Eutectic Solidification and Marginal Stability

J. S. Langer
Physics Department and Center for the Joining of Materials, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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A simple model of eutectic solidification is used to illustrate the marginal-stability theory of pattern selection in nonequilibrium processes. The nonlinear equation of motion which describes this model suggests a mechanism for noise amplification at the marginally stable operating point of the system.

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Some of the most interesting questions in the theory of nonequilibrium systems pertain to the mechanisms of pattern selection. A familiar example occurs in the Bénard problem[1] where the hydrodynamic equations of motion by themselves seem unable to provide a unique prediction for the spacing of convective cells.[2] These equations of motion predict the existence of stable steady-state convective patterns with a finite range of periodicities. Nature, however, seems to select only one of these patterns.

An almost identical situation occurs in the solidification of binary fluids with compositions at or near the eutectic point. Such systems generally solidify in the form of parallel lamellae of the two coexisting solid phases or, alternatively, rods of one phase in a matrix of the other. The lamellar version is illustrated in Fig. 1 where a periodic array of solid phases α and β is shown growing upward into the fluid. The situation that we shall consider is one in which the velocity of the solidification front is fixed by the imposition of a moving temperature gradient as in a zone-refining or directional-solidification process. It is known experimentally that the lamellar spacing λ is uniquely determined by the growth conditions. The steady-state theory for this system has been worked out in detail by Jackson and Hunt,[3] who find that solutions exist at all λ's and, further, argue on physical grounds that these solutions will be stable whenever λ is greater than some critical value λ_c.[4] It turns out that this critical λ_c coincides with the point of minimum undercooling of the solidification front (or equivalently, the point of maximum growth velocity at fixed temperature). The condition of minimum undercooling[5] has conventionally been assumed in the metallurgical literature to locate the operating point of this system; and the resulting predictions seem to be in good agreement with experiment. There has never been any really fundamental justification for this condition, however; nor has there even been a systematic study of the stability problem.[6]

The beauty of the eutectic model, in contrast to the Bénard or the single-phase solidification problems,[7] is that one can derive a useful equation of motion for the system with little more than dimensional considerations. To do this, we start by writing the steady-state result of Jackson and Hunt[3] in the form

$$\Delta T(\lambda) \propto \left(\frac{\lambda}{\lambda_c} + \frac{\lambda_c}{\lambda}\right), \tag{1}$$

where ΔT is the undercooling at the solidification front and λ_c, the critical λ mentioned above, has the standard form[7] for a stability length

$$\lambda_c{}^2 \propto D d_0 / v. \tag{2}$$

Here D is the diffusivity in the liquid, d_0 is a capillary length, and v is the growth velocity. Equation (1) can be understood qualitatively as follows: The first term on the right-hand side,

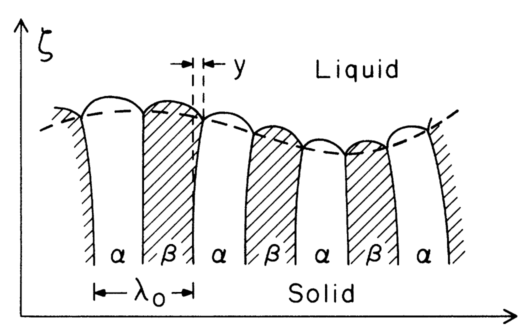

FIG. 1. Schematic illustration of a lamellar eutectic growing up the page with a deformed solidification front. The lamellae may be visualized as semi-infinite plates perpendicular to the plane of the paper. Experiments may also be performed in which the entire sample is a thin film in the plane of the page. The analysis in this paper is most directly applicable to the latter situation.

proportional to λ, arises because each advancing α region rejects β atoms and vice versa. Thus the fluid ahead of each solid region is supersaturated and the interfacial temperature is correspondingly depressed. The second term is a capillary effect. As shown in Fig. 1, the solidifying surfaces at the fronts of the lamellae must bulge forward in order that capillary forces balance at the triple points. This curvature, proportional to λ^{-1}, determines the second contribution to the undercooling *via* the Gibbs-Thomson relation.

