$$\mathbf{\Theta} = \begin{bmatrix} 0.1182 & 0 & -0.0050 \\ -0.0351 & 0.0785 & 0.0049 \\ -0.0135 & -0.0002 & 0.0662 \\ 0.0012 & 0 & -0.0058 \\ -0.0019 & 0.0016 & 0.0058 \end{bmatrix}$$

$$\mathbf{H} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Kalman Filter Gain Matrices

for $r/q = 1$:

$$\mathbf{K} = \frac{1}{1000} \begin{bmatrix} 137. & -6.83 & -18.3 & -0.554 \\ -24.4 & 5.26 & -7.76 & 20.8 \\ -6.83 & 34.4 & -5.76 & 5.98 \\ -18.3 & -5.76 & 90.3 & -31.3 \\ -0.554 & 5.98 & -31.3 & 36.7 \end{bmatrix}$$

For $r/q = 25$:

$$\mathbf{K} = \frac{1}{1000} \begin{bmatrix} 29.0 & -0.339 & -1.67 & 0.422 \\ -2.17 & 0.248 & -0.639 & 1.41 \\ -0.339 & 1.44 & -0.284 & 0.284 \\ -1.67 & -0.284 & 20.4 & -2.48 \\ 0.422 & 0.284 & -2.48 & 3.87 \end{bmatrix}$$

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Stability of Moving Surfaces in Fluid Systems with Heat and Mass Transport

II. Combined Effects of Transport and Density Difference between Phases

Stability of interfaces moving as a result of phase transformation or mass transfer is considered. Effects of transport and of the density difference between phases known to significantly influence stability during solidification and combustion respectively are here studied theoretically in fluid systems. The analysis indicates that instability is possible during vaporization of liquids under vacuum and perhaps during growth of cavitation bubbles. But except when interfacial tension is very low, instability is unlikely during mass transfer in liquid-liquid systems because the density difference between phases is small. A density difference can also produce cellular convection at an unstable interface during solidification.

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SCOPE

It is well known that spontaneously occurring convection near fluid interfaces can cause significant increases in heat and mass transfer rates. The convection may be accompanied by formation of small droplets of one phase in the other, for example, spontaneous emulsification. This latter feature may be desirable or undesirable, depending on circumstances.

Chemical engineers interested in such phenomena have, for the most part, limited their attention to convection generated by gradients in interfacial tension, the so-called "Marangoni effect." This paper presents results of a theoretical study carried out to determine whether other effects may sometimes lead to interfacial convection or break-up. One effect considered is that of transport on moving interfaces, the mechanism generally believed to be responsible for instabilities leading to dendrite formation during solidification. Another is convection which can arise near a moving interface between phases of differing densities, an effect known to influence stability of combustion fronts.

Neither of these effects has previously been considered in connection with instability of ordinary fluid interfaces. Both can exist only when an interface moves perpendicular to itself. The most familiar example of such motion is phase transformation; for example, the continuous decrease in size of an evaporating drop. Mass transfer which produces a continuous increase in volume of one phase at the expense of another, as when a solute diffuses between immiscible liquids, is another common example.

The present study was designed to provide information as to when moving interface effects on instability in fluid systems should be important and unimportant and to indicate directions for further research.

CONCLUSIONS AND SIGNIFICANCE

The small-amplitude stability analysis described below predicts that convection produced by the density difference between phases has a destabilizing influence during vaporization of a pure liquid. Only for rather large density *differences*, however, can the stabilizing effect of interfacial tension be overcome. Instability should be possible during vaporization of relatively nonvolatile liquids under vacuum or during growth of cavitation bubbles in liquids subjected to low or negative pressures. Further research on the latter possibility is suggested.

The analysis also suggests that both transport and density difference effects are much smaller than interfacial tension's stabilizing effect for most cases of mass transfer in liquid-liquid systems. The exception is when interfacial tension is extremely low, for example, near critical solution points or when special mixtures of surfactants are present, as in certain processes now under development for increasing oil recovery from underground reservoirs. One consequence of this result is elimination of moving interface effects as a possible cause of spontaneous emulsification in systems with mass transfer but without low tensions (see Ruschak and Miller, 1972). Phase transformation in supersaturated regions must have produced the emulsions observed.

Finally, it is found that a density difference between phases can cause cellular convection during solidification. This possible source of a frequently observed phenomenon seems heretofore to have been overlooked. Theoretical and experimental work are suggested which should provide information on importance of the density difference mechanism relative to natural convection mechanisms proposed by earlier workers.

During the past ten or fifteen years metallurgists have directed considerable attention toward understanding how transport effects can produce convection cells and dendrite formation at moving solidification fronts (Sekerka, 1968). A qualitative understanding of why such instabilities occur can be obtained from Figure 1. For the situation illustrated, the rate of solidification is limited by heat transport away from the interface into the liquid phase. When the interface experiences a small, wavy perturbation as shown, points such as *P* are exposed to a relatively large amount of liquid. As a result the rate of heat transport into the liquid increases there with a corresponding increase in local rate of phase transformation, that is, local interfacial velocity. A similar argument shows that local interfacial velocity decreases at points such as Q. As these changes in local speed of the interface produce an increase in perturbation amplitude, their effect is a destabilizing one. The effect is entirely due to transport processes in contrast to mechanical instability mechanisms, such as application of electric fields and ultrasonic vibrations, which are better known to chemical engineers.

