

Diffuse interface model of diffusion-limited crystal growth

Joseph B. Collins

Department of Physics, Brown University, Providence, Rhode Island 02912

Herbert Levine

*Schlumberger-Doll Research, Old Quarry Road,**Ridgefield, Connecticut 06877-4108*

(Received 11 February 1985)

A general approach to diffusion-limited crystal growth is proposed. It consists of a modified (nonequilibrium) Cahn-Hilliard representation of the interface coupled to a diffusion equation. Arguments are given as to its superiority over previous models. These are illustrated in a one-dimensional solution which shows how the system selects a unique interface velocity. This selection can be interpreted as the requirement of consistency between the interfacial undercooling as determined by the (microscopic) kinetics and as determined by the (macroscopic) diffusion equation.

At present, several unanswered questions about solidification morphology and dynamics are being vigorously addressed. Chief among these concern dendritic pattern-formation processes and selection of growth velocities in diffusion-limited growth. (Reference 1 is a good general review of the pre-1980 literature.)

Recently,^{2,3} progress had been made by looking at computationally and analytically tractable models and trying to extrapolate the results to more realistic systems. These models suggest that the appropriate physical considerations for dendritic growth are chemical- or thermal-diffusive transport, capillary effects, and crystalline anisotropy. Also, a new mechanism for velocity selection has been identified, that of "microscopic solvability."⁴ How well these ideas survive in models with true diffusive dynamics is not known, since there have been no exact solutions as yet. There are some indications, however, that these ideas will continue to apply.⁵

In this paper, we propose a generalized version of the usual diffusive model of crystal growth. In particular, we introduce the idea of a diffuse interface between the two equilibrium phases. This is not an arbitrary assumption, since the so-called "plastic" crystals that are observed to grow dendritically always have extended interfaces.⁶ Crystals with sharp interfaces most often have kinetically controlled rather than diffusion-limited growth. The purpose of this work is more, however, than just to include an additional physical effect. We will show that the introduction of a microscopic length into the problem allows us to demonstrate the aforementioned solvability mechanism for a planar interface. This will then be the first case whereby true crystal growth can be shown to behave in the same manner as the simple model systems discussed above. In addition, our model demonstrates a relatively simple manner of incorporating nonequilibrium interfacial kinetics into diffusive dynamics. This will be crucial in the future for the understanding of dendritic growth from the vapor phase, such as that which occurs for real snowflakes.

The basic idea is to introduce a ϕ^4 -theory representation of the interfacial free energy, and couple it to a diffusive-transport equation. The field ϕ should be thought of as an order parameter distinguishing the two phases. The ϕ^4 Landau-Ginsberg "potential" is intended to reflect both

bulk free-energy differences between the phases, and capillary effects (we will show, for instance, that it gives a realization of the Gibbs-Thomson effect). The equation of motion for the order parameter ϕ is a mean-field representation of the nonequilibrium interfacial kinetics. Solving the equation will then give rise to an extended interface. Since we are considering growth in a diffusion-controlled regime, we assume that the region of significant variation of ϕ (the interfacial region) will give rise to a source term in an accompanying diffusion equation. The resulting pair of coupled equations will be more physical than often-used singular-interface models, which neglect interfacial kinetics,¹ or pure ϕ^4 models, which neglect diffusion.^{7,8}

The first equation we write down represents the time evolution of a solid-liquid order parameter with Landau-Ginzburg-type time dependence (ignoring the noise term), i.e.,

$$\dot{\phi} \sim \frac{\delta F[\phi]}{\delta \phi} \quad (1)$$

The order-parameter-dependent free energy is chosen to have two definite phases at equilibrium, represented by Cahn-Hilliard terms,⁹ and a nonequilibrium linearly temperature-dependent driving term which is the bulk free-energy difference between phases. (See Fig. 1.) Explicitly, we have,

$$\begin{aligned} -\Gamma \dot{\phi} &= \frac{\delta}{\delta \phi} \left(\int [\alpha (\nabla \phi)^2 + \beta (\phi^2 - 1)^2 + cU\phi] d^3x \right) \\ &= -2\alpha \nabla^2 \phi + 4\beta (\phi^3 - \phi) + cU \quad (2) \end{aligned}$$

α, β are phenomenological constants which will be discussed shortly. Γ is the rate of relaxation to equilibrium. The dimensionless diffusion field U will take the form $(T - T_m)/(L/C_p)$ in the thermal case, where T is the temperature, T_m the melting temperature, L the latent heat, and C_p the specific heat. Note that we may immediately determine $c = L^2/2C_p T_m$ by identifying $cU\phi$ as the bulk free-energy difference between the two phases near the melting temperature.

