

INTERFACIAL INSTABILITIES IN DIRECTIONAL SOLIDIFICATION OF DILUTE BINARY ALLOYS: THE KURAMOTO-SIVASHINSKY EQUATION

A. Novick-Cohen

ABSTRACT:

Directional solidification processes are studied in the limit in which the imposed temperature profile is slack compared to the impurity diffusion-imposed velocity ratio. The dynamics of interfacial kinetics now become important and the phenomenological model of Coriell and Sekerka [1] is used to model these processes. In this limit, the Kuramoto-Sivashinsky equation is shown to be an asymptotically valid description of the interfacial dynamics. The Kuramoto-Sivashinsky equation is known to exhibit intermittency superimposed on a relatively stable array of cusps or wrinkles [2] and thus may serve as a reasonable limiting description of the solidification interface just before coherency is lost. Furthermore our result demonstrates that the Kuramoto-Sivashinsky equation may be a relevant framework in which to study Langer's proposed marginal stability criterion for dendritic growth [3].

INTRODUCTION:

Directional solidification has been the subject of much recent study and is important in many technological applications. In this process a dilute binary alloy is drawn through a temperature gradient, thereby causing the material to melt and refreeze. These processes may be roughly characterized by the slope of the gradient of the imposed temperature profile, G , and by the speed of the alloy transport v . Essentially low velocities and steep temperature profiles serve to stabilize the overall process and to cause an even planar interface to be produced.

Linear stability studies of the planar interface date back to Mullins and Sekerka [4] in 1965 and in 1970 weakly nonlinear stability treatments were

undertaken by Wollkind and Segel [5]. In Sivashinsky [6] and in Novick-Cohen and Sivashinsky [7] use was made of the fact that in a particular limit, the fastest growing mode of the solution of the linearly perturbed planar problem is asymptotically small. The limit considered there was when the slope G of the imposed temperature profile was just below G_c , the critical value of the slope above which there is always linear stability and when the distribution coefficient or the ratio of the equilibrium concentration of the impurity on the solid side of the interface to that on the liquid side, was small. In a neighborhood of this limit an effective separation of scales occurs since the modulations along the interface are much longer than the variations across the interface. This separation of scales allows an asymptotically valid equation for the evolution of a mildly nonplanar interface to be derived. The resultant equation for the interface $\phi(x, \tau)$ is [7] then

$$\phi_\tau + V^4 \phi + V^2 [2\phi - \phi^2] + \alpha \phi + \frac{1}{4\pi^2} f \frac{(1-n)}{(1+n)} V^2 \int_{-\infty}^{\infty} |k| [\phi(w, \tau) - \phi(x, \tau)] \exp(ik(x-w)) dw dk = 0. \quad (*)$$

Here both the dependent and the independent variables have been rescaled, and α and f are dimensionless parameters. Also, n is the ratio of the solid conductivity to the liquid conductivity.

In [7], it was demonstrated that if $-1 + f\sqrt{2/5} (1-n)(1+n)^{-1} > 0$, then equation (*) admits slowly travelling wave solutions. Furthermore, in one dimension if $f = 0$, then equation (*) possesses an associated Liapounov functional

$$F = \int \left\{ \frac{1}{2} |\nabla\phi|^2 + \phi^2 - \frac{1}{3} \phi^3 + \frac{1}{2} \alpha (\int \psi \phi)^2 \right\} dx,$$

where $\nabla\psi = \phi$. Note that F is not strictly a Liapounov functional since it is not bounded from below. Thus a relatively steady though perhaps sharply cusped

interface seems to be prescribed by equation (*). There does not seem to be any indication that such an equation would be capable of describing dendritic or chaotic behavior. This perhaps is to be expected since the asymptotics were undertaken in the neighborhood of the critical value G_c of the imposed temperature slope, above which there is linear stability for all values of the remaining parameters.

The results of this paper are based on the observation that whenever (a) the fastest growing mode is asymptotically small and (b) the mode $k = 0$ is a decaying mode according to linear stability, then a separation of scales may be possible. Examination of the linear dispersion relation obtained in [6] for the case of equal thermal conductivities, negligible latent heats, and a large thermal diffusivity to impurity diffusion rate,

$$\sigma = (1 - w - \beta k^2) \left(\sqrt{\frac{1}{4} + k^2 + \sigma} + K - \frac{1}{2} \right) - K$$

showed that conditions (a) and (b) held in some neighborhood of the limit $GD/V \ll 1$. Early attempts at repeating the former analysis in this second limit failed. Intuitively the reason for this failure is that when $GD/V \ll 1$ the interface starts to become diffuse. The diffusion process is no longer capable of stabilizing the interface and exponential instabilities develop. While in the extreme limit, it may in fact no longer be possible to stabilize the interface at all, some degree stabilization is effected by taking interfacial kinetics into account. It is this possibility which is explored in the remainder of this paper.

