

Phase-field models for anisotropic interfaces

G. B. McFadden, A. A. Wheeler,* R. J. Braun, and S. R. Coriell
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

R. F. Sekerka†

Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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The inclusion of anisotropic surface free energy and anisotropic linear interface kinetics in phase-field models is studied for the solidification of a pure material. The formulation is described for a two-dimensional system with a smooth crystal-melt interface and for a surface free energy that varies smoothly with orientation, in which case a quite general dependence of the surface free energy and kinetic coefficient on orientation can be treated; it is assumed that the anisotropy is mild enough that missing orientations do not occur. The method of matched asymptotic expansions is used to recover the appropriate anisotropic form of the Gibbs-Thomson equation in the sharp-interface limit in which the width of the diffuse interface is thin compared to its local radius of curvature. It is found that the surface free energy and the thickness of the diffuse interface have the same anisotropy, whereas the kinetic coefficient has an anisotropy characterized by the product of the interface thickness with the intrinsic mobility of the phase field.

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I. INTRODUCTION

Phase-field models [1–6] provide a convenient basis for the numerical solution of complicated solidification problems. In a phase-field model, in addition to the customary energy and/or concentration variables, an additional variable, the phase field, φ , is introduced to label explicitly the liquid and solid phases. The phase field takes on a constant value in each bulk phase, e.g., $\varphi = 0$ in the solid phase and $\varphi = 1$ in the liquid phase. The transformation from solid to liquid occurs over a thin transition region where φ varies smoothly from zero to one. The usual thermodynamic functions describing the system can then be modified to incorporate gradient energy terms; in particular, terms proportional to $|\nabla\varphi|^2$ can contribute to the surface excess quantities that play a fundamental role in Gibbs's formulation of surface thermodynamics [7]. In this sense, phase-field models are natural outgrowths of diffuse-interface models dating back to work by van der Waals [8], by Cahn and Allen [9,10], and by Cahn and Hilliard [11,12]. From a computational viewpoint, phase-field models are similar in some ways to the enthalpy method [13], in that explicit tracking of the solid-liquid interface is avoided. Phase-field models, however, are more versatile than enthalpy methods since such effects as undercooling of the melt and departures from thermodynamic equilibrium at the interface are included automatically (see, e.g., [14]).

An important example of the utility of phase-field models is given by the numerical studies of dendritic growth by Kobayashi [15–18] and by Wheeler, Murray, and Schaefer [19]. The phase-field treatments seem to capture successfully a broad variety of dendritic growth phenomena, including the correct relation between Peclet number and undercooling, the emission of sidearms, and the coarsening behavior of sidearms that are further re-

moved from the tip. The anisotropy of surface free energy or of interface kinetics is generally thought to play a fundamental role in the dynamics of dendritic growth [20,21].

Since in a phase-field formulation the interface is diffuse, the proper incorporation of surface free-energy anisotropy requires careful consideration. Phase-field models with anisotropy have been considered previously for specific choices of gradient energy. Caginalp and Fife [22,23] have considered models in which the isotropic "square gradient" expression is replaced by a more general quadratic form with different coefficients in each coordinate direction. For an isothermal system this leads to an elliptical equilibrium shape. In order to obtain more complicated anisotropies, Langer [2] proposed the addition to the gradient energy of terms involving the squares of higher derivatives of the phase field, and gave an example leading to cubic anisotropy. Cahn and Kikuchi [24] have considered discrete forms of diffuse-interface models, and have also included anisotropic effects through the choice of nearest-neighbor interactions (see also [25,26]). Both Kobayashi [17] and Wheeler, Murray, and Schaefer [19] include anisotropy by allowing the coefficient of the gradient energy to depend on the local orientation of the gradient of the phase field. Early numerical calculations were performed by Smith [27] and by Umantsev, Vinograd, and Borisov [28] in which no explicit anisotropy was included in the models; rather, anisotropy was provided implicitly by the underlying grid used in the numerical calculations.

In this paper we present an asymptotic analysis in the sharp-interface limit of the model studied by Kobayashi [17] and Wheeler, Murray, and Schaefer [19], including an anisotropic mobility. We consider a two-dimensional phase-field description for the solidification of a single-component material of uniform density, and assume that

there is no convection in the melt. We also assume that the anisotropy is mild enough that the resulting interface shape is smooth. In such an asymptotic analysis, the width of the transition region is thin compared to the radius of curvature of the lines $\varphi = \text{constant}$. Similar asymptotic analyses have been performed for the isotropic case [29–32] to recover the boundary condition

$$\frac{v_n}{\mu} = T_M - \frac{T_M}{L_V} \gamma K - T_I \quad (1)$$

that relates the normal velocity of the interface v_n (considered to be positive for the formation of solid), the mean curvature of the interface, K , and the interface temperature, T_I ; here μ is the interfacial kinetic coefficient, T_M is the bulk melting point, γ is the (isotropic) interfacial free energy, and L_V is the latent heat of fusion per unit volume. Our goal is to derive from an appropriate phase-field model the corresponding anisotropic form of this equation [33], which in two dimensions is

$$\frac{v_n}{\mu(\theta)} = T_M - \frac{T_M}{L_V} (\gamma + \gamma_{\theta\theta}) K - T_I, \quad (2)$$

where $\gamma = \gamma(\theta)$ denotes the dependence of the surface free energy on the local interface orientation, as measured by the angle θ between the interface normal and a given crystallographic direction, and $\mu = \mu(\theta)$ is an anisotropic kinetic coefficient that also depends on θ ; here $\gamma_{\theta\theta}$ denotes the second derivative of the function $\gamma(\theta)$.