The surface tension is just the additional free energy per unit area introduced by requiring the presence of a planar phase boundary between two phases in equilibrium,⁷ i.e., at

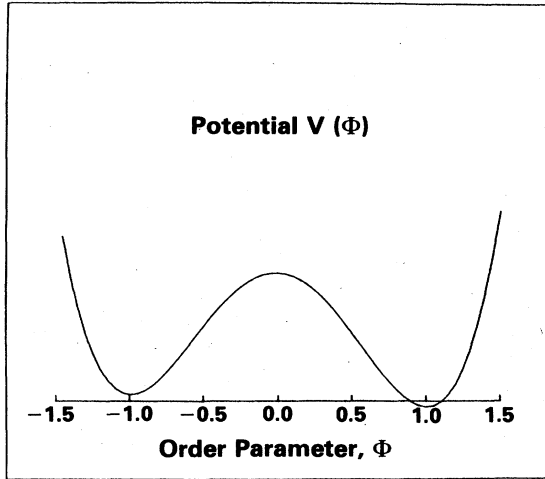


FIG. 1. Free energy as a function of the order parameter.

$U=0$. It is easy to check that, for an interface profile $\hat{\phi}$ of minimum free energy, $d\hat{\phi}/dx = (\beta/\alpha)^{1/2}(1-\hat{\phi}^2)$. Therefore, the additional free energy is given by

$$\sigma = \int_{-\infty}^{\infty} f_{PE} \hat{n} \cdot d\mathbf{x} = \int_1^1 2(\alpha f_0)^{1/2} d\phi = \frac{8}{3}(\alpha\beta)^{1/2},$$

where

$$f_{PE} = \alpha(d\hat{\phi}/dx)^2 + \beta(\hat{\phi}^2 - 1)^2$$

and $f_0 = \beta(\phi^2 - 1)^2$. Similarly, the interface thickness is proportional to $(\alpha/\beta)^{1/2}$. Measurement of these quantities, or the assumption of a specific microscopic model, will determine uniquely the exact values of the phenomenological parameters in Eq. (2). After making the rescalings

$$\tau = \frac{4\beta}{\Gamma} t, \quad y = \left(\frac{\beta}{\alpha}\right)^{1/2} x, \quad \delta = \frac{c}{4\beta},$$

Eq. (2) becomes

$$\frac{1}{2}\phi'' - \phi^3 + \phi + \dot{\phi} - \delta U = 0. \quad (3)$$

δ is a dimensionless parameter representing the ratio of the energy difference between the phases to the bulk free energy. It will be small whenever the system can be thought of as close to local thermodynamic equilibrium. This condition also ensures that the dimensionless interface velocity is small. This will be seen explicitly later.

The diffusion equation used for sharp interface models can be written

$$D\nabla^2 U - \dot{U} = v_n \delta(\mathbf{x} - \mathbf{x}_I(t)), \quad (4)$$

where D is the diffusivity, U is a dimensionless diffusion field, v_n is the normal velocity of the interface, and $\mathbf{x}_I(t)$ is the interface position. In this model the interface acts as a δ -function source of latent heat for the thermal case. This δ -function term is just the time derivative of a step-function order parameter

$$v_n \delta(\mathbf{x} - \mathbf{x}_I(t)) = -\frac{d}{dt} \theta(\mathbf{x} - \mathbf{x}_I(t)).$$

To complete our derivation, we merely substitute our new

order parameter in place of the old

$$D\nabla^2 U - \dot{U} = -\frac{d}{dt} \left(\frac{\phi}{2} \right), \quad (5)$$

where the $\frac{1}{2}$ is a normalization factor ($-1 \leq \phi \leq 1$, while $0 \leq \theta \leq 1$). This equation, together with (3), completely specifies the dynamics.

Let us first recall what happens if we consider Eq. (4) in one dimension with the usual equilibrium Gibbs-Thomson boundary condition $U(\mathbf{x}_I(t)) = 0$. A steady-state solution is only possible for a single undercooling $U(\infty) = -1$. With this undercooling, however, the velocity of interface propagation is arbitrary.¹ This is simply because of the absence of any length scale in the problem. For nonplanar interfaces, the Gibbs-Thomson boundary condition depends on the capillary length times the local curvature; for a planar interface there is no curvature. Physically, an arbitrary velocity cannot be correct, and must arise from some pathology in the model. Specifically, we believe that, while this singular interface model outlines the possible solutions allowed by the diffusion equation, it does not adequately represent the physical interfacial characteristics of the crystal-melt system. Our generalized system should therefore give rise to a unique, physical solution for at least this simple configuration.