THE MODEL:

We consider a one sided diffusion model in a frame which moves with velocity V ,

$$T_{L_t} = D_L \nabla^2 T_L + V \frac{\partial}{\partial z} T_L \quad z > \phi \quad (1)$$

$$T_{S_t} = D_S \nabla^2 T_S + V \frac{\partial}{\partial z} T_S \quad z < \phi \quad (2)$$

$$c_t = D \nabla^2 c + V \frac{\partial}{\partial z} c \quad z > \phi \quad (3)$$

with the boundary conditions

$$T_L = T_S \quad z = \phi \quad (4)$$

$$L_V V_n = k_S \frac{\partial T_S}{\partial n} - k_L \frac{\partial T_L}{\partial n} \quad z = \phi \quad (5)$$

$$V_n (c - c_S) = -D \frac{\partial c}{\partial n}, \quad z = \phi. \quad (6)$$

Here $z = \phi(x,t)$ denotes the location of the solidification interface, $c(x,z,t)$ denotes the impurity concentration in the liquid, and $T_L(x,z,t)$ ($T_S(x,z,t)$) denotes the temperature in the liquid (solid). Here D_L (D_S) is the thermal diffusivity in the liquid (solid), D is the diffusion coefficient for the impurity concentration, L_V is the latent heat, V_n is the normal velocity of the interface, k_L (k_S) is the thermal conductivity of the liquid (solid), c_S is the impurity concentration on the solid side of the interface and n is the unit normal to the interface. If the melting and refreezing process is proceeding slowly, then the interfacial kinetics are sufficiently rapid to equilibrate and the interface is locally at equilibrium. Then it is reasonable to assume that

$$c_S = k_0 c_i \quad (7)$$

and

$$T_i = T_e \equiv T_M - T_M^{IK} - g c_i. \quad (8)$$

Here c_i is the impurity concentration on the liquid side of the interface, c_S is the impurity concentration on the solid side of the interface, and k_0 is

known as the rejection coefficient. Likewise T_i is the temperature at the interface which if the system is near to local equilibrium, is given by the equilibrium melting temperature, T_e . The equilibrium melting temperature is given by the melting temperature at zero impurity concentration T_M together with a correction rising from minus the slope of the liquidus line, g , and a curvature correction or Gibbs-Thompson effect. Here k is the curvature and Γ is a capillary coefficient. Additionally, some suitable boundary condition must be imposed at infinity.

At faster speeds the constitutive relations on the boundary must be altered. In the spirit of Coriell and Sekerka we set

$$c_s = k(v, c_i)c_i \quad (9)$$

and

$$T_e - T_i = f(v, c_i). \quad (10)$$

Expressions (9,10) may be considered to include such models of interfacial kinetics as appear, for example, in the recent works of Aziz [8] or Caroli, Caroli, and Roulet [9].

Notice that equations (1-8) admit a planar interface $\phi = 0$, $c = c_1 + c_2 \exp(-VZ/D)$, $T_L = t_1 + t_2 \exp(-VZ/D_L)$ and $T_S = \hat{t}_1 + \hat{t}_2 \exp(-VZ/D_S)$. Five of the six coefficients are determined by the equations if we impose the boundary condition $c \rightarrow k_0 c_0$ as $z \rightarrow \infty$. We can interpret this to mean that an externally chosen temperature profile may be imposed, if the overall velocity of the system is taken so that $c \rightarrow k_0 c_0$. In this paper we limit our considerations to small perturbations around this planar interface. Thus, we linearize k and f about the planar interface

$$\begin{aligned} c_s &= (k_0 + k_v \Delta v + k_c \Delta c)c_i \\ \Delta(T_e - T_i) &= f_v \Delta v + f_c \Delta c \end{aligned}$$

where $\Delta g = g - g_{\text{planar}}$, and $k_0 = k_{\text{planar}}$ and we assume $k_0, k_v, k_c, (T_e - T_i)_{\text{planar}}, f_v$ and f_c to be known.

We now make a number of simplifying assumptions. While eventually it would be desirable to include all possible effects, the simplified model is presented here because it already exhibits rather rich behavior. Our assumptions are as follows: $D_L \gg D, D_S \gg D, L_V \ll 1$, and $k_S = k_L$. In this limit, as noted in [6], the temperature and the concentration equations decouple. The temperature profile is then given by