II. ISOTROPIC FORMULATION

Of prime consideration will be the surface free energy, γ , which is defined in terms of the surface excess of the Helmholtz free energy of the system. In a phase-field model, the bulk Helmholtz free-energy density, f , includes dependence on the phase field, φ , so that $f = f(T, \varphi)$, where T is the temperature. The free-energy density of the solid is then $f(T, 0)$ and that of the liquid is $f(T, 1)$, and at the bulk melting point, T_M , the two are equal. The Helmholtz free-energy functional that gives the free energy of an isothermal two-phase system of volume V is assumed to have the form [34]

$$\mathcal{F} = \int_V \left\{ f(T, \varphi) + \frac{\xi_0^2}{2} |\nabla \varphi|^2 \right\} dV, \quad (3)$$

where the constant ξ_0^2 that appears in the gradient energy coefficient has units of energy per unit length. If we adjust the bulk free energy so that $f(T_M, 0) = f(T_M, 1) = 0$, then for a one-dimensional system with $\varphi = \varphi(x)$ the surface excess free energy per unit area is given by

$$\gamma = \int \left\{ f(T_M, \varphi) + \frac{\xi_0^2}{2} \varphi_x^2 \right\} dx. \quad (4)$$

For an isothermal system, an evolution equation for the phase field is often postulated by requiring that φ evolve so as to minimize \mathcal{F} ; that is, by setting

$$\tau_0 \frac{\partial \varphi}{\partial t} = -\frac{\delta \mathcal{F}}{\delta \varphi} = \xi_0^2 \nabla^2 \varphi - \frac{\partial f}{\partial \varphi}, \quad (5)$$

where τ_0 is an empirical relaxation coefficient, whose inverse is an intrinsic interfacial mobility.

For the nonisothermal case, it is more appropriate to start with an entropy functional for the system [34,35],

$$S = \int_V \left\{ \tilde{s}(e, \varphi) - \frac{\xi^2}{2} |\nabla \varphi|^2 \right\} dV, \quad (6)$$

in which the entropy density \tilde{s} depends on the internal energy density and the phase. The parameter ξ that appears in the entropy functional may be related to the parameter ξ_0 of the Helmholtz free-energy functional by $\xi_0^2 = T \xi^2$ [34]. Evolution equations for the temperature and the phase field may be derived by requiring that e and φ evolve so as to ensure positive entropy production locally; for example, phase-field equations of the form

$$\frac{\partial e}{\partial t} = -\nabla \cdot \left[M_T \nabla \left(\frac{1}{T} \right) \right], \quad (7)$$

$$\tau \frac{\partial \varphi}{\partial t} = Q(T) p'(\varphi) - G'(\varphi) + \xi^2 \nabla^2 \varphi, \quad (8)$$

can be derived in this manner [34]. Here M_T is proportional to the thermal conductivity, and the internal energy density has the form

$$e(T, \varphi) = e_S(T) + p(\varphi) L(T) = e_L(T) + [p(\varphi) - 1] L(T), \quad (9)$$

where $L(T_M)$ is the latent heat of fusion per unit volume and $p(\varphi)$ is a smooth function with $p(0) = 0$ and $p(1) = 1$, so that $e(T, 1) - e(T, 0) = e_L(T) - e_S(T) = L(T)$. The energy equation may then be rewritten in the form

$$c(T, \varphi) \frac{\partial T}{\partial t} + L(T) p'(\varphi) \frac{\partial \varphi}{\partial t} = \nabla \cdot [k \nabla T], \quad (10)$$

where we have introduced

$$c(T, \varphi) = [1 - p(\varphi)] \frac{\partial e_S}{\partial T} + p(\varphi) \frac{\partial e_L}{\partial T}, \quad (11)$$

which is an interpolation of the bulk heat capacities per unit volume, and the thermal conductivity, $k = M_T/T^2$; the thermal conductivity may also be allowed to depend on temperature and phase in a general formulation. The function $Q(T)$ is given by the expression [34]

$$Q(T) = \int_{T_M}^T \frac{L(\zeta)}{\zeta^2} d\zeta = \frac{L(T_M)}{T_M^2} [T - T_M] + O([T - T_M]^2) \quad (12)$$

and the function $G(\varphi)$ is taken to be a double-well potential of the form

$$G(\varphi) = \frac{1}{4a} \varphi^2 (1 - \varphi)^2, \quad (13)$$

where a is a constant that determines the height of the intermediate maximum in the double-well potential; $1/a$ has dimensions of energy density per degree.

In the special case that $\partial e(T, 0)/\partial T = \partial e(T, 1)/\partial T = c_0$ and $L(T) = L_0$ are constant, and $p(\varphi) = \varphi$, Eqs. (7) and (8) become

$$c_0 \frac{\partial T}{\partial t} + L_0 \frac{\partial \varphi}{\partial t} = \nabla \cdot [k \nabla T], \quad (14)$$

$$\tau \frac{\partial \varphi}{\partial t} = \xi^2 \nabla^2 \varphi + \frac{1}{4a} \varphi(1 - \varphi)(\varphi - 1/2) + \frac{L_0}{TT_M} [T - T_M], \quad (15)$$

which is essentially equivalent to the form used by Langer [1,2] and Caginalp [4]. A disadvantage of the choice $p(\varphi) = \varphi$ is that the roots of the expression $Q(T)p'(\varphi) - G'(\varphi)$ appearing in Eq. (8) that determine the values of φ in the bulk phases then depend on temperature; choosing a more general form for $p(\varphi)$ that satisfies $p'(0) = p'(1) = 0$ allows the roots $\varphi = 0$ and $\varphi = 1$ for all temperatures [17,34,36,37].

For the isothermal case with $T = T_M$, the system admits a steady one-dimensional solution $\varphi(x)$ given by

$$\varphi(x) = \frac{1}{2} \left\{ \tanh \left[\frac{x}{2\sqrt{2}(\xi\sqrt{a})} \right] + 1 \right\}, \quad (16)$$

where we have chosen the origin so that $\varphi(0) = 1/2$. This solution shows that the width of the interfacial layer is proportional to the product $\xi\sqrt{a}$. The surface free energy (4) for this solution is given by

$$\gamma = T_M \xi^2 \int_{-\infty}^{\infty} \varphi^2 dx = \frac{T_M (\xi\sqrt{a})}{6\sqrt{2}a}. \quad (17)$$

Thus to maintain a finite surface free energy in the sharp-interface limit that $\xi\sqrt{a}$ tends to zero requires the constant a to tend to zero as well; i.e., the barrier height of the double-well potential becomes large.