To check this, we turn to the diffuse interface model and assume steady-state conditions. For a constant undercooling over all space, $U(\mathbf{x}) = -\Delta$, the order parameter solution to Eq. (3) to first order in δ is a constant-velocity traveling profile

$$\phi(y) \approx \frac{\delta\Delta}{2} - \tanh(y - 3\delta\Delta\tau/2). \quad (6)$$

Note that the velocity $v = \frac{3}{2}\delta\Delta$ depends linearly on the undercooling, a result that is well known for crystals with rough interfaces.^{6,10} Now, imagine having U vary over space, but very slowly on the scale of $\sqrt{\beta/\alpha}$. We expect that the velocity will still be a linear function of the interfacial undercooling, that is, of the value of U at the interface defined as where $\phi=0$. Let us denote this point as y_0 . On the other hand, we can determine the temperature distribution $U(y)$ for the constant-velocity phase boundary by integrating Eq. (5) with the above profile. This is sketched in Fig. 2. In particular, the value of U at the interface will be given by

$$\begin{aligned} U(y_0) &= -\frac{1}{2} \int G(y_0 - y', t - t') \dot{\phi}(y', t') dy' dt' \\ &= +\frac{1}{2} \int_0^{\infty} \left[\tanh\left(\frac{q}{4pv} - y_0\right) \right] e^{-q} dq - \frac{1}{2}, \end{aligned} \quad (7)$$

where $p = \alpha/4D\Gamma$, and the undercooling at infinity is necessarily chosen to equal 1. G is just the diffusive propagator. This is a second relation between v and the interfacial undercooling, which therefore suffices to determine them both. This idea of getting a nontrivial condition from the matching of microscopic and macroscopic considerations is quite similar to what has been proposed for dendritic growth, as discussed above. The analytical solution will reflect this heuristic argument.

We now find a perturbative solution by assuming a steady-state shape propagating with velocity $v = \delta\tilde{v}$. Equa-

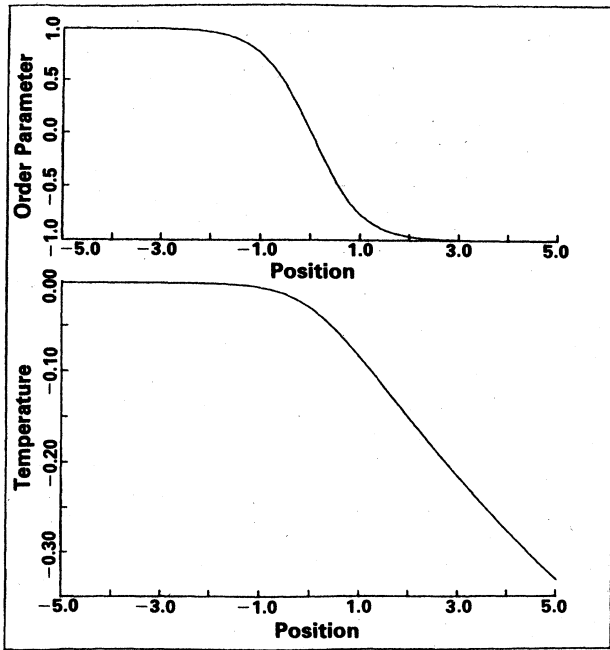


FIG. 2. Order-parameter and temperature profiles.

tion (3) can now be written as

$$\phi'' + \phi - \phi^3 + \delta(\tilde{v}\phi' - U(y)) = 0 \quad (8)$$

To zeroth order in δ , Eq. (8) has the form

$$\frac{1}{2}(\phi_0)_{yy} + \phi_0 - \phi_0^3 = 0 \quad (9)$$

and the solution is easily found to be

$$\phi_0 = -\tanh(y + a) \quad (10)$$

where a is an irrelevant constant. To next order we have to solve the equation

$$\frac{1}{2}(\phi_1)_{yy} + \phi_1(1 - 3\phi_0^2) = -\tilde{v}(\phi_0)_y + U \quad (11)$$

where U is given explicitly by integrating the diffusion Eq. (5) with the zeroth-order profile ϕ_0 . [The form of this integral has already been given as Eq. (7), above.] The key point to note is that, for arbitrary velocity, the solution of Eq. (11) will be secular, i.e., it will get arbitrarily large for large y . We must choose the velocity to prevent this from occurring. It is convenient to introduce an additional unknown Δ_I , and break up the temperature field via defining $U \equiv U^* - \Delta_I$. There are then two different terms on the right-hand side of (11):

$$[-\tilde{v}(\phi_0)_y - \Delta_I] + [U^*]$$

ϕ_1 has a corresponding two-term particular solution. The last piece of the right-hand side gives rise to a contribution to ϕ_1 of the form

$$\text{sech}^2 y \int_0^y dz \cosh^4 z \left[\int_{-\infty}^z \frac{U^*(z')}{\cosh^4 z'} dz' \right] \quad (12)$$

This will be secular unless the integral over z' decays rapid-

ly. This will fix Δ_I , which we interpret as the interfacial undercooling. We note that as $p \rightarrow 0$, $\Delta_I \rightarrow 0$, and, for very large p , $\Delta_I \rightarrow \frac{1}{2}$. Once we have a fixed value of Δ_I , we can compute the contribution to ϕ_1 from the first term on the right-hand side. This leads to the requirement that \tilde{v} equal $\frac{3}{2}\Delta_I$, a result similar to what we found in Eq. (6) for the constant undercooling case. We therefore have proven that there is a fixed velocity. This result is analogous to velocity determination in flame fronts.¹¹ Finally, we would like to note that small δ is not crucial for the selection, but in fact should occur in general for this system.

