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Stability of Dissolving or Depositing Surfaces

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In a previous paper, we have examined the variation of the mass transfer rate along a small amplitude wavy surface which is exchanging mass with a turbulently flowing fluid. We now use these results to show that a soluble flat surface is unstable in the presence of a turbulent flow. The wavelength of the most rapidly growing surface disturbance, made dimensionless with respect to the friction velocity and the kinematic viscosity, is found to be a very weak function of the Schmidt number. These results provide a possible explanation for wavelike dissolution patterns observed in caves and on the underside of river ice. The analysis predicts that deposition patterns should be quite different from dissolution patterns in that the most rapidly growing wave for deposition has a length of zero.

SCOPE

In this paper, we use results obtained in our laboratory on mass transfer to wavy surfaces to examine the stability of an initially flat surface which is dissolving or growing in a turbulent flow. A wavelike disturbance pattern with crests normal to the direction of mean flow is examined. Ranges of wavelengths are predicted over which disturbances on dissolving or depositing surfaces will grow. In addition, it is argued that the wavelength that eventually develops is close to that of the fastest growing wave.

The final wave pattern that develops on a dissolving surface is governed by nonlinear effects, such as flow separation, so that the linearized equations of stability theory are no longer applicable. By comparing predictions from stability theory with dissolution patterns observed in caves, we examine whether the final observed spacing between crests is determined by the stability of the surface, rather than the nonlinear effects. Therefore, stability theory can be used to predict the influence of system variables on the wavelength and velocity of dissolution patterns that initially appear on a dissolving surface and, perhaps, the wavelength of the final pattern.

CONCLUSIONS AND SIGNIFICANCE

The stability analysis of a surface dissolving in the presence of a turbulent flow shows that wavelike patterns can appear for wavelengths greater than a certain critical value. The wavelength of the most rapidly growing surface disturbance, made dimensionless with respect to the friction velocity and the kinematic viscosity, is found to be a very weak function of the Schmidt number. The wavelength of maximum growth is close to the wavelength of dissolution patterns observed in limestone caves and on melting ice. This comparison suggests that these patterns can be explained by a stability mechanism. For deposition processes, waves can occur, provided the wavelength is below the critical wavelength for the dissolution process. However, in this case the wavelength of maximum growth is zero. This suggests that deposition would be accompanied by a pattern with very small wavelength, possibly so small that it cannot be seen.

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The presence of dissolution patterns in an ice-water system is well documented in the carefully controlled laboratory experiments of Ashton and Kennedy (1972) and in observations of the underside of ice on rivers by Carey (1966) and on canals by Larsen (1969). The formation of wide crested wave patterns can also result from the dissolution of limestone caves by flowing water (Curl, 1966) and from the dissolution of ice walls (Goodchild, 1969) and glaciers (Czoernig-Czernhausen, 1926) by flowing air.

Both Ashton and Kennedy (1972) and Curl (1966) have pointed out that there is a preferred wavelength in observed two-dimensional dissolution patterns. Curl (1966) suggested that λ is related to the bulk average velocity U_b and the kinematic viscosity of the fluid ν and is not directly dependent on the dimensions of the system or the molecular diffusivity $Re_\lambda = \lambda U_b/\nu \cong 2.25 \times 10^4$. Later, Blumberg and Curl (1974) indicated that a more appropriate criterion might be a Reynolds number based on the friction velocity $Re^* = \lambda u^*/\nu = 2\,200$, where $u^* = U_b\sqrt{f/2}$.

In order for stable wavelike dissolution patterns to develop, there must be a maximum in the mass transfer rate at a point of maximum slope of the surface profile. A mass transfer variation of this type can occur because of flow separation at surface irregularities. For example, Blumberg and Curl (1974) suggested that the observed wavelength is proportional to the distance required for a separated laminar shear layer to become turbulent. This explanation seems consistent with the observation that Re_λ is approximately independent of Schmidt or Prandtl numbers.