III. ANISOTROPIC FORMULATION

To describe anisotropic surface free energies, we allow the coefficient ξ that appears in the gradient energy term $\xi^2 |\nabla \varphi|^2 / 2$ to depend on the orientation Θ of the contours of constant phase; i.e., we set $\xi = \xi(\Theta)$, where

$$\Theta = \arctan(\varphi_y / \varphi_x) \quad (18)$$

is the angle that the normal to these curves makes with the x axis. The angle Θ is thus defined throughout the domain; in the sharp-interface limit in which the crystal-melt interface is associated with the curve $\varphi = 1/2$, it reduces to the angle θ that the interface normal makes with a reference direction. The appropriate form for $\xi(\Theta)$ that is necessary to recover a given anisotropic surface free energy $\gamma(\theta)$ will be noted shortly. Practical difficulties in

defining Θ that are associated with the fact that $|\nabla \varphi|$ tends to zero in the bulk regions far from the interface are inconsequential to the asymptotic analysis, since the role of surface free energy is significant only in the neighborhood of the interface where $|\nabla \varphi|$ is non-negligible.

The term $\xi^2 \nabla^2 \varphi$ in Eq. (8), which arises from the variation

$$-\frac{\delta}{\delta \varphi} \left(\frac{\xi^2}{2} |\nabla \varphi|^2 \right) = \xi^2 \nabla^2 \varphi, \quad (19)$$

if ξ is constant, is then replaced by a more complicated expression,

$$-\frac{\delta}{\delta \varphi} \left(\frac{[\xi(\Theta)]^2}{2} |\nabla \varphi|^2 \right) = [\xi(\Theta)]^2 \nabla^2 \varphi + \text{additional terms}, \quad (20)$$

whose specific form we next compute.

The variation of the integral

$$I[\varphi] = \frac{1}{2} \int [\xi(\Theta)]^2 (\nabla \varphi)^2 dV \quad (21)$$

is given by (here $\xi' = d\xi/d\Theta$)

$$\begin{aligned} \delta I &= \int \{ \xi^2 \nabla \varphi \cdot \nabla \delta \varphi + (\nabla \varphi)^2 \xi \xi' \delta \Theta \} dV \\ &= \int \{ -\delta \varphi \nabla \cdot \{ \xi^2 \nabla \varphi \} + \xi \xi' [\varphi_x \delta \varphi_y - \varphi_y \delta \varphi_x] \} dV \\ &= - \int \{ \xi^2 \nabla^2 \varphi + 2 \xi \xi' \nabla \Theta \cdot \nabla \varphi \\ &\quad + ([\xi']^2 + \xi \xi'') [\varphi_x \Theta_y - \varphi_y \Theta_x] \} \delta \varphi dV, \end{aligned} \quad (22)$$

where we have integrated by parts and discarded the boundary term because it does not contribute to the functional derivative. In doing this, we have used the relation

$$\delta \Theta = \frac{\varphi_x \delta \varphi_y - \varphi_y \delta \varphi_x}{|\nabla \varphi|^2}. \quad (23)$$

By using the expression

$$\frac{\nabla \varphi}{|\nabla \varphi|} = (\cos \Theta) \hat{\mathbf{x}} + (\sin \Theta) \hat{\mathbf{y}}, \quad (24)$$

we obtain

$$\varphi_x \Theta_y - \varphi_y \Theta_x = |\nabla \varphi| \nabla \cdot \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right) \quad (25)$$

and

$$\nabla \Theta \cdot \nabla \varphi = |\nabla \varphi| \hat{\mathbf{z}} \cdot \nabla \times \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right); \quad (26)$$

here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors in the x , y , and z directions, respectively. The expression (20) therefore has the form

$$\begin{aligned} -\frac{\delta}{\delta \varphi} \left(\frac{1}{2} [\xi(\Theta)]^2 |\nabla \varphi|^2 \right) &= [\xi(\Theta)]^2 \nabla^2 \varphi + 2 \xi(\Theta) \xi'(\Theta) |\nabla \varphi| \hat{\mathbf{z}} \cdot \nabla \times \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right) \\ &\quad + \{ [\xi'(\Theta)]^2 + \xi(\Theta) \xi''(\Theta) \} |\nabla \varphi| \nabla \cdot \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right). \end{aligned} \quad (27)$$

An additional source of anisotropy is introduced by letting the empirical relaxation coefficient depend on orientation as well, so that $\tau = \tau(\Theta)$. The anisotropic form of the phase-field equations (8) and (10) then becomes

$$c(T, \varphi) \frac{\partial T}{\partial t} + L(T) p'(\varphi) \frac{\partial \varphi}{\partial t} = \nabla \cdot [k \nabla T], \quad (28)$$

$$\tau(\Theta) \frac{\partial \varphi}{\partial t} = Q(T) p'(\varphi) - G'(\varphi) - \frac{\delta}{\delta \varphi} \left(\frac{1}{2} [\xi(\Theta)]^2 |\nabla \varphi|^2 \right). \quad (29)$$

In the isothermal case with $T = T_M$, the equations admit steady, one-dimensional solutions of the form $\varphi = \varphi(\mathbf{x} \cdot \hat{\mathbf{n}})$, where $\hat{\mathbf{n}}$ is a constant unit vector and $\mathbf{x} \cdot \hat{\mathbf{n}} = x \cos \theta_0 + y \sin \theta_0$. The orientation is then constant, with $\Theta = \theta_0$, and the solution is given by [cf. Eq. (16)]

$$\varphi = \frac{1}{2} \left[\tanh \left(\frac{\mathbf{x} \cdot \hat{\mathbf{n}}}{2\sqrt{2}\xi(\theta_0)\sqrt{a}} \right) + 1 \right]. \quad (30)$$

The surface free energy for this orientation is then given by

$$\gamma(\theta_0) = \frac{T_M [\xi(\theta_0) \sqrt{a}]}{6\sqrt{2}a}. \quad (31)$$

This one-dimensional solution shows that interface width also varies with orientation; this width can be characterized by the parameter

$$\eta(\theta_0) = 6\sqrt{2} [\xi(\theta_0) \sqrt{a}] \quad (32)$$

which represents the width of the transition layer from $\varphi \approx 0.05$ to $\varphi \approx 0.95$. We note that $\gamma(\theta_0)$ and $\eta(\theta_0)$ are both proportional to $\xi(\theta_0)$, i.e., they have the same anisotropy.