Now suppose that this solidification front is slowly and gently deformed on a length scale much greater than λ. Let this deformation be described by the function $\zeta(x, t)$, the dashed curve in the figure, which measures the vertical displacement of the interface away from its undeformed position in the frame of reference moving with velocity v. If the moving temperature gradient which defines this frame of reference has magnitude G, then

$$G\zeta = -\Delta T(\lambda). \tag{3}$$

Next, define $y(x, t)$ to be the horizontal displacement of lamellae originally at position x. (See Fig. 1.) That is, the local lamellar spacing is

$$\lambda(x, t) \cong \lambda_0(1 + \partial y/\partial x), \tag{4}$$

where λ_0 is the original spacing of the undeformed system. Our basic assumption—one which was crucial to the stability argument of Jackson and Hunt—is that ζ and y are coupled by the condition that each lamella must grow in a direction which is locally perpendicular to the solidification front. Thus

$$\partial y/\partial t \cong -v\, \partial\zeta/\partial x. \tag{5}$$

Taking two derivatives with respect to x on both sides of (3), we obtain a nonlinear partial differential equation for $\lambda(x, t)$:

$$\frac{\partial\lambda}{\partial t} \cong \frac{v\lambda_0}{G}\frac{\partial^2}{\partial x^2}\Delta T(\lambda). \tag{6}$$

Equation (6) may conveniently be rewritten in the form

$$\frac{\partial\Lambda}{\partial\tau} = \frac{\partial}{\partial x}\mathfrak{D}(\Lambda)\frac{\partial\Lambda}{\partial x}, \tag{7}$$

where $\Lambda = \lambda/\lambda_c$ and $\mathfrak{D}$ plays the role of a Λ-dependent diffusion constant:

$$\mathfrak{D}(\Lambda) = 1 - \frac{1}{\Lambda^2} \propto \frac{d}{d\lambda}\Delta T(\lambda). \tag{8}$$

Note that several constant factors have been absorbed in the new timelike variable τ. The stability properties described by Jackson and Hunt are immediately apparent here. Constant-Λ solutions of (7) are differentially stable as long as $\mathfrak{D}$ is positive, that is, as long as $\Lambda > 1$ ($\lambda > \lambda_c$) so that the system is on the large-λ side of the minimum in ΔT. Nothing in the equation of motion by itself, however, seems to tell us which member of this continuous set of stable solutions is selected in nature.

The crucial fact here is that the point of minimum undercooling is also the point of marginal stability. In our recent work on dendritic solidification[7,8] (where an analogous maximum-velocity principle turned out *not* to be valid), we argued that a system of this kind, when driven by thermal fluctuations or other noise sources, generally drifts toward a state of marginal stability. The argument, as applied here, is simply that $\mathfrak{D}$ decreases with decreasing Λ, and thus a fluctuation which drives Λ downwards persists for a longer time than one which goes in the other direction. If there exists somewhere in the system some mechanism for creating new lamellae (defects, edges, etc.) then the time-averaged effect of noise must be to drive the system into new stable configurations with diminishing values of Λ.

We can make the above argument more precise by considering, in principle, what happens if we add a noise source to the right-hand side of (7). As it stands, Eq. (7) does not contain any sources or sinks for lamellae; it is a strict statement of local conservation of the field Λ, and therefore cannot describe any change in the average value of Λ over the entire system. We can circumvent this difficulty by applying the noise source to only a finite part of the system—in effect, using the infinite unperturbed part of the system as the "Λ bath"—and then looking to see whether lamellae flow into or out of the noisy zone. The required analysis is quite simple. Let $\overline{\Lambda}$ be the average value of Λ in the presence of noise; and write the exact Λ for any particular member of the ensemble of noise sources in the form $\overline{\Lambda} + \delta\Lambda$. Then expand (7) about $\overline{\Lambda}$ and average over this ensemble. The result is

$$\frac{\partial\overline{\Lambda}}{\partial\tau} = \frac{\partial}{\partial x}\mathfrak{D}(\overline{\Lambda})\frac{\partial\overline{\Lambda}}{\partial x} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\frac{d\mathfrak{D}}{d\overline{\Lambda}}\langle(\delta\Lambda)^2\rangle + \dots\,. \tag{9}$$

If $\overline{\Lambda}$ is roughly constant as a function of x and the noise is sufficiently weak that the higher-order terms in (9) are small, then the Λ flux driven by the noise source is

$$-\frac{1}{2}\frac{d\mathfrak{D}}{d\bar{\Lambda}}\frac{\partial}{\partial x}\langle(\delta\Lambda)^2\rangle.$$

Because $d\mathfrak{D}/d\bar{\Lambda}$ is positive, this flux flows out of the noisy zone as expected; that is, the lamellae flow *in*.