Ashton and Kennedy (1972) suggested that the formation of dissolution waves occurs in several stages. Small symmetric ripples form on an initially flat surface because the dissolving surface can be unstable to infinitesimal disturbances. The wavelength of the ripples is then the fastest growing wave predicted by a solution of the linearized mass balance equation. The ripples grow in size until they are large enough that separation occurs. Eventually, a steady state is reached in which the waves can have an asymmetric form. In their experiments on melting ice, Ashton and Kennedy showed that the wavelength of the waves formed on an initially plane surface is well established before the onset of separation. Their work suggests that the final wavelength observed is dictated by the stability process and not by the properties of the separated flow. This is the notion that is explored in this paper. A recent experimental study in our laboratory by Thorsness (1975) on mass transfer to small amplitude waves showed that for turbulent flows, a maximum transfer rate can occur in the wave trough. These results provide proof that dissolving surfaces can be unstable and is the main motivation for this study.

Wavelike variations in the concentration field can be induced by infinitesimal disturbances at the solid surface through a wave induced variation of the velocity normal to the surface or a wave induced variation in the turbulent transport. Ashton and Kennedy (1972) argued for a stability mechanism as the cause of dissolution waves by pointing out that flow accelerations and decelerations associated with the variation of the pressure gradient along the wave surface can cause variations in turbulent velocity fluctuations. Support for this explanation is obtained from the studies of Moretti and Kays (1965) on laminarizing of turbulent boundary layers. However, equilibrium relations for heat transfer in accelerating and decelerating flows predict amplitudes and phase lags for the heat transfer variation along a wavy surface which are much larger than are found in the experiments on melting ice. Ashton and Kennedy suggested that this discrepancy arises because in nonequilibrium situations that exist in flow over wavy surfaces, the turbulence does not respond instantaneously to flow accelerations and decelerations. No attempt was made by Ashton and Kennedy to calculate this lag so that it has not been possible to evaluate their explanation for the cause of the instability.

A rigorous analysis of the stability of dissolving surfaces requires solutions of the linearized momentum and mass balance equations. The chief difficulty is the modeling of the wave induced variations in the Reynolds stress and in the turbulent transport of mass. Thorsness, Morrisroe, and Hanratty (1978) recently showed that satisfactory solutions of the linearized momentum equations can be obtained by using a wave induced variation of the eddy viscosity predicted by a mixing length model suggested by Loyd, Moffat, and Kays (1970). An essential feature of this model is that variations of the thickness of the viscous wall region are induced by variations of the pressure gradient along the wave surface. Thorsness and Hanratty (1977) used an analogy between momentum transport and heat or mass transport to solve the linearized mass balance equations. Good agreement was obtained with measurements of the variation of the mass transfer along a small amplitude wavy surface.

We now use these recent results from our laboratory to examine the stability of dissolving surfaces, as well as of depositing surfaces.

STABILITY CRITERIA

The formation of dissolution waves on a flat surface can be considered as arising from minute bumps or hollows on the solid surface or from chance spatial variations in the mass transfer rate arising from disturbances in the flowing fluid. The spatial variation in the height of the surface can be considered as the sum of a number of Fourier components. If the initial surface disturbance is small enough, the rate of change of the individual components can be considered independent of one another so that the subsequent change of the surface structure can be calculated from solutions of the mass balance equation for single Fourier harmonics. It is assumed that the wave which ultimately appears on the surface is rather regular and is the harmonic whose amplitude is increasing most rapidly.

Consider a disturbance on the solid surface which is described by a single harmonic of wave number $\alpha = 2\pi/\lambda$ and which is propagating with velocity c. The surface height is then given as

$$h(t) = \bar{h}(t) + a(t)\cos(\alpha x - \alpha ct) \qquad (1)$$

where a rectangular coordinate system has been used, and $h(t)$ is the distance in the y direction above some arbitrary datum plane. The rate of dissolution of the surface per unit area is related to the mass flux from the surface to the fluid.