Let us now return to more general considerations. Our model has two parameters in addition to the undercooling, δ and p . The Stefan problem, as usually stated, with an equilibrium condition at the interface and with a sharp interface, corresponds to the limit $\delta \rightarrow 0$, $p \rightarrow 0$. We have already seen how, in this limit, the interface temperature approaches zero for a planar interface, and how p determines the relative size of the interface in units of the diffusion length. To complete our picture, we should show how to recover the idea that local equilibrium requires the interface temperature to be related to the curvature. We show how this arises directly from our order-parameter formulation.

Assume that a portion of a gently curved interface is in equilibrium with a melt at a constant temperature throughout, $U = -\Delta$. Equation (2) then becomes

$$2\alpha \nabla^2 \phi - 4\beta(\phi^3 - \phi) + c\Delta = 0 \quad (13)$$

Now in a coordinate system local to the interface, $\nabla^2 \sim \partial^2/\partial g^2 + \kappa\partial/\partial g$, where g is a coordinate normal to the interface and κ is the curvature of the interface. The first order (in curvature) solution is a *stationary* tanh profile, with the condition

$$\Delta = \frac{2\beta}{3c} \left(\frac{4\alpha}{\beta} \right)^{1/2} \kappa$$

where $(2\beta/3c)(4\alpha/\beta)^{1/2}$ has units of length, and we identify it with d_0 , the capillary length. This, we note, is precisely the Gibbs-Thomson condition, since this result for the capillary length can be rewritten using the above equations for c and σ as $d_0 \equiv \sigma C_p T_m / L^2$. This procedure can be straightforwardly extended to show that, in general, the growth velocity will depend on the deviation of the interface temperature from its curvature-dependent equilibrium value.

Much work needs to be done to see what advantages our approach will have over the usual methods. We foresee two possibilities. First, the fact that a planar interface already has a unique velocity may make the problem of deriving the velocity selection for parabolic "needle crystals" more tractable. Also, numerical simulations of the equations of motion can be attempted without having to explicitly keep track of a singular boundary. We are pursuing both of these ideas and hope to report on them soon.

We would like to acknowledge useful conversations with Y. Pomeau. After completion of this work we became aware of related ideas due to Fix,¹² who introduces a similar approach for the purpose of numerical simulation without the need for explicit boundary conditions.

- ¹J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).
- ²R. C. Brower, D. Kessler, J. Koplik, and H. Levine, *Phys. Rev. A* **29**, 1335 (1984); D. Kessler, J. Koplik, and H. Levine, *ibid.* **30**, 3161 (1984).
- ³E. Ben-Jacob, N. Goldenfeld, J. S. Langer, and G. Schön, *Phys. Rev. Lett.* **51**, 1930 (1983); *Phys. Rev. A* **29**, 330 (1984).
- ⁴D. Kessler, J. Koplik, and H. Levine, *Phys. Rev. A* **31**, 1712 (1985); E. Ben-Jacob, N. Goldenfeld, G. Kotliar, and J. Langer, *Phys. Rev. Lett.* **53**, 2110 (1984).
- ⁵R. C. Brower, D. Kessler, J. Koplik, and H. Levine, *Scr. Metall.* **18**, 463 (1984); D. Kessler, J. Koplik, and H. Levine, *Phys. Rev. A* **30**, 2820 (1984).
- ⁶D. P. Woodruff, *Solid-Liquid Interface* (Cambridge Univ. Press, Cambridge, England, 1973).
- ⁷S. M. Allen and J. W. Cahn, *Acta Metall.* **27**, 1085 (1979).
- ⁸S.-K. Chan, *J. Chem. Phys.* **67**, 5755 (1977).
- ⁹J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
- ¹⁰See, for example, R. F. Sekerka, in *Proceedings of the International School of Crystallography, Erice, 1981* (Reidel, Hingham, MA, 1982).
- ¹¹For a review, see P. Clavin and A. Linan, in *Theory of Gaseous Combustion*, NATO Advanced Studies Institute Series B, Physics (Plenum, New York, in press).
- ¹²G. Fix, in *Free Boundary Problems*, edited by A. Fasano and M. Primicerio, *Research Notes in Mathematics*, Vol. 2 (Pitman, New York, 1983).