It should be noted that the bulk liquid phase in Figure 1 is subcooled below the equilibrium solidification temperature, the latter being the temperature at the solid-liquid interface. In a similar manner transport-produced instabilities during melting, condensation, and vaporization are associated with superheated solid, subcooled vapor, and superheated liquid respectively. When there is appreciable transport in both phases, the correspondence between instability and superheating or subcooling is not exact, however, as shown by theoretical analyses of the solidification case (Mullins and Sekerka, 1963, 1964).

The transport effect just described is not the only possible destabilizing influence on a moving fluid interface. If the two phases have different densities, material crossing the interface experiences a change in volume. According to existing analyses of flame stability (Landau, 1944; Markstein, 1964), expansion accompanying combustion at a flame front has a destabilizing effect on the front. If the same result holds for phase transformation, expansion during vaporization should be destabilizing while contraction during condensation should be stabilizing. The flame stability work also indicates that instability due to the density difference between phases is accompanied by cellular convection. Indeed, it is shown below that the magnitude of the density difference effect on interfacial stability is influenced by changes in the convection pattern produced by transport. Thus, there is some interaction between density difference and transport effects.

Except for the first paper of this series (Miller and Jain, 1973) stability of moving interfaces in fluid systems has not previously been analyzed. That paper dealt with transport's effect on stability in situations where the density difference between phases was negligible and where there was no interfacial tension. Because of the latter restriction the analysis was not applicable to true fluid interfaces, that is, those separating phases in or near equilibrium. Instead, its results applied to situations where significant changes in temperature or composition occurred across a narrow region whose thickness could be neglected as a first approximation. For example, moving boundaries between regions of different ionic composition in a common solvent and between fog-containing and fog-free regions were considered.

A stability analysis is presented below for the case of phase transformation of a pure material. Both transport and density difference effects are included, as is the stabilizing effect of interfacial tension. After the governing equations and boundary conditions are given in the next three sections, a stability relation is derived. Instability during vaporization is discussed followed by some conclusions regarding convection during solidification and possible instability during mass transfer.

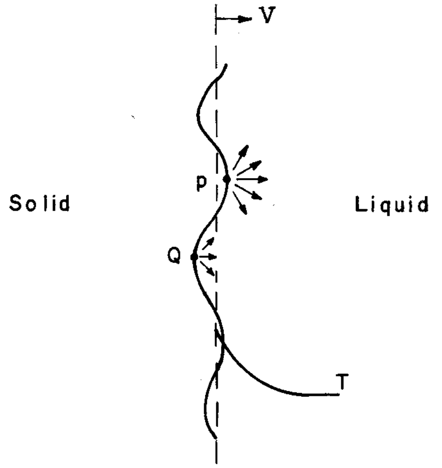

Fig. 1. Transport-produced instability during solidification of subcooled liquid.

INITIAL SITUATION

Consider the situation shown in Figure 2 where a plane interface moves toward the bulk of phase 2 with uniform velocity V due to phase transformation at the interface. The figure illustrates vaporization, phases 1 and 2 being vapor and liquid, respectively. For simplicity in analyzing the basic transport and density difference effects on stability, composition, and properties in each fluid are assumed uniform.

The initial temperature profile in phase 2 can be found by solution of the energy equation, taking, for convenience, a coordinate system moving with uniform and constant velocity V with respect to the bulk of phase 2:

$$-V\frac{\partial T_{2i}}{\partial z} = D_2\frac{\partial^2 T_{2i}}{\partial z^2} \qquad (1)$$

The solution of (1) is given by

$$T_{2i} = T_0 + \frac{G_2 D_2}{V}\left(1 - e^{-Vz/D_2}\right) \qquad (2)$$

In a similar manner the initial temperature profile in phase 1 is found to be

$$T_{1i} = T_0 + \frac{G_1 D_1}{V'}\left(1 - e^{-V'z/D_1}\right) \qquad (3)$$

Figure 2 illustrates the form of the temperature profiles for a situation where both phases help transport to the interface the heat required for vaporization. Note that the temperature far from the interface is unbounded in phase 1, a consequence of the assumption that V is constant. In actuality V will be time dependent as indicated, for example, by various solutions of the transport equations during phase transformation given by Carslaw and Jaeger (1959, Ch. 11). Assuming constant V greatly simplifies the mathematics, however, and should not strongly affect the temperature distribution in the immediate vicinity of the interface provided V does not change too rapidly. This assumption is employed in existing analyses of instabilities which occur during solidification.