For a small amplitude wave

$$\mp\rho_s\frac{dh}{dt} = N \qquad (2)$$

The negative sign signifies a dissolving surface and the positive sign a depositing surface. The surface flux for a dissolving surface can be decomposed into a mean and a fluctuating component defined in the following way:

$$N = \overline{N} + a|\hat{n}| \cos [(\alpha x + \theta) - \alpha ct] \qquad (3)$$

The term $\overline{N}$ is the mean flux and is a constant. The term $a(t)$ is the wave amplitude defined by (1). For a linear process, the amplitude of the mass transfer variation is linearly dependent on a. This dependence is expressed explicitly in (3) by designating the mass transfer amplitude as $a|\hat{n}|$. By comparing (1) and (3) it is seen that at a given time the spatial variation in the mass transfer rate is allowed to be out of phase with the wave profile. The phase angle θ is the number of degrees by which the maximum in the mass transfer rate precedes the maximum in the wave profile.

By using the trignometric relation for the cosine of the sum of two angles, (3) can be written in the alternate form

$$N = \overline{N} + a|\hat{n}| \cos\theta \cos(\alpha x - \alpha ct) - a|\hat{n}| \sin\theta \sin(\alpha x - \alpha ct) \qquad (4)$$

If (4) and (1) are substituted into (2), the following relations are obtained for a dissolving surface:

$$-\rho_s \frac{d\overline{h}}{dt} = \overline{N} \qquad (5)$$

$$-\rho_s \frac{da}{dt} = a|\hat{n}| \cos\theta \qquad (6)$$

$$c = \frac{|\hat{n}| \sin\theta}{\alpha \rho_s} \qquad (7)$$

Equation (6) can be solved to get

$$a = a_0 e^{\beta t} \qquad (8)$$

with

$$\beta = -|\hat{n}| \frac{\cos\theta}{\rho_s} \qquad (9)$$

If β is positive, the surface waves will grow, and if β is negative, they will decay. For a dissolution process, positive β requires $\cos\theta$ to be negative so that $\pi/2 < \theta < 3\pi/2$. This implies that for dissolution waves to grow, the maximum in the mass transfer rate must occur somewhere in the trough. If it is in the downstream half of the trough, the dissolution wave will propagate in the downstream direction, and if it is in the upstream half, it will propagate upstream.

For processes in which a surface is being deposited

$$\beta = +|\hat{n}| \frac{\cos\theta}{\rho_s} \qquad (10)$$

and the stability criterion is just opposite that for dissolution; that is, the maximum mass transfer rate must occur along the wave crest for waves to grow.

It is clear from the above considerations that the stability of dissolving surfaces is determined by the phase of the wave induced variation of the surface flux. For dissolution, where the transfer rate is controlled by convective processes at the surface, the prediction of instability requires a solution of the linearized mass balance equation for the perturbations in the concentration field caused by the presence of waves.

When a surface is melting instead of just dissolving, as is the case for ice, the analysis proceeds as indicated above except that $Q/\Delta H$ is substituted for N.

The analysis for this case is not so straightforward, since heat can be transferred by conduction through the ice, as well as by convection from the water flow over the ice surface. The inclusion of the heat due to gradients through the ice would require the determination of the temperature field in the solid, which in turn would require the specification of boundary conditions on the side of the ice not exposed to flowing water. We have chosen to ignore the conduction effect so that the results presented here will be applicable to melting ice only if conduction through the ice is small compared to convective heat transfer at the surface exposed to water. This condition is satisfied in most instances, particularly when the ice is thick.

INTERPRETATION OF DISSOLUTION PATTERNS

The measurements in Figure 9 of Thorsness and Hanratty (1977) clearly show a range of α for which the phase θ is greater than 90 deg. Thus, it is possible for the maximum in the mass transfer rate to exist somewhere in the trough of a small amplitude wave exchanging heat or mass with a turbulent fluid. From the arguments presented previously, we conclude that a dissolving flat surface is unstable.