$$T = T_0 + Gz \quad (1)$$

and the remaining equations are

$$c_t = D\nabla^2 c + V \frac{\partial}{\partial z} c \quad (2)$$

with the boundary and auxillary conditions

$$V_n = -D(\partial c / \partial n) / (c - c_s) \quad (3)$$

$$T_e = T_M - T_M \Gamma K - gc \quad (4)$$

$$c_s = (k_0 + k_v \Delta v + k_c \Delta c) c_i \quad (5)$$

$$\Delta(T_e - T_i) = f_v \Delta v + f_c \Delta c. \quad (6)$$

$$c \rightarrow k_0 c_i \quad z \rightarrow \infty$$

Combining (1), (4) and (6) and likewise (3) and (5), we obtain finally

$$c_t = D\nabla^2 c + V \frac{\partial}{\partial z} c \quad z > \phi$$

$$0 = T_M \Gamma K + G\phi + \Delta v f_v + \Delta c (f_c + g) \quad z = \phi$$

$$0 = D\partial c / \partial n + Vc(1 - \{k_{p\ell} + \Delta v k_1 + \Delta c_1 k_2\}) \quad z = \phi$$

$$c \rightarrow k_0 c_0 \quad z \rightarrow \infty$$

Introducing the dimensionless variables

$$\tilde{c} = c/c_0, \quad \tilde{x} = x(V/D), \quad \tilde{t} = t(V^2/D) \quad \tilde{\phi} = \phi V/D,$$

and dropping the tildas, we obtain,

$$c_t = V^2 c + \frac{\partial}{\partial z} c \quad z > \phi$$

$$c = 1 - \frac{\beta \phi_{xx}}{(1 + (\phi_x)^2)^{3/2}} + w\phi + \left\{ \frac{\phi_t + 1}{(1 + \phi_x^2)^{1/2}} - 1 \right\} F \quad z = \phi$$

$$0 = \partial c / \partial n + \frac{(1 + \phi_t) c}{(1 + \phi_x^2)^{1/2}} (1 - \{k_0 + (\frac{1 + \phi_t}{(1 + \phi_x^2)^{1/2}} - 1)R + (c-1)S\}) \quad z = \phi$$

$$c \rightarrow k_0 \quad z \rightarrow \infty$$

and the dimensionless planar state is given by

$$c = k_0 + (1 - k_0)e^{-z}$$

where

$$\beta = \frac{T_M \Gamma V/D}{c_0 [g + f_c]}, \quad w = \frac{GD/V}{c_0 [g + f_c]}, \quad A = \frac{V f_v}{c_0 [g + f_c]}, \quad R = V k_v, \quad \text{and} \quad S = c_0 k_c.$$

Noting that we may expect more impurity solute trapping and a lowering of the interfacial temperature below its equilibrium value as the external velocity is increased, k_c and f_v may be expected to be positive. Likewise, minus the slope of the liquidus line may be reasonably taken to be positive.

The technique of our analysis follows closely that which appeared in [6] and [7], however, slight differences appear at various steps, hence the details are given here for the sake of completeness. We look at linear stability of perturbations about the planar state, and obtain the dispersion relation

$$0 = \left[\frac{1}{2} - k_0 - S - \frac{1}{2} \sqrt{1 + 4(k_x^2 + \sigma)} \right] \left[(1 - k_0 - w) - \beta k_x^2 - \sigma A \right] + \left[(1 - k_0)(k_0 + S) + \sigma(1 - k_0 - R) \right]$$

and noting that when $w = \epsilon^2$ and $\beta(k_0 + c_0 k_2) - (1 - k_0) \sim \epsilon$, then in the unstable region $k_x \sim \epsilon^2$, and the dispersion relation is of the approximate form,

$$\sigma(w + (k_0 + S)A - k) \approx -k_x^4(1 - k_0 + w + \beta) + k_x^2(1 - k_0 + w - \beta(k_0 + S)) - w(k_0 + S).$$

Note that this dispersion relation is of the desired form; i.e., $k_{\max} \approx 0$ and $\sigma(k = 0) < 0$. From the approximate dispersion relation it is clear that the linear terms in the equation for ψ will be of the same form as appeared in [6] and [7] for the case $w \sim 1$ and $k_0 \ll 1$, although as it turns out, different nonlinearities appear.

Introducing the scaled variables

$$\tau = \epsilon^2 t, \quad \xi = \epsilon^{1/2} x, \quad z = z, \quad w = \epsilon^2, \quad \text{and} \quad (1 - k_0) = \beta(k_0 + S) + O(\epsilon),$$

then in curvilinear coordinates our system of equations becomes

$$0 = (c_z + c_{zz}) + \epsilon(c_{\xi\xi} + \phi_3^2 c_{zz} - 2\phi_\xi c_{\xi z} - \phi_{\xi\xi} c_z) + \epsilon^2(-c_\tau + \phi_\tau c_z) \quad z > 0$$

$$c = 1 + \frac{\epsilon\beta\phi_{\xi\xi}}{(1 + \epsilon\phi_\xi^2)^{3/2}} - \epsilon^2 w\phi - \left(\frac{1 + \epsilon^2\phi_\tau}{(1 + \epsilon\phi_\xi^2)^{1/2}} - 1 \right) A \quad z = 0$$