The velocities V and V' are related by the requirement that mass be conserved at the moving interface:

$$\rho_2 V = \rho_1 V' \qquad (4)$$

Moreover, the temperature gradients G_1 and G_2 must satisfy the requirement that energy be conserved there as well:

$$k_2 G_2 - k_1 G_1 - \rho_2 V \lambda = 0 \qquad (5)$$

TEMPERATURE AND VELOCITY PERTURBATIONS

Suppose now that the interface, initially the plane $z = 0$ in the moving coordinate system, receives a small, wavy perturbation to the position $\bar{z} = \delta(t)\, f(x, y)$. Here f is a periodic function satisfying

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = -\omega^2 f \qquad (6)$$

Suppose further that the perturbations in the normal components of velocity and vorticity and in the temperature have the asymptotic forms

$$v_z = W(z)\, \delta(t)\, f(x, y) \qquad (7)$$

$$Z_z = Z(z)\, \delta(t)\, f(x, y) \qquad (8)$$

$$T_p = T_p(z)\, \delta(t)\, f(x, y) \qquad (9)$$

It is convenient here, as in most small-amplitude analyses of hydrodynamic stability, to eliminate the pressure term in the equation of motion by employing the vorticity equation and its curl (Chandrasekhar, 1961, Ch. 2). When the normal components of these two equations are expressed in terms of (7) and (8), the results for phase 2 are

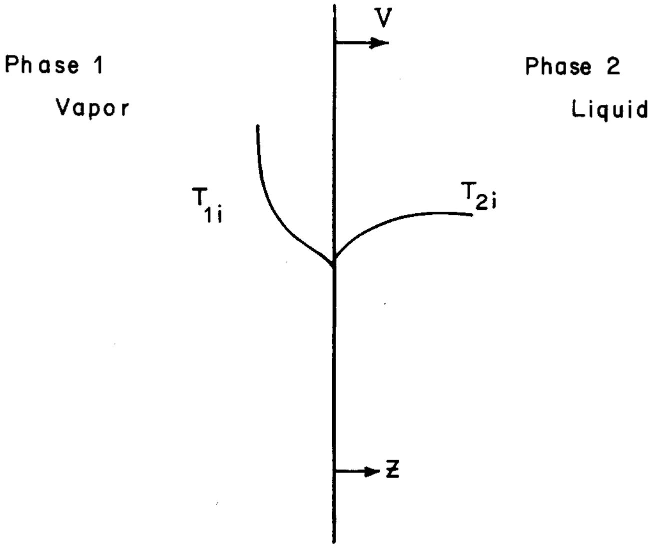

Fig. 2. Initial temperature distributions during vaporization of a pure liquid.

$$\left(\frac{\partial^2}{\partial z^2} + \frac{V}{\nu_2}\frac{\partial}{\partial z} - \omega^2\right) Z_2(z) = 0 \qquad (10)$$

$$\left(\frac{\partial^2}{\partial z^2} - \omega^2\right)\left(\frac{\partial^2}{\partial z^2} + \frac{V}{\nu_2}\frac{\partial}{\partial z} - \omega^2\right) W_2(z) = 0 \qquad (11)$$

These equations are based on the quasi steady state approximation used by Mullins and Sekerka (1963, 1964) in their analysis of interfacial instability during solidification, that is, the term $\partial v/\partial t$ in the momentum equation is neglected. The resulting solution will give the correct condition for marginal stability and a good approximation of time-dependent behavior for small deviations from marginal stability, but it will not adequately describe behavior of a general perturbation.

The solutions of (10) and (11) which vanish far from the interface are

$$Z_2(z) = M_2 e^{-\omega v_2 z} \qquad (12)$$

$$W_2(z) = M_5 e^{-\omega z} + M_6 e^{\omega v_2 z} \qquad (13)$$

By a similar procedure the solutions for phase 1 are found to be

$$Z_1(z) = M_1 e^{\omega v_1 z} \qquad (14)$$

$$W_1(z) = M_3 e^{\omega z} + M_4 e^{-\omega V_1 z} \qquad (15)$$

Tangential velocity and pressure distributions in both fluids may be calculated from (12) through (15) by the usual methods of hydrodynamic stability analysis (Chandrasekhar, 1961, Ch. 2).

Because variation of fluid properties with temperature has been neglected, the above equations for the velocity distribution were solved without knowledge of the temperature distribution. But the temperature distribution is influenced by convection. Effects of convection and the density difference between phases are important features included in the present analysis but not in existing analyses of solidification. Some boundary conditions are, of course, also different for the present fluid interface situation.

