MODELS OF PATTERN FORMATION IN FIRST-ORDER PHASE TRANSITIONS

J. S. Langer

Institute for Theoretical Physics
University of California
Santa Barbara, California 93106
USA

The study of simplified theoretical models is an important part of the search for a more general and systematic theory of natural pattern formation. Three qualitatively different kinds of models are considered here, each pertaining to the special class of situations in which patterns are formed during first-order phase transformations. The first of these models is the basic thermodynamic description of a solidifying system controlled by thermal diffusion and inter-facial attachment kinetics. The second is a continuum model which is the deterministic limit of "Model C" of Hohenberg, Halperin and Ma. The third is a contour dynamical, boundary-layer model that recently has proven useful for probing the fully nonlinear development of morphological instabilities. Insights concerning the mathematical mechanism for pattern selection in the relatively tractable boundary-layer model appear to be useful clues for understanding the behavior of the more complex and realistic models.

1. The Role of Models in the Search for a Systematic Theory of Pattern Formation

A systematic understanding of the mechanisms by which forms are generated in nature seems well beyond our grasp at present. We see a bewildering variety of patterns emerging even in inanimate phenomena — in solidification, hydrodynamics, chemical reactions, etc. — and we are only just beginning to comprehend the enormity of the task of understanding how patterns are formed in living systems. Eventually, we hope to know how to sort out these processes according to underlying mechanisms, to understand which phenomena are related to one another, to distinguish intrinsically complex situations from those which are fundamentally simple. We are not yet near the point where we can do such things, but it is always useful to think about what we need to learn in order to get there.

The most obvious classification of processes, one which has begun to be studied seriously in recent years, distinguishes physical situations which actually lead to regular, reproducible patterns from those which do not. For example, small slightly supercritical Rayleigh-Bénard convection cells exhibit sharp wavelength selection induced by boundary conditions (Whitehead, 1975). Selection of dendritic shapes and growth rates also seems to be sharp, but is independent of boundaries (Glicksman *et al.*, 1976; Huang and Glicksman, 1981; Langer, 1980). In larger Rayleigh-Bénard systems, wavelength selection is history dependent or nonexistent (Heutmaker *et al.*, 1985; Ahlers *et al.*, 1985). A growing number of theoretical models and experimental situations is currently being studied from this point of view, and I am optimistic that some specific questions will be answered in the next few years. Specific answers should lead to more general conclusions.

Another kind of classification that I think might be achievable , probably on a longer time scale, would involve the amount of information required to specify a pattern-forming event. For example, complicated dendritic structures are formed during solidification of simple substances in which both the intrinsic properties of the material such as thermal conductivity and surface tension as well as externally controlled parameters such as the temperature of the melt are held constant throughout the process. Natural snowflakes, on the other hand, owe some of their diversity to slight changes in the temperature and humidity of their environments during the history of their formation (Hobbs, 1974). In biological processes, the pattern-forming media themselves apparently change their properties in response to complex sequences of external stimuli. Might it not be possible to learn how to recognize some external signatures of these different levels of intrinsic complexity? Equivalently, might it not be possible

to deduce from the external features of a pattern forming process what are the minimum ingredients of an underlying physical model of the phenomenon?

Another example of the kind of classification that I think would be useful has to do with the precision with which pattern formation is controlled. Dendrites, convection patterns, and the like are stable against thermal fluctuations, but are never more precise in their features than is consistent with the noise in their environments. Some biological processes, on the other hand, appear to do better[1]. I think that we are on the verge of understanding how some inanimate processes may be acutely sensitive to small systematic changes in growth conditions without actually amplifying environmental noise; but the mechanisms by which living systems approach quantum limits of precision — if indeed they do so — constitute scientific *terra incognita*. As in the case of complexity, systematic characterization of these various levels of precision is equivalent to specifying minimum ingredients of adequate physical models.

If we are far from possessing a systematic theory of morphogenesis, the reason, I think, is that we still do not understand very well the properties of even the simplest models of pattern formation. Accordingly, my intention in this essay is to write about one special class of models, those that are based on first-order phase transitions, and to encourage the reader to consider with me how the information that we are obtaining about these models may ultimately fit into a bigger picture. As I shall argue later, association with a true thermodynamic phase transition is not likely to be a deep, distinguishing feature of pattern-forming systems in the sense outlined above. The choice of this class of models simply serves to narrow the discussion to manageable dimensions, and also lets me touch upon some work of Shang-Keng Ma (Halperin *et al.*, 1974; Hohenberg and Halperin, 1977), to whose memory this essay is dedicated.

My plan is to start by describing what I shall call the basic model of solidification. In fact, this is a fairly general model of what happens when two phases of a system are in contact with each other at a well defined boundary, and when the departure from equilibrium between these two phases causes that boundary to move. To emphasize the generality of this physical situation, I shall then move one step backwards toward a more fundamental description by showing how this model is related to the Ginzburg-Landau or Cahn-Hilliard models of phase transitions that have become so familiar to physicists in the last three decades. Finally, I shall move forward in time to describe a drastically truncated

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[1] The biological literature is so huge and foreign to this author that it does not seem possible to insert an exactly appropriate reference here. A classic text is that of D' Arcy W. Thompson (1944). For a more recent review, see Belintsev (1983a, 1983b). The problem of precision in biological systems has been addressed by Bialek (1983).