Having argued that fluctuations cause the eutectic system to drift toward $\Lambda = 1$, we must inquire about what happens when the system actually reaches this point. Equation (7) suggests a very interesting answer to this question. Suppose that, as illustrated by the solid curve in Fig. 2(a), the system has reached a point where $\Lambda \gtrsim 1$ almost everywhere but a fluctuation has caused Λ to drift to slightly subcritical values in some finite region. At the minimum of this curve, $\partial\Lambda/\partial x = 0$, $\partial^2\Lambda/\partial x^2 > 0$, and $\mathfrak{D} < 0$; thus Λ decreases. Another useful point to consider is x_1, defined by $\Lambda(x_1, t) = 1$. Differentiating this relation and using (7), we find

$$\frac{dx_1}{dt} = -\frac{\partial\Lambda/\partial t}{\partial\Lambda/\partial x} = -2\left[\frac{\partial\Lambda}{\partial x}\right]_{x=x_1}. \tag{10}$$

The sign of the right-hand side implies that the pair of points labeled x_1 in the figure are approaching each other. The resulting behavior is indicated by the arrows and dashed curve in Fig. 2(a) and by the schematic illustration of the actual event in Fig. 2(b). What is happening here is that all of the intensity of an initially diffuse and shallow fluctuation is being concentrated at a point. When Λ touches zero, the lamella at that point disappears, and the equation of motion loses its validity. The physical system presumably reverts to a state with fewer lamellae and larger average Λ, from which configuration the entire process must start all over again.

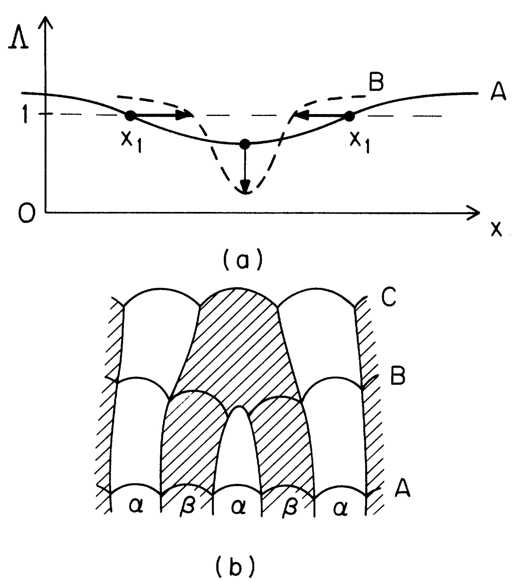

FIG. 2. Schematic illustration of an unstable fluctuation which terminates a lamella. Part (a) shows the function Λ at two successive instants A and B. The corresponding sequence of solidification fronts is shown in part (b). Front C occurs sometime later when the system has restabilized at a larger average value of Λ.

The process just described is a mechanism for the amplification of small fluctuations near the marginal-stability point. In general, if the marginal-stability principle is valid, one expects pattern-forming systems to be strongly sensitive to perturbations simply because the linear restoring force for some class of deformations vanishes at the operating point. In the eutectic system, this sensitivity shows up in the way that weak fluctuations are able to trigger macroscopic events, i.e. the termination of lamellae. It is tempting to speculate that a similar mechanism is present in the Bénard system. Perhaps extended Bénard systems are intrinsically noisy[9] because they are operating at a marginal-stability point where microscopic fluctuations are capable of inducing random macroscopic defects in the convection pattern.

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ERRATUM

STUDY OF THE DECAY $K_L{}^0 \to \pi^+\pi^-\gamma$. A. S. Carroll, I-H. Chiang, T. F. Kycia, K. K. Li, L. Littenberg, M. Marx, P. O. Mazur, J. P. de Brion, and W. C. Carithers [Phys. Rev. Lett. 44, 529 (1980)].

On page 531, column 2, lines 9 and 10 should read as follows: "... the θ distribution of the direct decay would be $\sin^2\theta(1+\alpha\cos^2\theta)$ ...". The expression for $d^2W/dk\,d\cos\theta$ on line 19 of the same page should read as follows:

$$\frac{d^2W}{dk\,d\cos\theta}=\frac{\alpha}{\pi}\,\Gamma(K_S\to\pi^+\pi^-)\frac{k^3\beta^3}{8\beta_0}\sin^2\theta\left\{\frac{16}{k^4}\frac{|\eta_{+-}|^2}{(1-\beta^2\cos^2\theta)^2}-\frac{8}{k^2}\frac{|\eta_{+-}|\sin(\varphi_{+-}+\delta_0-\delta_1{}^1)}{1-\beta^2\cos^2\theta}X_E+(X_E{}^2+X_M{}^2)\right\}.$$