When (7) and (9) are substituted into the energy equation for phase 2 and when the quasi steady state approximation is made, the result is

$$\frac{W_2(z)}{D_2}\,\frac{\partial T_{2t}}{\partial z} = \left(\frac{\partial^2}{\partial z^2} + \frac{V}{D_2}\,\frac{\partial}{\partial z} - \omega^2\right) T_{2p}(z) \quad (16)$$

The solution to (18) which vanishes far from the interface is

$$T_{2p}(z) = A_2\, e^{-\omega_2 z} + M_5\, F_2(z) + M_6\, \Phi_2(z) \quad (17)$$

$$F_2(z) = \frac{G_2}{\omega V}\, e^{-\left(\omega + \frac{V}{D_2}\right) z} \quad (18)$$

$$\Phi_2(z) = \frac{G_2\, e^{-\left(\omega_{V2} + \frac{V}{D_2}\right) z}}{D_2\left(\omega_{V2}{}^2 - \omega^2 + \omega_{V2}\dfrac{V}{D_2}\right)} \quad (19)$$

The corresponding results for phase 1 are

$$T_{1p}(z) = A_1\, e^{\omega_1 z} + M_3\, F_1(z) + M_4\, \Phi_1(z) \quad (20)$$

$$F_1(z) = \frac{-\,G_1}{\omega \epsilon V}\, e^{\left(\omega - \frac{\epsilon V}{D_1}\right) z} \quad (21)$$

$$\Phi_1(z) = \frac{G_1\, e^{\left(\omega_{V1} - \frac{\epsilon V}{D_1}\right) z}}{D_1\left(\omega_{V1}{}^2 - \omega^2 - \omega_{V1}\dfrac{\epsilon V}{D_1}\right)} \quad (22)$$

BOUNDARY CONDITIONS AND STABILITY RELATION

The eight constants M_1 through M_6, A_1, and A_2 introduced in solving the governing equations must be determined from boundary conditions at the fluid interface. The nine pertinent boundary conditions are conservation of mass and energy, conservation of momentum (three scalar equations), continuity of temperature, continuity of tangential velocity (two scalar equations), and equality between interfacial temperature and equilibrium vaporization temperature. Eight of these conditions can be used to determine the constants. The last condition can then be used to express the rate of growth or decay of the wavy perturbation in terms of wave number ω, interfacial velocity V, initial temperature gradients G_1 and G_2, and fluid and transport properties.

The boundary conditions take the forms:

Mass Balance

The rate of accumulation of mass in a volume element of the moving coordinate system which contains part of the interface (see Figure 3) must equal the net mass entering the element from the two phases:

$$\begin{aligned} &\rho_2(V - W_2(0)\,\delta(t)\,f(x, y)) \\ &\quad - \rho_1(\epsilon V - W_1(0)\,\delta(t)\,f(x, y)) \\ &\qquad = \delta(t)\,f(x, y)\,(\rho_1 - \rho_2) \end{aligned} \quad (23)$$

Energy Balance

The same approach applies as for the mass balance. Both conduction and convection of energy are considered.

$$\begin{aligned} &- k_1 \frac{\partial T_1}{\partial z}\bigg|_{\bar z} + k_2 \frac{\partial T_2}{\partial z}\bigg|_{\bar z} \\ &\quad - \rho_2\lambda(V - W_2(0)\,\delta(t)\,f(x, y)) = \delta(t)\,f(x, y)\,\rho_2\lambda \end{aligned} \quad (24)$$

Interfacial Temperature Conditions (Two Scalar Equations)

Interfacial temperature evaluated in both phases must be the equilibrium vaporization temperature T_0.

$$T_0 = T_1(\bar z) = T_2(\bar z) \quad (25)$$

Continuity of Tangential Velocity (Vector Equation Equivalent to Two Scalar Equations)

$$\mathbf{v}_{t1} - \epsilon V\,\delta(t)\,\nabla_{II} f = \mathbf{v}_{t2} - V\,\delta(t)\,\nabla_{II} f \quad (26)$$

The terms in V and ϵV stem from projection of the initial uniform velocities in phases 1 and 2 onto the wavy interface.

Normal Component of Momentum Balance

$$\begin{aligned} &p_1(\bar z) + 2\mu_1 \frac{\partial v_{z1}}{\partial z}(0) - p_2(\bar z) - 2\mu_2 \frac{\partial v_{z2}(0)}{\partial z} \\ &\quad + \rho_1(\epsilon^2 V^2 - 2\epsilon V\, W_1(0)\,\delta(t)\,f(x, y)) \\ &\quad - \rho_2(V^2 - 2V\, W_2(0)\,\delta(t)\,f(x, y)) \\ &\qquad = \gamma\omega^2\,\delta(t)\,f(x, y) \end{aligned} \quad (27)$$

This equation includes hydrodynamic pressure and normal viscous stresses in both fluids, momentum entering and leaving the volume element of Figure 3 due to convection (typically a rather small contribution), and the effect of the interfacial tension γ between fluids.

Tangential Component of Momentum Balance (Vector Equation Equivalent to Two Scalar Equations)

$$\begin{aligned} &\mu_1\left[\frac{\partial \mathbf{v}_{t1}(0)}{\partial z} + \delta(t)\,\nabla_{II} f\, W_1(0)\right] \\ &\qquad = \mu_2\left[\frac{\partial \mathbf{v}_{t2}(0)}{\partial z} + \delta(t)\,\nabla_{II} f\, W_2(0)\right] \end{aligned} \quad (28)$$

Since temperature and hence interfacial tension along the interface are uniform, (28) is merely a statement of continuity of shear stress.