"boundary-layer" model (Ben-Jacob *et al.*, 1983, 1984b), that I and my colleagues have proposed recently for the purpose of probing the fully nonlinear behavior of solidifying systems. This newer model has led to some interesting and surprising results which, if confirmed in the case of more realistic systems, may provide useful clues about a more general theory.

2. The Basic Model of Solidification Theory

In the conventional thermodynamic model of the solidification of a pure substance from its melt, the fundamental rate-controlling mechanism is the diffusion of latent heat away from the interface (Chalmers, 1964; Woodruff, 1973). The dimensionless thermal diffusion field is conveniently chosen to be

$$u = \frac{T - T_M}{(L/c)} , \qquad (2.1)$$

where T_M is the melting temperature and the ratio of the latent heat L to the specific heat c is an appropriate unit of undercooling. The field u satisfies the diffusion equation

$$\frac{\partial u}{\partial t} = D \nabla^2 u , \qquad (2.2)$$

where D is the diffusion constant which can, if we choose, be taken to have different values in the liquid and solid phases.

The crucial ingredients of the model are the boundary conditions imposed on u at the solidification front. First, there is heat conservation:

$$v_n = - [D\hat{n} \cdot \nabla u] , \qquad (2.3)$$

where $\hat{n}$ is the unit normal directed outward from the solid, v_n is the normal growth velocity, and the square brackets denote the discontinuity in the heat flux across the boundary. The physically more interesting condition is a statement of thermodynamic equilibrium — or small departure therefrom — which determines the temperature u_s at the two-phase interface:

$$u_s = - d_0 \kappa - \beta(v_n) . \qquad (2.4)$$

The right-hand side of (2.4) describes deviations from the state of thermodynamic equilibrium between two bulk phases in contact at a flat interface. The first term is the Gibbs-Thomson correction for a curved surface; κ is the sum of the principle curvatures, and $d_0 = \gamma c T_M / L^2$ is a capillary length, ordinarily of order Ångstroms, which is proportional to the surface tension γ.

The second term in (2.4) accounts for departures from local equilibrium associated with motion of the interface. To see this more generally, rewrite the equation in the form

$$v_n = \beta^{-1}(\delta u_s) \, , \tag{2.5}$$

where $\delta u_s \equiv -d_0 \kappa - u_s$ is the effective undercooling at the interface and $\beta^{-1}(\delta u_s)$ is the functional inverse of $\beta(v_n)$. The special choice $\beta^{-1} = \delta u_s/\beta_0$ implies linear response with a kinetic coefficient β_0^{-1}. A linear law of this kind might be accurate for a molecularly rough interface, in which case $\beta_0 = 0$ would describe the limit of pure diffusion control. For facetted interfaces, on the other hand, β^{-1} may be a highly nonlinear function of δu_s. In the latter case it is clear that β^{-1} must depend strongly on the orientation of the interface relative to the axes of symmetry of the growing crystal. Even in the linear, nonfacetted situation, both the inverse kinetic coefficient β_0 and the capillary length d_0 may be orientation-dependent and such effects of crystalline anisotropy seem to be extremely important in pattern selection.

The above equations, supplemented by initial data and boundary conditions on u far from the solidification front, constitute a complete statement of a physically realistic moving-boundary problem. In principle, these equations could be programmed into a computer and, with proper choices of parameters, the computer would predict the snowflake-like patterns seen experimentally when pure substances are solidified from undercooled melts[2]. The model does omit some physical effects such as hydrodynamics of the fluid phase and any elastic, plastic, or dynamic properties of the solid; but I think it highly unlikely that any of these effects will be of central importance for dendritic pattern formation. In practice, however, this model has been too difficult for extensive numerical analysis except in special cases which are, for our purposes, too simple to be interesting. The advent of parallel-processing computers, adaptive-grid algorithms, and the like should improve this situation in the near future, and the ability to make accurate simulations of the basic solidification model with various geometries and choices of parameters ultimately should prove very useful in developing and testing basic theory. I want to emphasize, however, that the role of numerical simulation at best is not essentially different from that of carefully controlled experimentation, especially in situations like this where the underlying physical model seems well understood. Experiments, both real and numerical,

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[2] So far as I know the closest that anyone has come to seeing dendritic behavior in a numerical solution of the basic solidification model is the work of Oldfield (1973). Oldfield's methods, although subject to some uncertainties, seem to have been about ten years ahead of their time. For a more recent attempt, see Smith (1981).

can test existing theoretical ideas and inspire new ones, but cannot substitute for fundamental theory.

3. The Phase-Field Model

The phase-field model, except for its neglect of stochastic forces, is identical to what Halperin, Hohenberg, and Ma (1974) have called "model C" in their studies of nonequilibrium critical phenomena; that is, it is a phenomenological model of the class of phase transitions which can be described by a nonconserved scalar order parameter coupled to a conserved noncritical thermal field.

There are two special reasons for discussing model C at this point in this essay. First, the classification of critical-point models that has emerged from a fundamental understanding of their distinguishing dynamical characteristics is a good example of the kind of systematization that I should like to see for models of pattern formation. I do not mean to imply that there is any particular similarity between the two kinds of problems, or that the problem of pattern formation as a whole might be amenable to such a complete systematization. However, in the next several paragraphs, we shall observe that the basic solidification model is a limiting case of model C; and this fact may help us to recognize similarities within this class of pattern-forming processes. For example, the role of the rate-limiting thermal field could be played by diffusing impurities, or diffusion of the primary substance through an inert secondary medium, without changing the mathematical statement of the model. On the other hand, this model of a true phase transition appears to be subtly different from, say, diffusion-limited aggregation (Witten and Sander, 1983).