Dimensionless equations

It is convenient to work in dimensionless units. We choose a length scale ℓ that represents a geometrical length in the system, such as a typical radius of curvature of the macroscopic phase boundaries. We choose a diffusive time scale $c_L \ell^2 / k_L$, where k_L is the liquid thermal conductivity and $c_L = \partial e_L / \partial T$ is the heat capacity per unit volume of the liquid, both evaluated at the melting point. We measure temperature relative to the melting point in units of T_M , and measure energy density in units of $L(T_M)$.

Appropriate scalings for the width of the interfacial layer and the double-well barrier height are incorporated by introducing the small dimensionless parameter ϵ , defined by

$$\epsilon = \frac{aL(T_M)}{T_M}, \quad (33)$$

where $L(T_M)$ is the latent heat per unit volume at the melting point. A thin interfacial layer is obtained by setting

$$\frac{\xi(\Theta) \sqrt{a}}{\ell} = \epsilon \Gamma(\Theta), \quad (34)$$

where $\Gamma(\Theta)$ is of order unity and is a dimensionless form of $\xi(\Theta)$. The dimensionless governing equations may then be written in the form

$$\tilde{c} \frac{\partial u}{\partial t} + \frac{1}{\tilde{S}} \tilde{L} p'(\varphi) \frac{\partial \varphi}{\partial t} = \nabla \cdot [\tilde{k} \nabla u], \quad (35)$$

$$\begin{aligned} \epsilon^2 \tilde{\tau}(\Theta) \frac{\partial \varphi}{\partial t} &= \frac{1}{4} \varphi(1 - \varphi)(\varphi - 1/2) + \epsilon \tilde{Q}(u) p'(\varphi) \\ &\quad - \epsilon^2 \frac{\delta}{\delta \varphi} \left(\frac{1}{2} [\Gamma(\Theta)]^2 |\nabla \varphi|^2 \right), \end{aligned} \quad (36)$$

where the space and time variables are now dimensionless, and the variational derivative in the latter expression is given by Eq. (27) with $\Gamma(\Theta)$ replacing $\xi(\Theta)$. Here $u = (T - T_M) / T_M$ is the dimensionless temperature, $\tilde{k}(u, \varphi) = k(T, \varphi) / k_L$, $\tilde{c}(u, \varphi) = c(T, \varphi) / c_L$, $\tilde{L}(u) = L(T) / L(T_M)$, and

$$\tilde{S} = \frac{T_M c_L}{L(T_M)}, \quad (37)$$

$$\tilde{\tau}(\Theta) = \frac{k_L T_M^2 \tau(\Theta)}{a \ell^2 c_L [L(T_M)]^2}, \quad (38)$$

$$\tilde{Q}(u) = \int_0^u \frac{\tilde{L}(\bar{u})}{(1 + \bar{u})^2} d\bar{u} = u + O(u^2). \quad (39)$$

To retain the effects of interface kinetics, $\tilde{\tau}(\Theta)$ should be assumed to be of order unity. The dimensionless Helmholtz free-energy functional for $T = T_M$ has the form

$$\frac{\mathcal{F}}{\ell^3 L(T_M)} = \int_V \left\{ \frac{\epsilon}{2} [\Gamma(\Theta)]^2 |\nabla \varphi|^2 + \frac{1}{4\epsilon} \varphi^2 (1 - \varphi)^2 \right\} dV. \quad (40)$$

From Eqs. (31)–(34), we see that the dimensionless surface free energy for orientation $\Theta = \theta_0$ is

$$\frac{\gamma(\theta_0)}{L(T_M) \ell} = \frac{\Gamma(\theta_0)}{6\sqrt{2}}. \quad (41)$$

IV. MATCHED ASYMPTOTIC EXPANSIONS

An asymptotic expansion of the dimensionless phase-field equations (35) and (36) in the sharp-interface limit allows the identification of appropriate forms for the coefficients $\xi(\Theta)$, $\tau(\Theta)$, and a in order to recover the anisotropic generalization (2) of the Gibbs-Thomson equation. The formal procedure is similar to that employed by Caginalp [29] for the isotropic case, so we provide an abbreviated version of the asymptotic expansion. To perform the expansion, two subregions of the domain are identified: in the *inner region*, which represents the

vicinity of the interfacial layer, the gradient of the phase field is large and the temperature varies slowly, and in the *outer region*, which represents the bulk phases, the phase field is essentially constant. In each phase, the solution can be represented by an asymptotic expansion in terms of appropriately scaled inner or outer variables. The inner and outer regions share a common region of overlap, and in this intermediate region, the asymptotic expansions for the inner and outer solutions can be matched to determine the solution. Roughly speaking, the outer solution determines the far-field boundary conditions for the inner solution, and the inner solution determines the appropriate interfacial jump conditions for the outer solution.

A. Outer solution

The outer solution is defined in the bulk phases where the spatial variation of φ is small, and this variation is on an $O(1)$ length scale. The solution is formally expanded in powers of ϵ ,

$$u = u^{(0)} + \epsilon u^{(1)} + \epsilon^2 u^{(2)} + \dots, \quad (42)$$

$$\varphi = \varphi^{(0)} + \epsilon \varphi^{(1)} + \epsilon^2 \varphi^{(2)} + \dots \quad (43)$$

The leading-order solution is given by $\varphi^{(0)} = 1$ and $\varphi^{(0)} = 0$ in the liquid and solid regions, respectively, and the leading-order temperature in each region satisfies the usual diffusion equation

$$\tilde{c}^{(0)} \frac{\partial u^{(0)}}{\partial t} = \nabla \cdot [\tilde{k}^{(0)} \nabla u^{(0)}], \quad (44)$$

where $\tilde{c}^{(0)}$ and $\tilde{k}^{(0)}$ have values appropriate to the respective bulk phases.

Far-field boundary conditions for the thermal field are assumed to be known, but interfacial jump conditions, that hold in the limit that the interfacial layer becomes sharp, must be determined by matching with the inner solution. The higher-order corrections for the thermal field may be computed by continuing the procedure, but are not required for the subsequent analysis. From Eq. (36) we see that the first-order correction for the phase field vanishes identically under the assumption that $p'(0) = p'(1) = 0$. The formal expansion for

the outer solution breaks down near the interfacial layer, where the variation of φ is large.

