpha\beta} \qquad \text{(A. 3-10)}$$

we may write the normal component of the surface momentum equation as

$$\overset{0(\delta)}{[T^{ij}{}_{(1)} - T^{ij}{}_{(2)}]}\;n_{(1)i}\,n_{(1)j} + \overset{0(\delta)}{2H}\;\overset{0(\delta)}{[\sigma + (\kappa - \epsilon)\,S^\omega{}_\omega]} + 2\epsilon\,\overset{0(\delta)}{b_{\alpha\beta}}\;\overset{0(\delta)}{S^{\alpha\beta}} = 0 \qquad \text{(A. 3-11)}$$

Dropping terms of $0(\delta^2)$ gives

$$[T^{ij}{}_{(1)} - T^{ij}{}_{(2)}]\,n_{(1)i}\,n_{(1)j} + 2H\sigma = 0 \qquad \text{(A. 3-12)}$$

Writing the bulk phase stress tensor at $y = l$ as

$$T^{ij}|_{y=l} = \bar{T}^{ij}|_{y=0} + l\left(\frac{\partial \bar{T}^{ij}}{\partial y}\right)_{y=0} + \widetilde{T}^{ij}|_{y=0} \qquad \text{(A. 3-13)}$$

where we have now switched to the x, y coordinates allows us to express Equation (A. 3-12) as

$$\left\{ l\left[\frac{\partial \bar{T}^{ij}{}_{(1)}}{\partial y} - \frac{\partial \bar{T}^{ij}{}_{(2)}}{\partial y}\right] + [\widetilde{T}^{ij}{}_{(1)} - \widetilde{T}^{ij}{}_{(2)}]\right\} n_{(1)i}\,n_{(1)j} + 2H\sigma = 0, y = 0 \qquad \text{(A. 3-14)}$$

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[*] $\dfrac{\delta}{\delta t}$ represents the material derivative.

Here we have used the fact that

$$\bar{T}^{ij}{}_{(1)} = \bar{T}^{ij}{}_{(2)}, y = 0 \qquad (A.\ 3\text{-}15)$$

Specifying the stress tensors as

$$T^{ij}{}_{(1)} = -\, g^{ij}\, p + \mu\, (v^{i,j} + v^{j,i}) \qquad (A.\ 3\text{-}16a)$$

$$T^{ij}{}_{(2)} = g^{ij}\, p_o \qquad (A.\ 3\text{-}16b)$$

where p_o is the constant ambient pressure yields

$$\left.\begin{aligned} \frac{\partial \bar{T}^{ij}{}_{(1)}}{\partial y} &= -\, g^{ij}\, \rho_{(1)}\, g \cos\theta && (A.\ 3\text{-}17a) \\ \frac{\partial \bar{T}^{ij}{}_{(2)}}{\partial y} &= 0 && (A.\ 3\text{-}17b) \end{aligned}\right\} y = 0$$

By using Equations (A. 3-10), (A. 3-7), (A. 2-2), and (A. 2-14) we may write the mean curvature as

$$2H = \frac{\partial^2 l}{\partial x^2} + 0(\delta^2) \qquad (A.\ 3\text{-}18)$$

Referring again to Equations (A. 2-14) for the components of the unit normal, and dropping terms of $0(\delta^2)$ allows us to write Equation (A. 3-14) as

$$-\, l\, \rho_{(1)}\, g \cos\theta - \widetilde{p} + 2\mu \left(\frac{\partial \widetilde{v}_y}{\partial y} \right) + \sigma \left(\frac{\partial^2 l}{\partial x^2} \right) = 0, y = 0 \qquad (A.\ 3\text{-}19)$$

This result is the normal stress condition for the Orr-Sommerfeld equation.

By considering now the tangential component of the surface momentum equation, we write Equation (A. 3-4) as

$$a^{\alpha\beta}\, g_{ik} \left(\frac{\partial y^k}{\partial u^\beta} \right) [T^{ij}{}_{(1)} - T^{ij}{}_{(2)}]\, n_{(1)j} + a^{\alpha\beta} \left[\frac{\partial \sigma}{\partial u^\alpha} + (\kappa - \epsilon)\, S^{\omega}{}_{\omega,\beta} \right] + 2\epsilon S^{\alpha\beta}{}_{,\beta} = 0 \qquad (A.\ 3\text{-}20)$$