The good agreement between the calculations and the measurements has encouraged us to use this analysis to determine the influence of α on the growth factor β and the wave velocity c. Figure 9 of Thorsness and Hanratty (1977) also presents the calculated dimensionless amplitude of the mass transfer variation vs. the dimensionless wave number for Schmidt number = 729 and for Prandtl number equal to 13.7. In terms of the nomenclature used in this paper, the ordinate of Figure 9 of Thorsness and Hanratty (1977) is $|\hat{n}|\nu/\overline{N}u^*$, and the abscissa is $\alpha\nu/u^* = \alpha^+$. Equations (7) and (9) can be rearranged in the dimensionless form suggested by this plot to give

$$c^* = \frac{c\rho_s}{\overline{N}} = \left(\frac{|\hat{n}|\nu}{\overline{N}u^*}\right) \frac{\sin\theta}{\alpha^+} \qquad (11)$$

$$\beta^* = \frac{\beta\nu\rho_s}{\overline{N}u^*} = -\left(\frac{|\hat{n}|\nu}{\overline{N}u^*}\right) \cos\theta \qquad (12)$$

Since both $|\hat{n}|\nu/\overline{N}u^*$ and θ are functions of α^+, the dependence of the wave velocity on the wave number is not immediately evident from (11).

From (12) it is seen that the maximum in β^* is determined by two competing factors. Large values of $|\hat{n}|\nu/\overline{N}u^*$ are favored by large values of α^+. However, at large α^+, the phase angle decreases to zero. For waves to grow, $\cos\theta$ must be positive 90 deg $< \theta <$ 270 deg, and the most favorable value is 180 deg. Consequently, it would be expected that the maximum in β^* will occur at large values of α^+, but not so large that the wave induced variation in the mass transfer rate will have an unfavorable phase.

Values of β^* and c^* determined from the calculated results presented in Figure 9 of Thorsness and Hanratty (1977) are shown in Figures 1 and 3 for Z = 729 and in Figures 2 and 4 for Z = 13.7. The reference to model D parameters on the figures refers to the two parameters used in the turbulence model used in carrying out the calculations as described by Equations (33) to (36) in Thorsness and Hanratty (1977). It is to be noted that

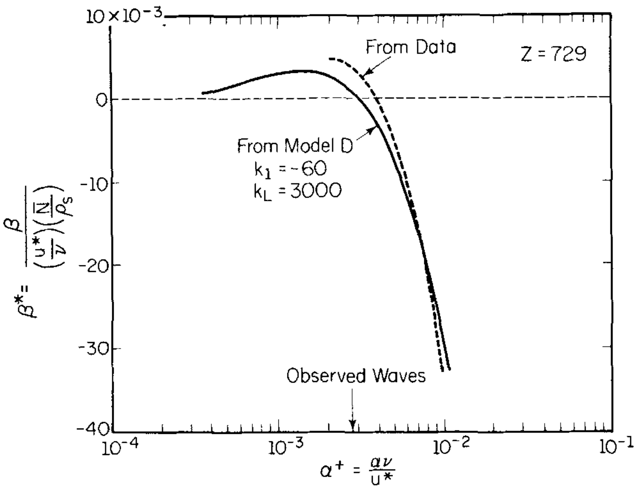

Fig. 1. Growth factors for a Schmidt number of 729.

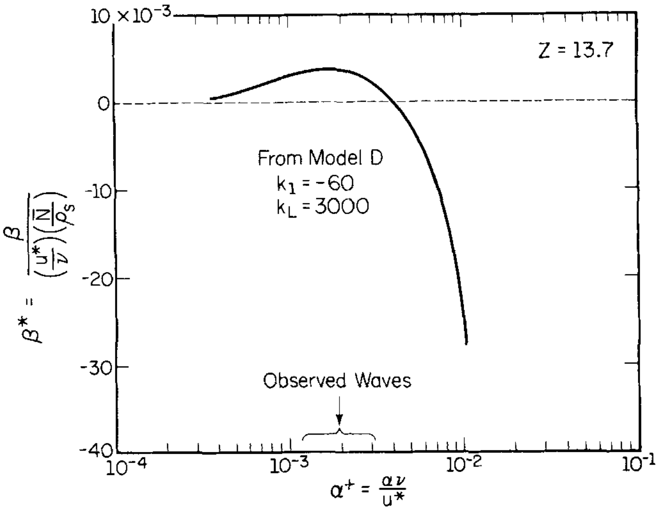

Fig. 2. Growth factors for a Prandtl number of 13.7.