B. Inner solution

To perform the inner expansion in the interfacial layer, it is convenient to introduce a local coordinate system based on a parametrization of the curve $\varphi(x, y, t) = 1/2$. In terms of the arclength s , this curve may be expressed in the form $x = X(s, t)$ and $y = Y(s, t)$. The curve has a tangent vector (X', Y') , a normal vector $(Y', -X')$, and a normal velocity $v_n = Y'X_t - X'Y_t$, where the prime denotes the derivative with respect to arclength and time derivatives are indicated by subscripts. We use s as one of the local coordinates, and use the distance r along the normal as the other coordinate, so that

$$x(r, s, t) = X(s, t) + rY'(s, t), \quad (45)$$

$$y(r, s, t) = Y(s, t) - rX'(s, t). \quad (46)$$

The orientation of the curve is chosen so that the solid lies on the left if the curve is traversed in the direction of increasing s , and the normal then points into the liquid; the coordinate system is described in more detail in the Appendix. The governing equations in the local coordinates are further transformed by introducing the scaled variable $\rho = r/\epsilon$ and writing $\hat{\varphi}(\rho, s, t) = \varphi(x, y, t)$ and $\hat{u}(\rho, s, t) = u(x, y, t)$ in the inner region, with corresponding expansions

$$\hat{u} = \hat{u}^{(0)} + \epsilon \hat{u}^{(1)} + \epsilon^2 \hat{u}^{(2)} + \dots, \quad (47)$$

$$\hat{\varphi} = \hat{\varphi}^{(0)} + \epsilon \hat{\varphi}^{(1)} + \epsilon^2 \hat{\varphi}^{(2)} + \dots \quad (48)$$

in terms of the inner variables.

1. Matching conditions

Matching conditions provide the far-field boundary conditions for the inner solution. The outer solution $u(x, y, t)$ at a point near the curve $\varphi = 1/2$ is written as a function of the inner variables, and the resulting expressions are expanded in ϵ to obtain

$$u(X + \epsilon\rho Y', Y - \epsilon\rho X', t) = u_{\pm}^{(0)}(X, Y, t) + \epsilon \left\{ u_{\pm}^{(1)}(X, Y, t) + \rho \frac{\partial u_{\pm}^{(0)}}{\partial n}(X, Y, t) \right\} + O(\epsilon^2), \quad (49)$$

where the plus or minus subscript indicates the limiting behavior of the outer solution as ρ tends to zero through positive or negative values, respectively, to allow for the possibility of discontinuous behavior of the outer solution in the sharp-interface limit. The limiting behavior of the phase field is simply $\varphi = 1 + O(\epsilon^2)$ for $\rho > 0$ and $\varphi = O(\epsilon^2)$ for $\rho < 0$.

2. Transformation to inner variables

The orientation angle Θ , which in the inner region satisfies

$$\tan \Theta(\rho, s, \hat{\varphi}_\rho, \hat{\varphi}_s) = \frac{-(X' + \epsilon\rho Y'')\hat{\varphi}_\rho + \epsilon Y' \hat{\varphi}_s}{(Y' - \epsilon\rho X'')\hat{\varphi}_\rho + \epsilon X' \hat{\varphi}_s}, \quad (50)$$

can be expanded in the form

$$\Theta = \Theta^{(0)} + \epsilon\Theta^{(1)} + O(\epsilon^2), \quad (51)$$

with

$$\tan \Theta^{(0)} = -X'/Y' = \tan \theta(s), \quad (52)$$

i.e., to leading order, $\Theta^{(0)}$ is simply the normal angle $\theta(s)$ to the interface, and is independent of the variable ρ . A short calculation shows that the first-order correction is given by

$$\Theta^{(1)} = \widehat{\varphi}_s^{(0)}/\widehat{\varphi}_\rho^{(0)}; \quad (53)$$

we note that $\widehat{\varphi}_s^{(0)}(\rho, s)$ vanishes when $\rho = 0$, but is not necessarily zero if $\rho \neq 0$.

The governing equations may be transformed by using the results given in the Appendix; here we note some of the intermediate expressions before presenting the final

results. The time derivative transforms according to

$$\frac{\partial \varphi}{\partial t} = \frac{-v_n}{\epsilon} \frac{\partial \widehat{\varphi}^{(0)}}{\partial \rho} + O(1). \quad (54)$$

The transformed Laplacian assumes the form

$$\begin{aligned} \nabla^2 \varphi &= \frac{1}{(1 + \epsilon\rho K)} \left\{ [(1 + \epsilon\rho K)\varphi_r]_r + \left[\frac{1}{(1 + \epsilon\rho K)} \varphi_s \right]_s \right\} \\ &= \frac{1}{\epsilon^2} (\widehat{\varphi}_{\rho\rho}^{(0)} + \epsilon\widehat{\varphi}_{\rho\rho}^{(1)}) + \frac{K(s)}{\epsilon} \widehat{\varphi}_\rho^{(0)} + O(1), \end{aligned} \quad (55)$$

and the gradient is given by

$$|\nabla \varphi| = \sqrt{\varphi_r^2 + \varphi_s^2 / (1 + \epsilon\rho K)^2} = \frac{1}{\epsilon} \widehat{\varphi}_\rho^{(0)} + O(\epsilon); \quad (56)$$

here we assume that the coordinates are oriented so that $\widehat{\varphi}_\rho^{(0)} > 0$ when simplifying the square root.

We also have the expansions

$$\begin{aligned} \nabla \cdot \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right) &= \frac{1}{(1 + \epsilon\rho K)} \left\{ \frac{1}{\epsilon} \left[\frac{(1 + \epsilon\rho K)\varphi_\rho}{\sqrt{\varphi_\rho^2 + \epsilon^2 \varphi_s^2 / (1 + \epsilon\rho K)^2}} \right]_\rho + \epsilon \left[\frac{\varphi_s / (1 + \epsilon\rho K)}{\sqrt{\varphi_\rho^2 + \epsilon^2 \varphi_s^2 / (1 + \epsilon\rho K)^2}} \right]_s \right\} \\ &= K(s) + O(\epsilon) \end{aligned} \quad (57)$$

and

$$\begin{aligned} \widehat{\mathbf{z}} \cdot \nabla \times \left(\frac{\nabla \varphi}{|\nabla \varphi|} \right) &= \frac{1}{(1 + \epsilon\rho K)} \left\{ \frac{1}{\epsilon} \left[\frac{\epsilon\varphi_s}{\sqrt{\varphi_\rho^2 + \epsilon^2 \varphi_s^2 / (1 + \epsilon\rho K)^2}} \right]_\rho - \left[\frac{\varphi_\rho}{\sqrt{\varphi_\rho^2 + \epsilon^2 \varphi_s^2 / (1 + \epsilon\rho K)^2}} \right]_s \right\} \\ &= \frac{\varphi_{\rho s}^{(0)}}{\varphi_\rho^{(0)}} - \frac{\varphi_s^{(0)} \varphi_{\rho\rho}^{(0)}}{(\varphi_\rho^{(0)})^2} + O(\epsilon). \end{aligned} \quad (58)$$