Here we have assumed that the spatial variations of κ and ϵ are of $0(\delta)$ or less, and we have used the fact that derivatives of $a^{\alpha\beta}$ are $0(\delta^2)$. We now apply Equation (A. 2-20) to this result and use Equation (A. 3-15) to obtain

$$a^{\alpha\beta}\, g_{ik} \left(\frac{\partial y^k}{\partial u^\beta} \right) \left[l \frac{\partial \bar{T}^{ij}{}_{(1)}}{\partial y} + \widetilde{T}^{ij}{}_{(1)} \right] n_{(1)j} + a^{\alpha\beta} \left[\frac{\partial \sigma}{\partial u^\beta} + (\kappa - \epsilon)\, \widetilde{S}^{\omega}{}_{\omega,\beta} \right] + 2\epsilon \widetilde{S}^{\alpha\beta}{}_{,\beta} = 0 \qquad (A.\ 3\text{-}21)$$

where we have used the fact that

$$\widetilde{T}^{ij}{}_{(2)} = 0 \qquad (A.\ 3\text{-}22)$$

Noting that

$$\frac{\partial y^k}{\partial u^\beta} = \left(\begin{array}{c} 1 \\ 0(\delta) \\ 0 \end{array} \right) \begin{array}{l} k = 1, \beta = 1 \\ k = 2, \beta = 1 \\ k = 3, \text{ or } \beta = 2 \end{array} \qquad (A.\ 3\text{-}23)$$

and keeping Equations (A. 2-14) in mind allows us to write Equation (A. 3-21) as

$$l \left(\frac{\partial \bar{T}^{12}{}_{(1)}}{\partial y} \right) + \widetilde{T}^{12}{}_{(1)} + \frac{\partial \sigma}{\partial u^1} + (\kappa - \epsilon) \left(\frac{\partial S^{\omega}{}_{\omega}}{\partial u^1} \right) + 2\epsilon \left(\frac{\partial S^{1\beta}}{\partial u^\beta} \right) = 0 \qquad (A.\ 3\text{-}24)$$

where the covariant derivatives have been replaced by partial derivatives according to Equation (A. 2-8). Since the components of the surface velocity vector are equal to the components of the spatial velocity vector to within $0(\delta^2)$, the final form of Equation (A. 3-24) reduces to

$$\mu l \left(\frac{\partial^2 \bar{v}_x}{\partial y^2} \right) + \mu \left(\frac{\partial \widetilde{v}_x}{\partial y} + \frac{\partial \widetilde{v}_y}{\partial x} \right) + \frac{\partial \sigma}{\partial x} + (\kappa - \epsilon) \frac{\partial^2 \widetilde{v}_x}{\partial x^2} = 0 \qquad (A.\ 3\text{-}25)$$

which is the tangential stress condition for the Orr-Sommerfeld equation.

NOTATION

$a_{\alpha\beta}$ = surface metric tensor
a = determinant of the surface metric tensor
$b_{\alpha\beta}$ = second fundamental surface tensor, cm.$^{-1}$
c = complex growth rate constant, cm./sec.
$\mathcal{D}$ = bulk phase diffusion coefficient, sq.cm./sec.
$\mathcal{D}_s$ = surface phase diffusion coefficient, sq.cm./sec.
f^i = body force vector, sq.cm./sec.^{2}
g_{ij} = three-space metric tensor
h = film thickness, cm.
H = mean curvature, cm.$^{-1}$
l = position of interface, cm.
p = fluid pressure, dynes/sq.cm.
p_o = ambient pressure, dynes/sq.cm.
$S_{\alpha\beta}$ = surface rate of deformation tensor, sec.$^{-1}$
t = time, sec.
$T^{\alpha\beta}$ = surface stress tensor, dyne/cm.
T^{ij} = three-space stress tensor, dyne/sq.cm.
u_o = undisturbed surface velocity, cm./sec.
u^α = surface coordinates, cm.
$u^\beta{}_{(A)}$ = surface diffusion velocity of species A, cm./sec.
$u^i{}_{(AK)}$ = bulk diffusion velocity of species A in phase k, cm./sec.
v^i = three-space mass average velocity, cm./sec.
v^α = surface mass average velocity, cm./sec.
w^i = three-space surface velocity, cm./sec.
x, y = rectangular Cartesian coordinates, cm.
y^i = position vector

Greek Letters

α = $2\pi h/\lambda$, dimensionless wave number
γ = surface density, g./sq.cm.
δ = dimensionless number $<<1$
ϵ = surface shear viscosity coefficient, (dyne)(sec.) cm.
κ = surface dilational viscosity coefficient, (dyne)(sec.) cm.
λ = wave length, cm.
μ = bulk fluid viscosity coefficient, (dyne)(sec.) sq.cm.
ρ = bulk fluid density, g./cc.
σ = surface tension, dyne/cm.
θ = angle of inclination, radians

Subscripts

(A) = species A on the surface
(k) = phase k
(Ak) = species A in phase k

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