When the constants M_1 through M_6, A_1 and A_2 are eliminated among (23) to (28), the result can be expressed in the following form:

$$\begin{aligned} \frac{\dot\delta}{\delta} = &-\frac{\beta^{*2}(\rho_1 + \rho_2)}{\Delta\omega} \begin{vmatrix} 1 - \omega_1{}^* & 1 - \omega_2{}^* & \omega_2{}^* + \epsilon\omega_1{}^* \\ 1 - \omega_1{}^{*2} & S(\omega_2{}^{*2} - 1) & a_9 \\ a_1 & a_3 & a_4 \end{vmatrix} \\ &+ \frac{\omega V(\epsilon - 1)}{\Delta} \begin{vmatrix} 1 - \omega_1{}^{*2} & S(\omega_2{}^{*2} - 1) & a_9 \\ a_1 & a_3 & a_4 \\ a_5 & a_7 & a_8 \end{vmatrix} \\ &- \frac{G}{\Delta} \begin{vmatrix} 1 - \omega_1{}^* & 1 - \omega_2{}^* & \omega_2{}^* + \epsilon\omega_1{}^* \\ 1 - \omega_1{}^{*2} & S(\omega_2{}^{*2} - 1) & a_9 \\ a_5 & a_7 & a_8 \end{vmatrix} \end{aligned} \quad (29)$$

According to (29), the fractional rate of growth ($\dot\delta/\delta$) of the interfacial perturbation can be found by adding three terms. The first term is proportional to β^{*2} and is basically the usual stabilizing effect of interfacial tension and gravity on a fluid interface. The second term is proportional to interfacial speed V and to the fractional density difference between phases ($\epsilon - 1$). It represents the density difference effect on interfacial stability. The third term is, roughly speaking, proportional to the rate of heat transfer to or from the interface. It represents the transport effect on stability and is the only term which appears in the usual analysis of instability during solidification.

The condition for marginal stability can be found from

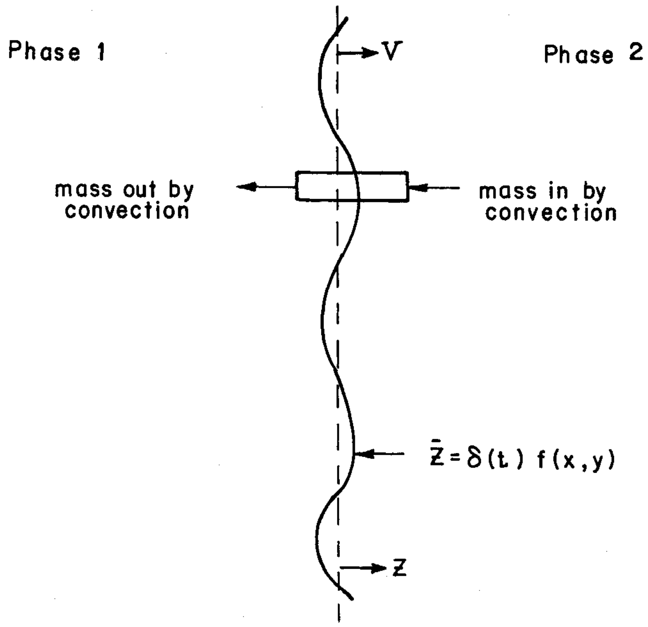

Fig. 3. Conservation of mass at moving interface after perturbation.

(29) by requiring that $(\dot{\delta}/\delta)$ vanish. Clearly instability occurs when $(\dot{\delta}/\delta)$ is positive while the interface is stable when $(\dot{\delta}/\delta)$ is negative.

VAPORIZATION

The case of vaporization is particularly interesting because expansion during vaporization should make the density difference effect destabilizing. Equation (29) can be simplified because the density ratio ϵ and viscosity ratio S between fluids are large. Further simplification can be achieved by neglecting heat transport in the vapor phase in comparison with heat transport in the liquid phase. This assumption should be reasonable in many cases of interest. It has the additional advantage of eliminating any possible difficulties which might arise from the unrealistic initial temperature distribution in the vapor phase at large distances from the interface (see Figure 2 and earlier discussion). Finally, the radicals in the expressions for ω_1^*, ω_2^*, and (ω_2/ω) can be expanded by restricting consideration to small wave numbers ω (long wave lengths), for which $(V/D_2\omega)$, $(V/\nu_2\omega)$ and $(\epsilon V/\nu_1\omega)$ are much greater than unity. With these simplifications (29) reduces to

$$(\dot{\delta}/\delta) = -\frac{\beta^{*2}(\rho_1+\rho_2)D_2}{2S\,\rho_2\,\omega V(D_2+\nu_2)}\left(\frac{\nu_2\omega}{V}\right)^2 + \frac{3\epsilon\omega V D_2}{2S(D_2+\nu_2)}\left(\frac{\nu_2\omega}{V}\right)^2 + \omega V\left(\frac{D_2\omega}{V}\right) \qquad (30)$$

As expected, the last two terms of (30), which represent density difference and transport effects respectively, are positive and hence destabilizing. The term in β^{*2} is negative, indicating that interfacial tension has its usual stabilizing effect.