The second reason for current interest in model C is that it may provide the most natural algorithm for numerical solutions of the basic solidification model. This is the context in which the term "phase-field model" has been introduced by Fix (1983)[3]. A serious difficulty with the basic model is that it requires the computer to track a moving boundary, a procedure which is frought with numerical hazards. The idea which Fix has pursued is to replace the dynamics of the boundary by an equation of motion for a phase-field — in other words, an order parameter — which changes from one value to another quickly but smoothly at the two-phase interface. The obvious way of inventing such an equation is to go back to the physics, that is, to use model C. The new partial

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[3] Fix and Lin (unpublished) have demonstrated the feasibility of their technique for studying the onset of instabilities but have not yet used it to generate more complex solidification patterns. A similar idea has been developed independently by Collins and Levine (1985), and also by Deutsch (1985).

differential equation for the phase field is necessarily much stiffer than the diffusion equation for the thermal field; but stiff equations may turn out to be easier to control numerically than moving boundaries. The results are not known yet.

My purpose in the next few paragraphs is to provide a simple, intuitive description of the phase-field model without any attempt at rigor or completeness. Most of the ideas probably would have seemed familiar to Gibbs or van der Waals, but I think that they are worth repeating in a modern context.

Let $\phi(x, t)$ be the phase field, a function of position x and time t. Its equation of motion can be chosen to be

$$\frac{\partial \phi}{\partial t} = -\Gamma \frac{\delta F}{\delta \phi} \quad , \tag{3.1}$$

where Γ is a kinetic coefficient and F is a free energy with the standard form:

$$F\{\phi\} = \int dx \left[\frac{K}{2} (\nabla \phi)^2 + f(\phi) - \alpha u \phi \right] . \tag{3.2}$$

Here, $f(\phi)$ is a free-energy density which we can choose to have minima with $f = 0$ at $\phi = \pm \Delta \phi$, so that the latter quantities are the equilibrium values of ϕ in the coexisting "liquid" ($+$) or "solid" ($-$) phases. The gradient-energy coefficient K determines the shape in equilibrium of the interfacial profile $\phi_s(x)$, which satisfies (3.1) with $d\phi_s/dt = 0$ and $u = 0$:

$$K \frac{d^2 \phi_s}{dx^2} = \frac{df}{d\phi_s} \quad , \tag{3.3}$$

and has associated with it the interfacial energy (Cahn and Hilliard, 1958)

$$\gamma = K \int_{-\infty}^{\infty} \left(\frac{d\phi_s}{dx} \right)^2 dx . \tag{3.4}$$

The coupling coefficient α can be determined from considerations of thermodynamic equilibrium to be $L^2/T_M c \Delta \phi$.

The phase-field model reduces to the basic solidification model in the limit where the thermal field u varies much more slowly than the phase-field ϕ in both space and time. An easy — and easily generalizable — way to see how this works is to consider a growing d-dimensional sphere in a region of constant

$u < 0$, and to look for an interfacial profile of the form $\phi \equiv \phi_s(r - R)$, where r is the radial coordinate, R is the slowly time dependent radius of the sphere, and ϕ_s is almost but not quite the same function that was defined in (3.3). Specifically, for r near R, ϕ_s now is a solution of

$$K \frac{d^2 \phi_s}{dr^2} \simeq \frac{d}{d\phi_s}(f - \alpha u \phi_s) - \eta \frac{d\phi_s}{dr} \, , \tag{3.5}$$

where

$$\eta = \frac{(d-1)K}{R} + \frac{v}{\Gamma} \, , \tag{3.6}$$

and $v = dR/dt$. When $|u|$ is sufficiently small, Eq. (3.5) can be solved by eye by the usual mechanical analogy; r becomes time and ϕ_s becomes the displacement of an object of mass K moving in the potential $-f + \alpha u \phi_s$ with damping constant η. The particle stays for a time R at the "solid" peak near $\phi = -\Delta\phi/2$ and then drops abruptly to the "liquid" peak near $+\Delta\phi/2$, losing an energy $\alpha|u|\Delta\phi$ in the process. The situation is illustrated in Fig. 1. The requirement that the friction constant η be just right to achieve this energy loss is:

$$-\alpha u(\Delta\phi) \simeq \eta \int \left(\frac{d\phi_s}{dr}\right)^2 dr \simeq \frac{\eta \gamma}{K} \quad . \tag{3.7}$$

In writing the final expression on the right-hand side of (3.7), I have used (3.4) and have ignored the small u-dependence of γ. This result is, in effect, a condition for the solvability of (3.5). It is conveniently rewritten in the form:

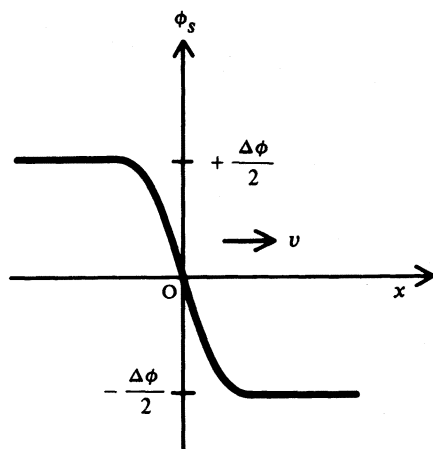$$v = -\frac{(d-1)\Gamma K}{R} - \frac{\Gamma K \alpha u \Delta\phi}{\gamma} \quad . \tag{3.8}$$

Equation (3.8) is the same as (2.4) or (2.5) in the case of linear response if we identify $\beta_0^{-1} = \Gamma K L^2 / \gamma C T_M$, set $u = u_s$, and generalize $(d-1)/R$ to be the curvature κ. Note that we have also recovered the Gibbs-Thomson condition by this procedure.