We therefore have

$$\begin{aligned} -\epsilon^2 \frac{\delta}{\delta \varphi} \left(\frac{1}{2} [\Gamma(\Theta)]^2 |\nabla \varphi|^2 \right) &= [\Gamma(\Theta)]^2 \widehat{\varphi}_{\rho\rho}^{(0)} + \epsilon \left\{ [\Gamma(\Theta)]^2 \widehat{\varphi}_{\rho\rho}^{(1)} + [\Gamma(\Theta)]^2 K(s) \widehat{\varphi}_\rho^{(0)} + 2\Gamma(\Theta) \Gamma'(\Theta) \left[\widehat{\varphi}_{\rho s}^{(0)} - \frac{\widehat{\varphi}_s^{(0)} \widehat{\varphi}_{\rho\rho}^{(0)}}{\widehat{\varphi}_\rho^{(0)}} \right] \right. \\ &\quad \left. + \{ [\Gamma'(\Theta)]^2 + \Gamma(\Theta) \Gamma''(\Theta) \} K(s) \widehat{\varphi}_\rho^{(0)} \right\} + O(\epsilon^2) \\ &= [\Gamma(\theta)]^2 \widehat{\varphi}_{\rho\rho}^{(0)} + \epsilon \left\{ [\Gamma(\theta)]^2 \widehat{\varphi}_{\rho\rho}^{(1)} + [\Gamma(\theta)]^2 K(s) \widehat{\varphi}_\rho^{(0)} + 2\Gamma(\theta) \Gamma'(\theta) \widehat{\varphi}_{\rho s}^{(0)} \right. \\ &\quad \left. + \{ [\Gamma'(\theta)]^2 + \Gamma(\theta) \Gamma''(\theta) \} K(s) \widehat{\varphi}_\rho^{(0)} \right\} + O(\epsilon^2), \end{aligned} \quad (59)$$

where in the final expression we have expanded $\Gamma = \Gamma(\Theta)$ using

$$\Theta = \theta(s) + \epsilon \frac{\widehat{\varphi}_s^{(0)}}{\widehat{\varphi}_\rho^{(0)}} + O(\epsilon^2) \quad (60)$$

to simplify the result.

3. Leading-order solution

The leading-order equations take the form

$$\frac{\partial}{\partial \rho} \left(\tilde{k}^{(0)} \frac{\partial \widehat{u}^{(0)}}{\partial \rho} \right) = 0, \quad (61)$$

$$[\Gamma(\theta)]^2 \frac{\partial^2 \widehat{\varphi}^{(0)}}{\partial \rho^2} - g(\widehat{\varphi}^{(0)}) = 0, \quad (62)$$

where

$$g(\widehat{\varphi}^{(0)}) = \frac{1}{4} \widehat{\varphi}^{(0)} (\widehat{\varphi}^{(0)} - 1) (\widehat{\varphi}^{(0)} - 1/2). \quad (63)$$

Here $\tilde{k}^{(0)} = \tilde{k}(\widehat{u}^{(0)}, \widehat{\varphi}^{(0)})$ denotes the thermal conductivity evaluated with the leading-order solution.

The thermal matching conditions for the inner problem,

$$\widehat{u}^{(0)}(\rho, s, t) \rightarrow u_\pm^{(0)}(X, Y, t) \quad (64)$$

as $\rho \rightarrow \pm\infty$ implies that $\tilde{k}^{(0)} \partial \hat{u}^{(0)} / \partial \rho = 0$, and so $\hat{u}^{(0)}$ is independent of ρ . It follows that the leading-order thermal field for the outer solution is continuous across the interface.

The leading-order solution for the phase field is [cf. Eq. (16)]

$$\hat{\varphi}^{(0)}(\rho, s) = \frac{1}{2} \left\{ \tanh \left(\frac{\rho}{2\sqrt{2}\Gamma(\theta)} \right) + 1 \right\}; \quad (65)$$

here the s dependence of $\hat{\varphi}^{(0)}$ enters through the function Γ , whose argument is the normal angle $\theta(s)$ along the interface.

4. First-order solution

The first-order inner problem has the form

$$\frac{\partial}{\partial \rho} \left(\tilde{k}^{(0)} \frac{\partial \hat{u}^{(1)}}{\partial \rho} \right) = -v_n \frac{\tilde{L}(\hat{u}^{(0)})}{\tilde{S}} p'(\hat{\varphi}^{(0)}) \hat{\varphi}_\rho^{(0)}, \quad (66)$$

$$\begin{aligned} [\Gamma(\theta)]^2 \frac{\partial^2 \hat{\varphi}^{(1)}}{\partial \rho^2} - g'(\hat{\varphi}^{(0)}) \hat{\varphi}^{(1)} &= -v_n \tilde{\tau}(\theta) \hat{\varphi}_\rho^{(0)} - \tilde{Q}(\hat{u}^{(0)}) p'(\hat{\varphi}^{(0)}) - [\Gamma(\theta)]^2 K(s) \hat{\varphi}_\rho^{(0)} - 2\Gamma(\theta) \Gamma'(\theta) \hat{\varphi}_{\rho s}^{(0)} \\ &\quad - \{[\Gamma'(\theta)]^2 + \Gamma(\theta) \Gamma''(\theta)\} K(s) \hat{\varphi}_\rho^{(0)}. \end{aligned} \quad (67)$$

The thermal matching conditions for the inner problem imply that

$$\frac{\partial \hat{u}^{(1)}}{\partial \rho}(\rho, s, t) \rightarrow \frac{\partial u_\pm^{(0)}}{\partial n}(X, Y, t) \quad (68)$$

as $\rho \rightarrow \pm\infty$. Integration of the thermal equation then gives the equation

$$-v_n \frac{\tilde{L}(\hat{u}^{(0)})}{\tilde{S}} = \tilde{k}_L \frac{\partial u_+^{(0)}}{\partial n} - \tilde{k}_S \frac{\partial u_-^{(0)}}{\partial n}, \quad (69)$$

which is the appropriate heat-flux boundary condition for the outer solution.