β^* is a strong function of α^+ but only weakly dependent on Schmidt number of Prandtl number. We, therefore, find that a stability mechanism is consistent with the observation of Blumberg and Curl (1974) that $\lambda u^*/\nu$ characterizing dissolution patterns should be approximately constant.

For $Z = 729$, the calculated wave induced mass transfer variation indicates that dissolution waves are possible for $\alpha^+ < 0.0003$ and that a maximum in β^* occurs at $\alpha^+ = 0.001$ to 0.002. Values of β^* determined from the mass transfer measurements presented in Thorsness and Hanratty (1977) are also shown in Figure 1. The measurements were not carried out over a wide enough range of α to establish the maximum in β^*. However, they do suggest that the calculated α^+ for maximum growth could be somewhat low because of errors in modeling the wave induced variation of turbulent transport. The arrow in Figure 1 indicates the value of α^+ suggested as representative of naturally occurring limestone dissolution patterns (Blumberg and Curl, 1974). The wave number characterizing these dissolution patterns is somewhat larger than the calculated α^+ for maximum growth and about in line with what would be expected from measured mass transfer variations. This agreement gives further support for a stability mechanism as the cause of the dissolution patterns.

Calculated values of β^* for $Z = 13.7$ shown in Figure 2 give unstable waves for $\alpha^+ < 0.004$ and a maximum in β^* at $\alpha^+ = 0.002$. The range of wave numbers characterizing the ice waves observed by Ashton and Kennedy in their experiments with melting ice is also indicated in Figure 2. Again, good agreement is obtained between the calculated wave number for maximum growth and the observed number of the dissolution patterns.

Calculated values of the dimensionless wave velocity $c^* = c\rho_s/\overline{N}$ are also given in Figures 1 and 2. Ashton and Kennedy (1972) reported a value of $c^* = 2.2$ for ice waves. The curve in Figure 2 indicates a range of values of $c^* = 0.84$ to 3.2, over the range of α^+ where observations were made, in good agreement with measurements.

POSSIBILITY OF DEPOSITION PATTERNS

The criterion for deposition patterns, Equation (10), shows that growth is possible provided $-\pi/2 < \theta < \pi/2$ and that most favorable phase angle for wave growth is $\theta = 0$ deg. From Figures 1 and 2 it is found that deposition patterns are possible provided $\alpha^+ > 0.003$ to 0.004. The results given in Thorsness and Hanratty (1977) show that $|\hat{n}|$ becomes arbitrarily large, and $\theta \rightarrow 0°$ for $\alpha^+ \rightarrow \infty$. Consequently, the wave number for maximum growth of deposition waves is $\alpha^+ \rightarrow \infty$. This implies that deposition waves will be of very small length, possibly so small that they will not be observed.

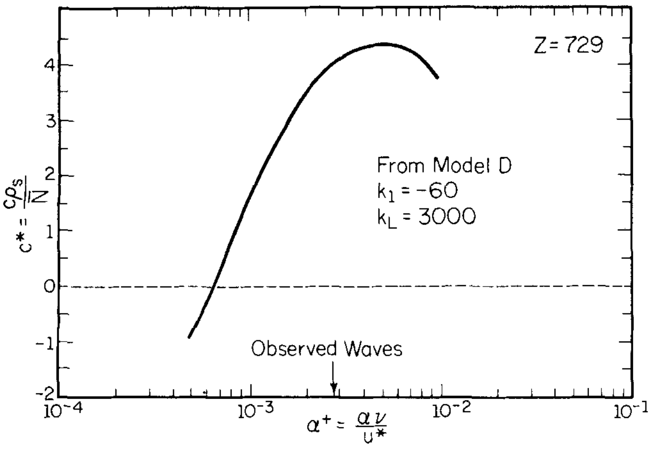

Fig. 3. Wave velocity for a Schmidt number of 729.