It remains to look at variations of the thermal field u. Let σ be the entropy density. Up to a ϕ-independent constant, σ is given by

$$\sigma = -\frac{\partial f}{\partial \tau} = \frac{\alpha C}{L} \phi = \frac{L\phi}{T_M \Delta\phi} \, , \tag{3.9}$$
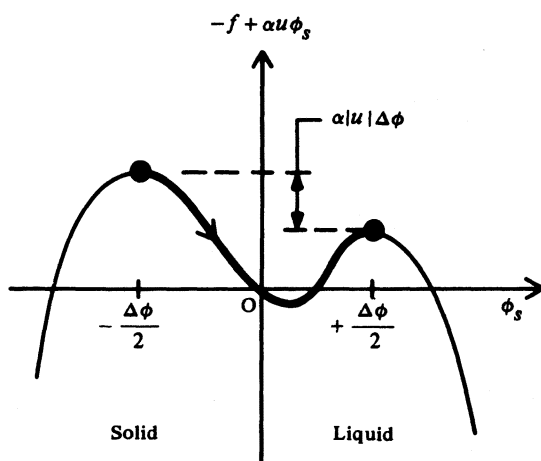
(a)

(b)

Fig. 1 (a) Schematic effective potential for the mechanical analogy used in the derivation of the equation of motion (3.8) for an interface in the phase-field model.
(b) Equilibrium interfacial profile $\phi_s(x)$.

which provides an interesting interpretation of the phase-field ϕ. The equation of motion for σ is just heat conservation:

$$T\frac{d\sigma}{dt} = T\frac{\partial\sigma}{\partial T}\frac{dT}{dt} + T\frac{\partial\sigma}{\partial\phi}\frac{d\phi}{dt} = cD\nabla^2 T \ . \tag{3.10}$$

With (2.1), (3.9), and $c = T\partial\sigma/\partial T$, (3.10) becomes

$$\frac{\partial}{\partial t}\left(u + \frac{\phi}{\Delta\phi}\right) = D\nabla^2 u \ . \tag{3.11}$$

Away from the interface, ϕ is a constant, and (3.11) reduces to the diffusion equation (2.2). Suppose that a flat section of interface is moving in the x direction with velocity v, so that

$$\phi(x, t) \simeq \phi_s(x - vt) \ ; \qquad \frac{\partial\phi}{\partial t} \simeq -v\frac{\partial\phi_s}{dx} \ . \tag{3.12}$$

Remembering that u must be continuous and slowly varying on the scale of the thickness of the interface, we can use (3.12) to integrate (3.11) from a point just on the solid side, say $x \lesssim 0$, to a neighboring point in the liquid at $x \gtrsim 0$. The result is the continuity condition (2.3). Thus the combination of equations (3.1) and (3.11) does reproduce, in the limit of a sharp interface and slowly varying thermal field, most of the features of the basic solidification model described in Sec. 2.

One crucial feature of solidification that has been missing so far in this description of the phase-field model is any effect of crystalline anisotropy. The simplest way that I know to add such effects is to include higher derivatives in the free energy; for example, the addition to the gradient energy of a term proportional to

$$\sum_{i=1}^{d}\left(\frac{\partial^2\phi}{\partial x_i^2}\right)^2 \ ,$$

would produce a cubic anisotropy[4]. This term would add fourth derivatives to equations (3.3) or (3.5) but apparently does not change the above results in any essential way other than causing the surface tension to become anisotropic.

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[4] Deutsch (1985) has demonstrated that a four fold anisotropy can stabilize the direction of growth of an embryonic dendritic protrusion.

The effect is the same as that of adding next-neighbor interactions along the symmetry axes in an Ising-like discretization of this model. One unnatural feature of this procedure is that the anisotropy pertains equally to the "liquid" as well as "solid" phases although it has a strong effect only at the interface. If that turned out to be unacceptable for some purposes, one could make the new term vanish in the "liquid" phase by multiplying it by an appropriate function of ϕ.

Because the phase-field model is a purely thermodynamic description of a first-order phase transition, one might expect that there exists a thermodynamic free energy functional which is a non-increasing function of time and which, therefore, serves as a Lyapunov functional for the coupled system of equations (3.1) and (3.11). Indeed, the appropriate free energy is

$$\mathscr{F} = \int dx \left\{ \frac{K}{2}(\nabla\phi)^2 + f(\phi) + \tfrac{1}{2}\alpha\Delta\phi u^2 \right\} \ . \tag{3.13}$$

To see this, let the independent fields be ϕ and $U = u + \phi/\Delta\phi$, in terms of which the equations of motion (3.1) and (3.11) can be written

$$\frac{\partial\phi}{\partial t} = -\Gamma\frac{\delta\mathscr{F}}{\delta\phi} \ , \tag{3.14}$$

$$\frac{\partial U}{\partial t} = \frac{D}{\alpha\Delta\phi}\nabla^2\frac{\delta\mathscr{F}}{\delta U} \ . \tag{3.15}$$

Then, so long as there are no fluxes across boundaries at infinity,

$$\frac{d\mathscr{F}}{dt} = -\int dx \left\{ \Gamma\left(\frac{\delta\mathscr{F}}{\delta\phi}\right)^2 + \frac{D}{\alpha\Delta\phi}\left(\nabla\frac{\delta\mathscr{F}}{\delta U}\right)^2 \right\} \leqslant 0 \ ; \tag{3.16}$$

thus $\mathscr{F}$ is a Lyapunov function.