Equation (30) predicts that a vertical interface, for which the gravity term of β^{*2} vanishes, will be unstable with respect to perturbations having long wave lengths. The reason is that the transport term eventually dominates as $\omega \to 0$. Insertion of typical numbers shows, however, that the wavelengths where transport dominates are very long indeed, so long that they could not occur in most cases of interest because they exceed system dimensions.

For more realistic wavelengths it turns out that stability is determined by the relative magnitudes of the interfacial tension and density difference terms. According to (30), the ratio of these terms is given by

$$r = -\,\gamma\omega/3\,\rho_2\,\epsilon V^2 \qquad (31)$$

Numerical calculations indicate that for wavelengths of order 0.01 m, $|r|$ is quite large, that is, interfacial tension is able to stabilize the interface unless the density ratio ϵ has rather large values corresponding to system pressures well below atmospheric. The analysis thus suggests that instability during vaporization is likely to occur only when liquids of relatively low volatility are vaporized under vacuum. For exampe, a liquid mercury interface is unstable to perturbations with wavelengths of about 10 mm for a pressure of about 100 N/m^2 and a temperature gradient in the liquid of about 10^4 °K/m.

Since instability during vaporization is favored by high interfacial speeds, the density difference effect could be of importance during rapid growth of cavitation bubbles in liquids under low pressures or in tension. Instabilities observed during rebound of such bubbles, that is, secondary growth following collapse, have been attributed to destabilizing effects originating during the collapse process (Benjamin and Ellis, 1966). It may well be that the density difference effect plays an important role as well. Extension of the present analysis to explore this possibility would be of interest.

It is noteworthy that when a simpler analysis is carried out which includes the density difference effect but ignores details of heat transfer in the liquid, the ratio corresponding to (31) is basically the same but lacks the factor of 3 in the denominator. Thus, although the transport effect itself does not appreciably influence stability, transport does indirectly influence the stability condition. This result stems from the effect transport has on the velocity distribution. In the analysis, this effect appears in the boundary conditions. It would seem, therefore, that calling the density difference effect a simple consequence of expansion or contraction oversimplifies matters. Clearly, the effect is influenced by details of the flow pattern as well.

For a horizontal interface the term in β^{*2} includes gravity effects. These are able to stabilize the interface in the limit $\omega \to 0$. But the conclusion that very low densities of the vapor phase are required for instability at wavelengths which are physically reasonable remains unchanged. For systems such as drops or bubbles with spherical geometry, gravity plays no similar role and the above results for a vertical, plane interface should adequately describe stability behavior in a qualitative manner. The exact form of the stability condition for spherical interfaces could easily be derived using the same basic procedure as described above.

An equation analogous to (30) applicable to disturbances having short wavelengths, that is, $(V/D_2\omega)$, $(V/\nu_1\omega)$, and $(\epsilon V/\nu_1\omega) << 1$, can be derived. Since the increase in interfacial area produced by a perturbation increases with decreasing wavelength, it is found, as might be expected, that the interfacial tension effect dominates and the interface is stable under these conditions.

CELLULAR CONVECTION DURING SOLIDIFICATION

As mentioned previously, it is well known that transport can produce interfacial instability during solidification of subcooled liquids. The cellular convection which frequently accompanies instability is usually attributed to effects of density gradients in the liquid produced by temperature and/or concentration gradients (Hurle, 1972). Cellular convection can also be produced by the density difference between phases even where there are no density gradients in the liquid as can be shown using the present analysis.

Consider a situation where phase 1 of Figure 2 is a *solid* and phase 2 is a liquid, so that the viscosity ratio S is zero. For short wavelengths (29) reduces in this case to

$$(\dot{\delta}/\delta) = \frac{(k_1G_1 + k_2G_2)}{\rho_1\lambda\left[\,1 + (1-\epsilon)\left(\dfrac{k_2G_2}{\rho_2\lambda V}\right)\left(\dfrac{V}{2D_2\omega}\right)\right]} \tag{32}$$

Short wavelengths are of primary interest here because they are the least stable, a situation quite different from the vaporization case discussed above. During vaporization of a liquid interfacial tension stabilizes the interface with respect to perturbations having short wavelengths. But the rigidity of the solid precludes this effect during solidification, as indicated by the absence of β^{*2} in (32).