Differentiation of Eq. (62) with respect to ρ shows that the function $\hat{\varphi}_\rho^{(0)}$ is a homogeneous solution of Eq. (67). The right-hand side of this equation must then be orthogonal to this function, which provides the solvability condition

$$\begin{aligned} v_n \tilde{\tau}(\theta) \int_{-\infty}^{\infty} (\varphi_\rho^{(0)})^2 d\rho &= -\tilde{Q}(\hat{u}^{(0)}) - [\Gamma(\theta)]^2 K(s) \int_{-\infty}^{\infty} (\varphi_\rho^{(0)})^2 d\rho - \Gamma(\theta) \Gamma'(\theta) \frac{d}{ds} \left[\int_{-\infty}^{\infty} (\varphi_\rho^{(0)})^2 d\rho \right] \\ &\quad - \{[\Gamma'(\theta)]^2 + \Gamma(\theta) \Gamma''(\theta)\} K(s) \int_{-\infty}^{\infty} (\varphi_\rho^{(0)})^2 d\rho, \end{aligned} \quad (70)$$

or, using the relation

$$\int_{-\infty}^{\infty} (\hat{\varphi}_\rho^{(0)})^2 d\rho = \frac{1}{6\sqrt{2}\Gamma(\theta)}, \quad (71)$$

we have

$$\frac{v_n \tilde{\tau}(\theta)}{6\sqrt{2}\Gamma(\theta)} = -\tilde{Q}(\hat{u}^{(0)}) - \frac{1}{6\sqrt{2}} [\Gamma(\theta) + \Gamma''(\theta)] K(s), \quad (72)$$

which is our principal result.

V. DISCUSSION

The expression (72) is the dimensionless version of Eq. (2) if we take $\tilde{Q}(u) \approx u$ and revert to dimensional variables,

$$\frac{v_n}{\mu(\theta)} = T_M - \frac{T_M}{L(T_M)} (\gamma + \gamma_{\theta\theta}) K - T_I; \quad (73)$$

here we have identified

$$\mu(\theta) = \left(\frac{6\sqrt{2}L(T_M)}{T_M^2} \right) \frac{\xi(\theta)\sqrt{a}}{\tau(\theta)} \quad (74)$$

as the appropriate form for the kinetic coefficient, and we recall that the surface free energy is given by

$$\gamma(\theta) = \frac{T_M [\xi(\theta)\sqrt{a}]}{6\sqrt{2}a}. \quad (75)$$

Note that anisotropy in the parameter $\xi(\theta)$ induces anisotropy in both the surface free energy and the kinetic coefficient, even when the parameter τ is isotropic; note also that the anisotropy of the kinetic coefficient depends on the ratio of ξ and τ .

The expressions (74), (75), and (32) relate the physical parameters μ , γ , and the interface width η to the phase-field parameters ξ , τ , and a . These relations can be inverted to yield expressions for the phase-field parameters in terms of the physical parameters, viz.,

$$\tau(\Theta) = \frac{L(T_M)\eta(\Theta)}{T_M^2\mu(\Theta)}, \quad (76)$$

$$[\xi(\Theta)]^2 = \frac{\eta(\Theta)\gamma(\Theta)}{T_M}, \quad (77)$$

$$a = \frac{T_M\eta(\Theta)}{72\gamma(\Theta)}; \quad (78)$$

note that the latter expression implies a common functional dependence for η and γ in order for the resulting parameter a to be constant. Alternatively, the parameters τ and ξ may be expressed in terms of γ , μ , and the single parameter a by using Eq. (78) to eliminate η in Eqs. (76) and (77).

It is noteworthy that the relationship of the boundary condition Eq. (73) to the phase-field model has been investigated numerically in the context of the dendritic growth of nickel at an undercooling of $L(T_M)/2c_L$ by Wheeler, Murray, and Schaefer [19]. Specifically, numerically computed values of the tip temperature T_I were compared to those computed from Eq. (73) for several values of ϵ (see Table 3 of [19], in which $\epsilon = \bar{\epsilon}/2$). The agreement improves with decreasing ϵ , and for the smallest value of $\epsilon = 1.25(10^{-3})$ considered, the agreement was within 11%.

As mentioned in the Introduction, an anisotropic surface free energy can also be obtained by replacing the isotropic gradient energy term by the more general quadratic form $(\xi_x^2\varphi_x^2 + \xi_y^2\varphi_y^2)/2$ [23], where ξ_x^2 and ξ_y^2 are constants. In this case, the term $\xi^2\nabla^2\varphi$ in Eq. (8) would be replaced by

$$-\frac{\delta}{\delta\varphi} \left(\frac{\xi_x^2}{2}\varphi_x^2 + \frac{\xi_y^2}{2}\varphi_y^2 \right) = \xi_x^2\varphi_{xx} + \xi_y^2\varphi_{yy}. \quad (79)$$

If x is scaled by ξ_x and y is scaled by ξ_y , this expression reduces to that for the isotropic case. Since the isotropic equilibrium shape is given by a circle, the corresponding anisotropic equilibrium shape is therefore an ellipse. This choice of gradient energy leads to one-dimensional solutions of the form (30) with surface free energy (31), where

$$\xi(\theta_0) = \sqrt{\xi_x^2 \cos^2 \theta_0 + \xi_y^2 \sin^2 \theta_0}. \quad (80)$$

This particular form of gradient energy term thus leads to a surface free energy with two-fold axes of symmetry about the orientations $\theta = 0$ and $\theta = \pi/2$, and possessing only two degrees of freedom (ξ_x and ξ_y). The present approach for introducing anisotropy, wherein a *scalar function* $\xi = \xi(\theta)$ is instead employed, allows general surface energies $\gamma = \gamma(\theta)$ to be treated.