So far as I know, the variational principle (3.16) is of no special help in solving pattern-selection problems; nor do I know of any variational formulation that is more useful. In systems undergoing phase transformations, patterns are either transient phenomena, that is, nonequilibrium shapes like snowflakes which are *en route* to simpler equilibrium structures, or else they occur in systems which are being driven away from equilibrium by constraints — fluxes at infinity — which invalidate (3.16). An example of the latter situation is directional solidification (Langer, 1980) where one observes, say, cellular

solidification fronts in a moving frame of reference in which heat is being added at one end and extracted at the other. The resulting problem is very similar to the Rayleigh-Bénard problem in hydrodynamics (Whitehead, 1975) for which no Lyapunov function seems to exist (except, perhaps, in the limit of weak flow near the threshold of instability). The lesson to be learned from all of this is that the question of whether a pattern-forming system is undergoing a first-order phase transition is *not* likely to be of primary importance in a systematic theory of morphogenesis. The focus of attention must not be on the existence of a free-energy or the like, but rather on the dynamical properties of the equations of motion themselves.

4. The Boundary-layer Model

The feature of the basic solidification model that makes it so difficult mathematically is its spatial and temporal nonlocality. The latent heat released at one point on the solidification front determines the motion of distant points at later times. As a result, a complete mathematical description must retain either the full diffusion field $u(\mathbf{x}, t)$ or, equivalently, the entire history of configurations of the front. Thus, the solidification model is intrinsically different from, for example, models of viscous fingering in porous media or in Hele-Shaw cells where the diffusion equation (2.2) for the thermal field is replaced by the Laplace equation for the pressure (Hele-Shaw, 1898; Saffman and Taylor, 1958). The latter replacement exaggerates spatial nonlocality but eliminates memory effects; the motion of the interface is determined only by its current configuration, and numerical analysis is feasible (Tryggvason and Aref, 1983). If we try omitting $\partial u/\partial t$ in (2.2) to study solidification, however, we lose Ivantsov's steady-state "needle-crystal" solutions (Ivanstov, 1947; Horvay and Cahn, 1961) and, therefore, we probably lose the possibility of studying persistent, i.e., non-transient, dendritic behavior[5].

The boundary-layer model (Ben-Jacob *et al.*, 1983; 1984b) has been invented in an attempt to include some of the nonlocality associated with the thermal diffusion field in an otherwise purely contour-dynamical description of pattern formation. The range of the diffusion field in front of a moving interface is generally of order $l \sim D/v$. If this range is much smaller than the radius of curvature of the interface, $\kappa l \ll 1$, then diffusion is effectively confined to a narrow region which we call the boundary-layer. Our basic idea is to replace the dynamics of the full diffusion field by an equation of motion for the local heat content of the boundary-layer as a function of position on the interface.

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[5]With the addition of anisotropy, however, these systems have been shown to produce remarkable snowflake-like patterns. See Ben-Jacob *et al.* (1986).

This major simplification (oversimplification?) turns out to have great mathematical benefits. In particular, lateral diffusion within the boundary layer mimics the retarded nonlocal interactions between different points on the solidification front, and these interactions can be described mathematically in a relatively tractable manner.

It must be emphasized that what is being described here is a model, not a systematic approximation. There do exist physical situations in which the condition $\kappa l \ll 1$ might be valid, for example, dendritic tips at large undercooling; although this is not the regime in which accurate experiments have yet been performed. Even in this regime, however, the natural instabilities of the solidification front lead to situations in which curvature is large or in which points on the front that are well separated from each other in arc length — for example, points on different side branches of a dendrite — approach each other in real space. Either of the latter situations imply a breakdown of the boundary-layer assumption. My preference is to think of the boundary-like picture as a model in its own right, guided by the physics of solidification but not expected to produce quantitative experimental predictions, its main purpose being to provide new insights into mathematical mechanisms of pattern selection.

Given the special purposes of the boundary-layer model, it has been reasonable to confine detailed analyses to the two-dimensional situation in which the solidification front is a simply connected curve, i.e., a "string". We can represent this front by specifying its curvature κ as a function of arc length s and time t. If θ is the angle between the normal to the front and a fixed direction (perhaps the orientation of some axis of symmetry of the growing crystal), then the definition of curvature,

$$\kappa(s,t) = \frac{\partial \theta}{\partial s} \; , \tag{4.1}$$

is a differential equation whose solution determines the curve. The equation of motion for κ is

$$\left(\frac{\partial \kappa}{\partial t}\right)_n = -\left(\frac{\partial^2}{\partial s^2} + \kappa^2\right) v_n \; , \tag{4.2}$$

which must be supplemented by the metric condition

$$\left(\frac{ds}{dt}\right)_n = \int_0^s \kappa \, v_n \, ds' \; . \tag{4.3}$$

Here, the subscript n denotes differentiation along the outward normal and v_n is the same normal velocity defined previously. Equations (4.2) and (4.3) are purely geometric statements; all physical content is contained in the quantity v_n.