For liquid and solid phases of equal density ($\epsilon = 1$), it is easily shown that there is no flow in the liquid. In this case (32) gives interfacial growth rate when heat transport is due entirely to conduction. This situation is the one treated by existing analyses in the metallurgical literature. When liquid and solid densities are unequal ($\epsilon \neq 1$), cellular convection does arise. Even so, it can be seen from (32) that since $(V/D_2\omega)$ is small, convection does not appreciably affect the growth rate $(\dot{\delta}/\delta)$. This result can be understood by noting that a small value of $(V/D_2\omega)$ can be interpreted as a small value for the ratio of the time $(D_2\omega^2)^{-1}$ needed for energy to diffuse through a distance ω^{-1} to the time $(V\omega)^{-1}$ for convection of energy through the same distance. Thus, conduction still dominates the heat transport process.

The important result, however, is the prediction that cellular convection accompanies instability when a density difference between phases exists. Moreover, according to the predicted velocity distribution, flow in the cells should be in one direction when the liquid phase is denser than the solid, as for water, and in the opposite direction when the solid phase is denser, as for most other materials. It should be possible to compare this prediction with experimental observations of cellular convection in different systems. Also of interest would be a theoretical analysis including both the density difference between phases and density gradients in the liquid.

Finally, it should be noted that a straightforward extension of the present analysis to solidification of binary mixtures shows that a density difference between phases can cause cellular convection in this case as well.

MOVING INTERFACES DURING MASS TRANSFER

The discussion thus far has emphasized situations where interfacial motion is due to a phase transformation which is accompanied by heat transport to or from the interface. Interfacial motion can also be produced by mass transport, as when the volume of one phase increases at the expense of another due to diffusion of one or more species between them. Of course, heat and mass transport could occur simultaneously, for example, during vaporization of a liquid mixture.

The analysis for the mass transfer situation is quite similar to that presented above. Indeed, the differential equations describing mass transfer in a binary mixture are identical to those given previously if thermal diffusivities are replaced by appropriate diffusion coefficients. Boundary conditions are also the same except that concentration, unlike temperature, is discontinuous at the interface. In the component mass balance equation which replaces (24), the concentration difference between phases at the interface replaces $(\rho_2\lambda)$, the enthalpy difference between phases. Because of the similarity between analyses, general conclusions about the mass transfer case can be drawn without analyzing it in detail.

It is clear that any destabilizing effect due either to transport or to the density difference between phases increases with increasing interfacial velocity V. In liquid-liquid systems diffusion coefficients are typically small (about 10^{-9}m^2/s), leading to low values of interfacial velocity V. For purposes of comparison the thermal diffusivity of liquid water is about 10^{-7}m^2/s and liquid metals have even higher values. Moreover, the density difference in liquid-liquid systems is usually rather small so that its effect on stability is small as well. Hence, in most liquid-liquid systems of interest, interfacial tension can overcome any destabilizing effects due to transport or the density difference between phases. One exception is situations where interfacial tension is extremely low (less than about 10^{-6} N/m). Low tensions occur near critical solution points, in biological systems, or when special mixtures of surfactants are present, as in certain oil recovery processes now under development (Foster, 1972). Thus, moving interface effects, like electrical double layer effects (Miller and Scriven, 1970), may significantly influence stability of low-tension interfaces although they are unimportant for more familiar interfaces of higher tension.

A recent paper (Ruschak and Miller, 1972) suggested moving interface effects as one possible mechanism for spontaneous formation of emulsions in ternary liquid-liquid systems. This mechanism seems to be the cause of interfacial instability in ternary solid systems (Coates, 1970). Since interfacial tensions were not low in the systems studied, the present work clearly rules out this mechanism of emulsion formation. The emulsions observed must have been produced by the other mechanism suggested by Ruschak and Miller, namely, nucleation and growth or spinodal decomposition in regions of local supersaturation.

One additional aspect of the mass transfer case is that interfacial tension gradients would arise due to concentration gradients along the wavy interface. The resulting effect on stability would likely be much larger than moving interface effects except in low-tension systems. As mentioned previously, interfacial tension gradients do not arise during phase transformation of a pure material because interfacial temperature is uniform.

SUMMARY

Because of interfacial tension's large stabilizing effect, moving interface effects are important for a smaller class of situations in the fluid systems considered here than in the solid systems considered previously by metallurgists. But moving interface effects should significantly influence stability during vaporization of low-volatility fluids, during growth of cavitation bubbles, and during processes where mass is transferred across interfaces of very low tension.

For the case of solidification the present analysis suggests the density difference between phases as a possible source of cellular convection, a mechanism not heretofore considered.