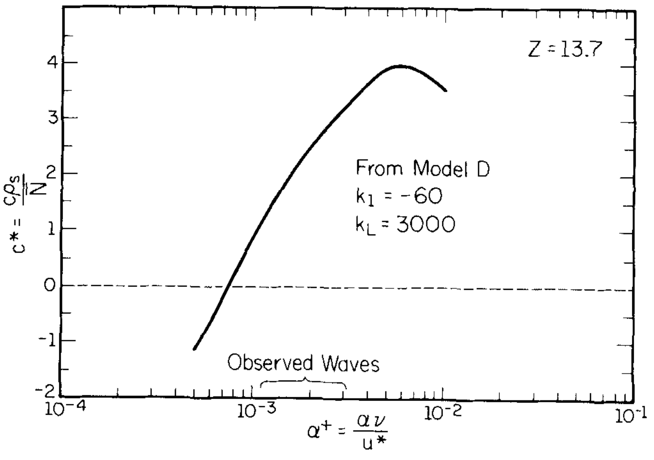

Fig. 4. Wave velocity for a Prandtl number of 13.7.

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NOTATION

a = wave amplitude, m
c = wave velocity, m/s
c^* = $c\rho_s/\overline{N}$
f = friction factor = $\tau_W/\frac{1}{2}U^2{}_b$, dimensionless
h = surface height, cm
ΔH = heat of fusion
N = mass flux from the surface or heat flux to surface in the units of mass or heat per unit area per unit time
Q = surface heat flux
Re^* = Reynolds number based on the friction velocity = $\lambda u^*/\nu$
t = time, s
U_b = bulk averaged velocity, m/s
u^* = friction velocity equal to $(\overline{\tau}_W/\rho)^{1/2}$, m/s
x = coordinate in the direction of mean flow
y = coordinate perpendicular to mean solid surface, m

Greek Letters

α = wave number, m^{-1}
α^+ = wave number made dimensionless using u^* and ν
β = time constant for growth, s^{-1}
β^+ = $\rho\nu\rho_s/Nu^*$
θ = phase angle to be defined by (8)
λ = wave length, m
ν = kinematic viscosity, m^2/s
ρ = density of the fluid, kg/m^3
ρ_s = density of solid, kg/m^3
τ_W = shear stress acting on the wave surface, N/m^2
$\overline{\tau}_W$ = average value of τ_W over one wavelength, N/m^2

Other symbols

$\overline{N}(y)$ = average value of N over one wavelength
$a|\hat{n}|$ = amplitude of wave induced variation of N, $n = N - \overline{N}$
Z = Schmidt number of Prandtl number

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An Equation of State for Polyatomic Fluids

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An equation of state has been developed for convex nonspherical particles with nonpolar and multipolar forces. The effects of nonsphericity and multipolarity on phase behavior are characterized by a geometric shape parameter and an energy fluctuation parameter, respectively. The equation performs for real fluids better than the Van der Waals equation and as well as the Redlich-Kwong and Peng-Robinson equations.

SCOPE

An equation of state is developed for attracting, nonspherical particles with rigid, convex cores. The method makes use of mean field approximations and the scaled particle theory. The effect of nonsphericity and polarity on phase behavior is investigated. Spherocylindrical, tetragonal, and hexagonal cores are considered. The equation of state is tested for nitrogen, carbon dioxide, methane, and benzene and is compared to the Van der Waals, Redlich-Kwong, and Peng-Robinson equations as well as new variations of these equations.

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