The essence of the boundary-layer model is the assumption that $v_n(s, t)$ must depend only on local properties of the system at the position s and time t. The simplest assumption is that v_n is a function only of the local geometry; for example, v_n could have the form

$$v_n = (1 + \epsilon \cos m\theta)\left(\kappa + A\kappa^2 - B\kappa^3 + \gamma \frac{\partial^2 \kappa}{\partial s^2} \right) , \qquad (4.4)$$

where A, B, γ and ϵ are constants and m is an integer, say $m = 4$ or 6, which determines the crystalline symmetry. This is the "geometrical model" of Brower *et al.* (1983; 1984), which has proven to be immensely useful because it is simple enough to be analyzed in great detail and turns out to have interesting — if not quite dendritic — pattern forming properties.

The geometrical model (4.4) is missing the memory effects that I have advertized as being so important. For example, a flat interface ($\kappa = 0$) never moves. In real life, the velocity of such an interface can be finite, but must decrease like $t^{-1/2}$ because of the gradual build-up of latent heat in the fluid ahead of it. A related feature is that, although the geometrical model does have steady-state needle-crystal solutions when the "surface tension" γ vanishes, these needles have stationary straight sides instead of the parabolic shape characteristic of models with diffusion control. The principal success of the geometrical model is that the growth rates of its needle crystals at finite γ are selected *via* a solvability mechanism which can be studied in great detail (Kessler *et al.*, 1984). Disappointingly, these needle crystals do not undergo persistent side branching oscillations except at one special value of the anisotropy strength ϵ for which, as it turns out, the tip of the needle is just marginally unstable. The geometrical model is not, strictly speaking, a direct representation of a first-order phase transition; therefore I shall say no more about it except to emphasize again its importance as a mathematical example.

In the boundary-layer model proposed by Ben-Jacob *et al.* (1983; 1984b), the velocity v_n is determined by l, the thickness of the layer. We suppose that the thermal field u in front of the interface looks something like

$$u(x) \sim -\Delta + (\Delta + u_s)e^{-x/l} , \qquad (4.5)$$

where x is the distance into the fluid measured along the unit normal $\hat{n}$, $\Delta = (T_M - T_\infty)/(L/c)$ is the undercooling at infinity in units L/c, and u_s is the value

of u at the interface given by (2.4) or, equivalently, (3.8). The continuity condition (2.3) suggests that we use the ansatz (4.5) to write

$$v_n = \frac{D(\Delta + u_s)}{l} \quad . \tag{4.6}$$

It remains to devise an equation of motion for l. This is best done in terms of the quantity

$$h(s, t) = \int_0^\infty dx (\Delta + u) \simeq (\Delta + u_s) l , \tag{4.7}$$

which we interpret as the heat content per unit length of the interface. Our proposed equation of motion for h is a phenomenological statement of heat balance within the boundary layer:

$$\left(\frac{\partial h}{\partial t}\right)_n = v_n (1 - \Delta - u_s) - v_n \kappa h + D \frac{\partial}{\partial s} \left(l \frac{\partial u_s}{\partial s} \right) . \tag{4.8}$$

Equation (4.8) is the crux of the boundary-layer model, and each of the three terms on the right-hand side deserves some comment. The first term is the rate at which latent heat is being added to the boundary layer. It accounts for the fact that a fraction $\Delta + u_s$ of this heat must be used to warm the solid from $u(\infty) = -\Delta$ to $u = u_s$. The second term is geometrical in origin and contains the mechanism for the diffusive instability that is responsible for pattern formation in these systems (Langer, 1980). It expresses the fact that a piece of interface with positive curvature increases in length as it grows outward, thus decreasing the amount of heat per unit length, h. Because the corresponding decrease in l implies an increase in v_n, this term causes an outward bulge to accelerate. Conversely, the heat h accumulates in an inward pointing groove, causing it to fall behind the neighboring parts of the interface. The last term on the right-hand side of (4.8) describes lateral diffusion, and it is *via* this effect that capillary forces control the diffusive instability just described. Remember that, apart from the kinetic correction, u_s is equal to $-d_0 \kappa$, so that this third term couples the thermal field to the curvature with a strength proportional to the surface tension. More precisely, a forward bulge, $\kappa > 0$, must be cooler than its surroundings by an amount $d_0 \kappa$, and therefore heat must flow toward it, retarding its growth. The specific form chosen for the lateral diffusion term depends strongly on the presumed locality of the diffusion field, and it is probably at this point that the boundary-layer model is least realistic.

The dynamical system defined by Eqs. (4.6) and (4.8), supplemented by the thermodynamic relation (2.4), has many features in common with the basic solidification model of Sec. 2. Generally, the two models are in good agreement when the boundary-layer condition, $\kappa l \ll 1$, is satisfied. Flat interfaces move with the appropriate $t^{1/2}$ law and needle-crystals in the Ivantsov limit, $d_0 = 0$, are parabolas. The dynamics of the diffusive instability, in the long-wavelength limit, is the same in both models. There are also important discrepancies, mostly associated with failure of $\kappa l \ll 1$. For example, stable, short-wavelength deformations of a flat interface relax much too slowly because there is no mechanism in this model to account for the fact that such deformations perturb the diffusion field only out to distances less than l. Another awkward feature of the boundary-layer model is that it does not, in its present form, include diffusion in the solid. As a result, heat accumulating in grooves cannot escape, and the growing instabilities tend toward sharp cusps which may be physically realistic but have been major impediments to numerical analysis.

Although analytic and numerical work on the boundary-layer model has not yet been carried as far as that on the geometrical model (Kessler et al., 1984), a number of very interesting results have been obtained. I want to devote the last few paragraphs of this essay to a qualitative description of some of those results because I think they illustrate the role of model building in the search for more general theories of pattern formation.