$$0 = (1 + \epsilon\phi_\xi^2) c_z - \epsilon c_\xi \phi_\xi + \left[(1 + \epsilon^2\phi_\tau) c \left(1 - \left\{ k_0 + \left(\frac{1 + \epsilon^2\phi_\tau}{(1 + \epsilon\phi_\xi^2)^{1/2}} - 1 \right) R + (c - 1) S \right\} \right) \right] \quad z = 0$$

$$c \rightarrow k_0 \quad z \rightarrow \infty.$$

Formally expanding $c = c_0 + \epsilon c^1 + \dots$ and $\phi = \epsilon F^1 + \epsilon^2 F^2 + \dots$, then substituting and solving the $O(1)$, $O(\epsilon)$, and $O(\epsilon^2)$ equations, we find that

$$c^0 = k_0 + (1 - k_0)e^{-z},$$

$$c^1 = 0$$

and

$$c^2 = \beta F_{\xi\xi}^1 c^{-z} + F_{\xi\xi}^1 (1 - k_0) z e^{-z}.$$

At $O(\varepsilon^3)$, solvability conditions require $F^1(\varepsilon, t)$ to satisfy the equation

$$\begin{aligned} (A(k_0+S)-R)F_{\tau}^1 + \frac{1}{2} (R-(k_0+S)A)(F_{\xi}^1)^2 + ([1-k_0] - [k_0+S]\beta)F_{\xi\xi}^1 + \\ + (k_0+S)WF^1 + (\beta + (1-k_0))F_{\xi\xi\xi\xi}^1 = 0. \end{aligned}$$

Invoking symmetry and invariance we obtain that in two dimensions the governing equation should be

$$S_1 F_{\tau}^1 + S_1 |\nabla F^1|^2 + S_2 \nabla^2 F^1 + S_3 \nabla^4 F^1 + S_4 F = 0.$$

Recalling that

$$S_1 = A(k_0+S)-R = vk_v \left[\frac{(k_0 + c_0 k_c)}{c_0(g + f_c)} - 1 \right],$$

we obtain that $S_1 > 0$ if c_0 is sufficiently small. Likewise

$S_2 = ([1 - k_0] - [k_0 + S]\beta) > 0$ if β is sufficiently small. Also $S_3 > 0$ if $S = c_0 k_c$ is not too large. Lastly, since $k_0 < 1$, $S_4 > 0$. Rescaling $t = (S_4/S_1)\tau$, $x = (S_4/S_2)^{1/2}\xi$, and $G = (S_1/S_2)F^1$, then

$$G_{\tau} = |\nabla G|^2 + \nabla^2 G + \alpha \nabla^4 G + G = 0 \quad (**)$$

where $\alpha = S_3 S_4 / S_2^2$. Note that if we make the further transformation $\hat{G} = -G$, then the Kuramoto-Sivashinsky equation [10,11] is obtained.

DISCUSSION:

The Kuramoto-Sivashinsky equation is known to exhibit intermittancy superimposed on a relatively stable array of cusps or wrinkles [2]. The inversion $\bar{G} \rightarrow -G$ would then give downward cusps, precisely the direction which could be expected on a solidification front. Furthermore this intermittancy is perhaps to be expected in the limit as the imposed temperature profile becomes more gradual just before the interface becomes diffuse.

It should not be difficult to alter our analysis to include small latent heat effects, and non-equal thermal conductivities. This will be done in a forthcoming analysis.

Lastly perhaps equation (*) could provide an appropriate context in which to test Langer's principle of marginal stability, although the intention would be to forward as opposed to side propagation.

REFERENCES

1. Coriell, S.R., and Sekerka, J. *Cryst. Growth*, 61 (1983) 499-508.
2. Michelson, D.M., and Sivashinsky, G.I., *Acta Astronautica*, 4 (1977) 1207-1221.
3. Dee, G., and Langer, J.S., *Phys. Rev. Lett.* 50 (1983), 383.
4. Mullins, W.W., and Sekerka, J. *Appl. Phys.* 35 (1964) 444.
5. Wollkind, D.J., and Segel, L.A., *Phil. Trans. Roy. Soc. (London)* 268A (1970) 351-380.
6. Sivashinsky, G.I., *Physica* 8D (1983) 243-248.
7. Novick-Cohen, A., and Sivashinsky, G.I., to appear in *Physica D*.
8. Aziz, M.J., *J. Appl. Phys.* 53 (1982), 1158.
9. Caroli, B., Caroli, C., and Roulet, B., to appear.
10. Sivashinsky, G.I., *Acta Astronautica*, 4 (1977), 1177-1207.
11. Kuramoto, Y., *Prog. Theor. Phys.*, 63 (1980) 1885-1903.