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NOTATION

a_1 = term in Equation (29) =

$$\frac{k_1G_1}{\epsilon V}[1-(\omega_1/\omega)-N_1]-a_2,\ \mathrm{J/m^3}$$

a_2 = term in Equation (29) =

$$\frac{-k_1G_1N_1[\omega_1{}^*-N_1-(\omega_1/\omega)]}{\epsilon V(\omega_1{}^{*2}-N_1\omega_1{}^*-1)},\ \mathrm{J/m^3}$$

a_3 = term in Equation (29) =

$$\frac{-k_2G_2}{V}[1-(\omega_2/\omega)+N_2]-a_4+\epsilon a_2,\ \mathrm{J/m^3}$$

a_4 = term in Equation (29) =

$$\epsilon a_2-\frac{k_2G_2N_2[\omega_2{}^*+N_2-(\omega_2/\omega)]}{V(\omega_2{}^{*2}+N_2\omega_2{}^*-1)},\ \mathrm{J/m^3}$$

a_5 = term in Equation (29) = $\mu_1\omega[(\epsilon V/\nu_1\omega)-2]-2\rho_2V-a_6$, N/m³ · s

a_6 = term in Equation (29) = $\mu_1\,\omega_1{}^*\omega[\omega_1{}^{*2}+\omega_1{}^*(\epsilon V/\nu_1\omega)-3]-2\rho_2V$, N/m³ · s

a_7 = term in Equation (29) = $\mu_2\omega[2+(V/\nu_2\omega)]+2\rho_2V-a_8+\epsilon a_6$, N/m³ · s

a_8 = term in Equation (29) = $\epsilon a_6+\mu_2\omega\,\omega_2{}^*[\omega_2{}^{*2}-\omega_2{}^*(V/\nu_2\omega)-3]$, N/m³ · s

a_9 = term in Equation (29) = $\epsilon(1+\omega_1{}^{*2})-S(1+\omega_2{}^{*2})$, dimensionless

D = thermal diffusivity, m²/s

f = function describing spatial periodicity of perturbation

G = term in Equation (29) = $k_1G_1\omega_1(1+N_1)+k_2G_2\omega_2(1-N_2)$, W/m³

G_i = initial temperature gradient at interface in phase i, K/m

k = thermal conductivity, W/m · K

N_1 = $(\epsilon V/D_1\omega)$, dimensionless

N_2 = $(V/D_2\omega)$, dimensionless

p = pressure, N/m²

S = viscosity ratio = (μ_2/μ_1), dimensionless

t = time, s

T = temperature, K

T_0 = equilibrium temperature for phase transformation, K

v = velocity, m/s

V = initial velocity of moving interface with respect to bulk of phase 2, m/s

W = perturbation function for normal velocity (see Equation (7)), $\mathrm{s^{-1}}$

x, y = coordinates in plane of unperturbed interface, m

z = coordinate perpendicular to unperturbed interface, m

Z = perturbation function for normal vorticity (see Equation (8)), $(\mathrm{m\cdot s})^{-1}$

$\overline{z}$ = position of interface after perturbation, m

Greek Letters

β^* = oscillation frequency in absence of viscous and moving interface effects =

$$\left[\frac{\gamma\omega^3+(\rho_2-\rho_1)g\omega\mathrm{COS}\theta}{(\rho_1+\rho_2)}\right]^{1/2},\ \mathrm{s^{-1}}$$

γ = interfacial tension, N/m

δ = function describing variation of perturbation amplitude with time, m

$\dot{\delta}$ = $\partial\delta/\partial t$, m/s

Δ = term in Equation (29) = $(\epsilon-1)$

$$\begin{vmatrix} 1-\omega_1{}^* & \omega_1{}^* & 1-\omega_2{}^* & \omega_2{}^*+\epsilon\omega_1{}^* \\ 1-\omega_1{}^{*2} & 1+\omega_1{}^{*2} & S(\omega_2{}^{*2}-1) & a_9 \\ a_1 & a_2 & a_3 & a_4 \\ a_5 & a_6 & a_7 & a_8 \end{vmatrix} - \rho_2\lambda \begin{vmatrix} 1-\omega_1{}^* & 1-\omega_2{}^* & \omega_2{}^*+\epsilon\omega_1{}^* \\ 1-\omega_1{}^{*2} & S(\omega_2{}^{*2}-1) & a_9 \\ a_5 & a_7 & a_8 \end{vmatrix},$$

N²/m⁵ · s

ϵ = density ratio = (ρ_2/ρ_1), dimensionless

θ = angle between unperturbed interface and horizontal, rad.

λ = latent heat of phase transformation, J/kg

μ = viscosity, N · s/m²

ν = kinematic viscosity, m²/s

ρ = density, kg/m³

ω = wavenumber, $\mathrm{m^{-1}}$

ω_1 = $-(\epsilon V/2D_1)+\sqrt{\omega^2+(\epsilon V/2D_1)^2}$, $\mathrm{m^{-1}}$

ω_{V1} = ω_1 with D_1 replaced by ν_1, $\mathrm{m^{-1}}$

ω_2 = $(V/2D_2)+\sqrt{\omega^2+(V/2D_2)^2}$, $\mathrm{m^{-1}}$

ω_{V2} = ω_2 with D_2 replaced by ν_2, $\mathrm{m^{-1}}$

$\omega_i{}^*$ = (ω_{Vi}/ω), dimensionless

∇_{II} = surface gradient operator = $\mathbf{i}\dfrac{\partial}{\partial x}+\mathbf{j}\dfrac{\partial}{\partial y}$

Subscripts

1 = phase 1

2 = phase 2

i = initial value, that is, before perturbation

p = change from initial value due to perturbation

t = tangential

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