One surprising result that emerged early in our numerical studies of the boundary-layer model was the crucial role played by crystalline anisotropy. The existence of Ivantsov's needle-crystal solutions in the absence of anisotropy had led to the expectation that its role, while important as a symmetry-selecting perturbation, was somehow secondary to the dynamical interaction between diffusive instabilities and capillary forces. Our first numerical simulations made it clear that such was not the case.

Figure 2 shows a sequence of solidification fronts computed with no crystalline anisotropy; that is, $\beta = 0$ and d_0 is independent of θ in (2.4). The initial shape is a circle with a small six-fold anisotropy, and six-fold symmetry is enforced at all later stages. Note that we have been able to follow the morphological instability far into the nonlinear regime where the outward bulges flatten and the heat accumulates in deep grooves. This behavior is generally characteristic of unstable solidification fronts observed in experiments but, so far as I know, this is the first time that it has been reproduced theoretically. Also apparent in the figure is that this process does not produce a snowflake. As verified by further computation, the next grooving instability occurs at the flattened centers of the outward bulges, producing a pair of fingers which, themselves, will later flatten and split. If continued indefinitely, this system
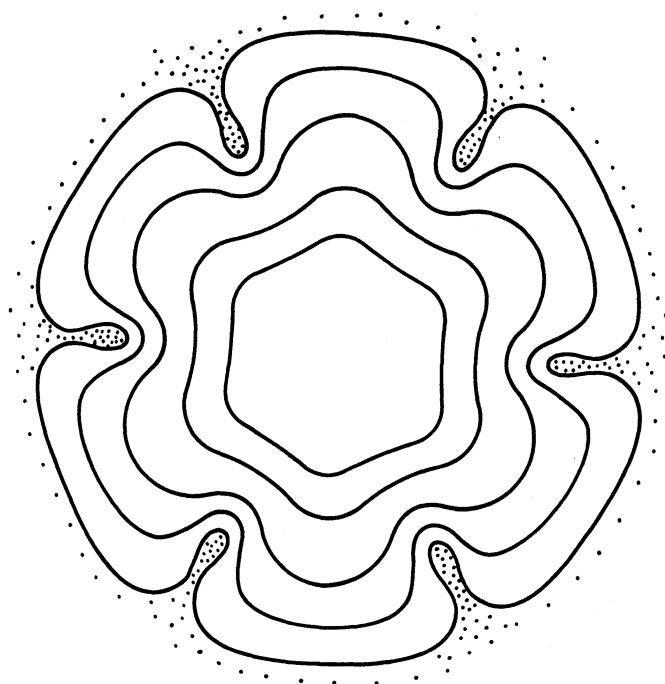
Fig. 2 Sequence of solidification fronts generated by the boundary-layer model with isotropic growth kinetics. The initial state contains a small six-fold anisotropy. The dots indicate schematically the accumulation of heat in the grooves.

would produce an increasingly complex, possibly fractal, structure which might be of some interest in biology but probably not in crystal growth. Moreover, the symmetry of this structure is almost certainly unstable. Although we have not pursued this line of investigation in any detail, I am fairly sure that a small symmetry breaking perturbation would cause this system to produce an intrinsically chaotic picture more reminiscent of seaweed than any regular pattern.

Figure 3 shows what happens when anisotropy is added to the equations of motion. Here we have started with an unperturbed circle (the dashed curve in the figure, one sixth of which is shown); we have let d_0 be constant again, but have chosen a linear kinetic coefficient β_0 proportional to $1 - \cos 6\theta$. The circle first grows slowly almost into a hexagon, then becomes unstable at its corners and emits dendritic structures which propagate rapidly outward along the growth directions favored by $\beta_0(\theta)$. The dynamical effect of the anisotropy is to cause these dendritic tips to lock almost immediately into a state with sharply defined velocity and tip radius, both of the latter parameters being the same as those which are selected when the system is set into motion from different
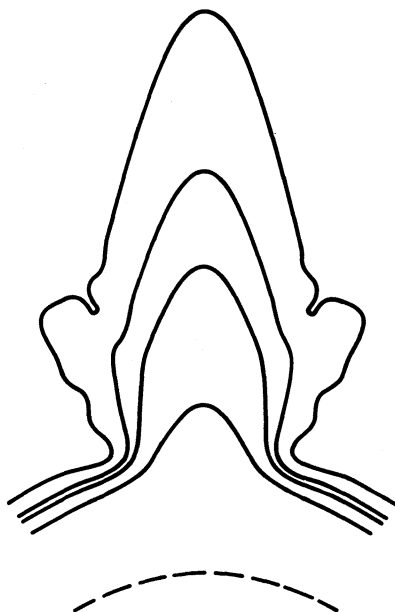
Fig. 3 Sequence of solidification fronts (unequal time intervals) generated by the boundary-layer model with a six-fold anisotropy in the growth kinetics. The initial state (dashed curve) is an unperturbed circle.

initial configurations. The pair of large side branches visible in the figure is reminiscent of structures seen in real snowflakes (Nakaya, 1954) and is apparently a transient phenomenon generated by the initial instability at the hexagonal corners. The parabolic tips do seem to be emitting weak side-branching oscillations which are best seen in graphs of curvature *versus* arc length; but we have not been able to continue the computation long enough to discover whether or not these are also transients as in the geometrical model.

By far the most stunning surprise to emerge so far from work on the boundary-layer model and the geometrical model as well has been the discovery that the velocities and tip radii of dendrites selected by dynamical simulations like those just described can be predicted by examining the solvability of the steady-state equations (Ben-Jacob *et al.*, 1984a). In our first paper on the boundary-layer model (Ben-Jacob *et al.*, 1983; 1984b), we pointed out that surface tension is a singular perturbation, and that the continuous family of Ivantsov needle crystals must break down when d_0 is nonzero. The trouble is that the shape of

the tip, which is no longer parabolic if there are capillary corrections, cannot necessarily be matched smoothly onto a parabola behind it except possibly for special values of the velocity. My initial interpretation of this situation was that dendritic velocities had to be selected by dynamical properties of the tip, and that consistency with steady-state parabolic solutions far behind the tip had to be irrelevant. Real dendrites, with side branches, simply do not look like that. It turns out, however, that whenever we have found a propagating tip in a dynamical simulation, the velocity and radius of curvature of that tip have had precisely those special values for which there exist needle-crystal solutions of the steady-state equations. Side branching dendrites without an associated needle crystal might occur in this model; but so far we have not seen such behavior.

The picture that now seems to us to be emerging from ongoing analytic and numerical work is the following. Think of the equations of motion for the boundary-layer model as a dynamical system which describes trajectories in a space of functions $[\kappa(s, t), h(s, t)]$. Depending on the values of the system parameters Δ, $d_0(\theta)$, $\beta_0(\theta)$, this space may (or may not) contain stationary states, that is, dynamical fixed points $[\kappa^*(s), h^*(s)]$ which describe needle crystals and which satisfy

$$\left(\frac{\partial \kappa^*}{\partial t}\right)_s = \left(\frac{\partial h^*}{\partial t}\right)_s = 0 \ . \tag{4.9}$$

A special property of the boundary-layer model is that these fixed points, if they exist at all, can be no more stable than marginally stable. One can show analytically that there always exist modes of deformation of a needle crystal which relax infinitely slowly. Physically, these modes are a result of the slow dynamics of the boundary layer which becomes indefinitely thick as one moves away from the tip. (No such dynamical feature occurs in the geometrical model.) If more than one fixed point exists, the most nearly stable one will be that with the largest velocity and smallest tip radius; slower, flatter dendritic tips are more likely to be unstable against tip splitting deformations. It can happen that even the fixed point with largest velocity is strongly unstable, for example, if the crystalline anisotropy is too weak. In that case, no dendritic pattern formation occurs, and the morphology probably becomes increasingly irregular as the system evolves. It might also happen that the leading fixed point is stable, that even the marginal trajectories in $[\kappa, h]$ space are attracted to it but approach algebraically rather than exponentially. Then the boundary-layer model would behave like the geometrical model (Kessler *et al.*, 1984) and produce propagating

needles with only transient or fluctuation-induced side branching activity. It is possible that this is a correct physical picture, that side branching occurs because dendritic tips have just enough instability to amplify special fluctuations in their environments.

The most interesting possibility is that the leading fixed point is weakly, or perhaps just marginally, unstable. I think that this also could correspond to physical reality. Real dendrites are not needle-crystal fixed points but, rather, might be visualized as limit cycles in $[\kappa, h]$ space. Near the tip, the dendritic shape may repeat itself with a period equal to the interval between emission of side branches. [By using the κ representation, we consider only the shape of the interface and avoid problems associated with translational motion in real space. Note the time derivatives at fixed s in (4.9).] Irregular coarsening of side branches behind the tip means that this limit cycle would have to be weakly unstable; but that instability could have little to do with the velocity-selection mechanism. The apparent role of the fixed point would be to serve as an almost stable center for the limit cycle. All small perturbations of the needle crystal, that is, all dynamical trajectories starting near the fixed point, would be attracted onto the limit cycle. For this to happen, the fixed point must be almost but not quite stable, a situation which looks something like marginal instability, but which I do not know how to define precisely.

In each of these dynamical pictures of dendrites, the solvability condition serves as a selection principle because the fixed point possesses some average properties of the nearby dynamical trajectory. In order to use this scheme to make practical calculations, one need not solve the full dynamical problem. One simply solves the steady-state equations, which can now be thought of as a nonlinear eigenvalue problem for the velocity, and checks to see whether that solution is sufficiently (marginally?) stable. There remains some vestige of the earlier marginal-stability hypothesis (Langer, 1980; Langer and Müller-Krumbhaar, 1978) here, along with the hint of a connection between marginal stability and the sensitivity of pattern forming systems to small changes in growth conditions. But the picture is clearly very different from anything that has been proposed previously.

I remarked at the beginning of this section that the main purpose of the boundary-layer model — and the geometrical model as well — was to provide new insight into mathematical mechanisms of pattern selection. The investigations described above certainly have produced new ideas; but it remains to be seen whether these ideas are relevant to reality as defined by the basic model in Sec. 2. A crucial question is whether the breakdown of the Ivantsov solutions, and therefore the existence of a solvability condition, might be a special feature of the local contour-dynamical models. It is conceivable that the fully nonlocal

basic model behaves quite differently, that the continuous family of Ivantsov solutions survives the effects of capillarity, and that some more complex dynamical mechanism is responsible for dendritic pattern selection. This question is being studied actively by a number of people (including this author) as this essay is being written. No results are certain yet, but there are strong indications in favor of a solvability condition for the fully nonlocal model. If this result is confirmed, then we shall be on our way toward fitting one small piece into a very large puzzle.

Acknowledgments

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