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APPENDIX

We collect some pertinent facts about the local coordinate system used in the inner expansion of the matching procedure. The orthogonal coordinates r and s are defined relative to the moving curve $x = X(s, t)$ and $y = Y(s, t)$, where s is arclength along the curve. The coordinate transformation is given by

$$x(r, s, t) = X(s, t) + rY'(s, t), \quad (A1)$$

$$y(r, s, t) = Y(s, t) - rX'(s, t). \quad (A2)$$

Thus

$$x_r = Y'(s, t), \quad y_r = -X'(s, t), \quad (A3)$$

$$x_s = X'(s, t) + rY''(s, t), \quad y_s = Y'(s, t) - rX''(s, t). \quad (A4)$$

If the angle that the normal to the interface makes with respect to the x axis is denoted by $\theta(s)$, then $\theta_s = \mathcal{K}(s)$ is the local curvature of the interface. We have

$$X' + iY' = ie^{i\theta}, \quad (A5)$$

and by differentiating we have

$$X'' + iY'' = -e^{i\theta}K. \quad (A6)$$

It follows that

$$K = -(X'' - iY'')e^{i\theta} = X'Y'' - Y'X'', \quad (A7)$$

and

$$(X'')^2 + (Y'')^2 = K^2. \quad (A8)$$

For the unit circle, this expression gives a positive curvature $K = 1$.

We have the Jacobian

$$h(r, s) = x_r y_s - x_s y_r = 1 + rK(s). \quad (A9)$$

Since $x_r x_s + y_r y_s = 0$, the coordinates are orthogonal, and the square of the element of differential arclength dS in the three-dimensional set of orthogonal coordinates (r, s, z) is given by

$$dS^2 = dr^2 + h^2 ds^2 + dz^2. \quad (A10)$$

The gradient of a function $\psi(r, s)$ transforms according to

$$\nabla\psi = \psi_r \hat{\mathbf{r}} + \frac{1}{h}\psi_s \hat{\mathbf{s}}, \quad (A11)$$

and the Laplacian is given by

$$\nabla^2\psi = \frac{1}{h} \left\{ (h\psi_r)_r + \left(\frac{1}{h}\psi_s \right)_s \right\}. \quad (A12)$$

Given a vector

$$\mathbf{A}(r, s) = u(r, s)\hat{\mathbf{r}} + v(r, s)\hat{\mathbf{s}}, \quad (\text{A13})$$

we have

$$\nabla \cdot \mathbf{A} = \frac{1}{h} \{(hu)_r + v_s\}, \quad (\text{A14})$$

and

$$\hat{\mathbf{z}} \cdot \nabla \times \mathbf{A} = \frac{1}{h} \{(hv)_r - u_s\}. \quad (\text{A15})$$

[These relations are analogous to those in cylindrical coordinates, if $h(r, s)$ is identified with the radius in the corresponding expressions.]

If we regard the coordinates r and s as functions of x , y , and t , we note that inverting the Jacobian matrix

gives the relations

$$hr_x = Y'(s) - rX''(s), \quad hr_y = -X'(s) - rY''(s), \quad (\text{A16})$$

$$hs_x = X'(s), \quad hs_y = Y'(s). \quad (\text{A17})$$

We also have

$$hr_t = -(X_t Y' - Y_t X') + r(X_t X'' + Y_t Y'') \\ + r^2(Y_t X'' - X_t Y'') = -v_n + O(r), \quad (\text{A18})$$

$$hs_t = -(X_t X' + Y_t Y') + r(Y_t X'_t - X_t Y'_t) \\ = -v_{\text{tan}} + O(r), \quad (\text{A19})$$

where $v_n = Y'X_t - X'Y_t$ is the normal velocity of the curve and $v_{\text{tan}} = Y'Y_t + X'X_t$ is a tangential velocity which depends on the specific choice of arclength parametrization.

* Permanent address: School of Mathematics, University of Bristol, Bristol BS8 1TW, United Kingdom.

† Also at National Institute of Standards and Technology.

- [1] J. S. Langer (private communication).
 [2] J. S. Langer, in *Directions in Condensed Matter Physics*, edited by G. Grinstein and G. Mazenko (World Scientific, Philadelphia, 1986), p. 165.
 [3] B. I. Halperin, P. C. Hohenberg, and S-K. Ma, *Phys. Rev. B* **10**, 139 (1974).
 [4] G. Caginalp, in *Applications of Field Theory to Statistical Mechanics*, edited by L. Garrido, Lecture Notes in Physics Vol. 216 (Springer-Verlag, Berlin, 1985), p. 216.
 [5] J. B. Collins and H. Levine, *Phys. Rev. B* **31**, 6119 (1985).
 [6] A. R. Umantsev and A. L. Roitburd, *Fiz. Tverd. Tela* (Leningrad) **30**, 1124 (1988) [*Sov. Phys. Solid State* **30**, 651 (1988)]; A. Umantsev and G. B. Olson, *Phys. Rev. A* **46**, R6132 (1992).
 [7] J. W. Gibbs, *The Collected Works of J. Williard Gibbs* (Longmans, Green, New York, 1928), Vol. I, pp. 55–353.
 [8] J. D. van der Waals, *Konink. Akad. Wet. Amsterdam* (Sec. 1), **1**, 8 (1893) (in Dutch) [English translation (with commentary): J. S. Rowlinson, *J. Stat. Phys.* **20**, 197 (1979)].
 [9] J. W. Cahn and S. M. Allen, *J. Phys. (Paris) Colloq. Suppl.* **C7**, 51 (1977).
 [10] S. M. Allen and J. W. Cahn, *Acta Metall.* **27**, 1085 (1979).
 [11] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
 [12] J. W. Cahn, *Acta Metall.* **9**, 795 (1961).
 [13] M. E. Rose, *Math. Comput.* **14**, 249 (1960).
 [14] A. A. Wheeler, W. J. Boettinger, and G. B. McFadden, *Phys. Rev. E* **47**, 1893 (1993).
 [15] R. Kobayashi, *Bull. Jpn. Soc. Ind. Appl. Math.* **1**, 22 (1991).
 [16] R. Kobayashi, *Abst. Pap. Am. Math. Soc.* **12**, 163 (1991), and associated videotape.
 [17] R. Kobayashi, *Physica D* **63**, 410 (1993).
 [18] R. Kobayashi, in *Pattern Formation in Complex Dissipative Systems*, edited by S. Kai (World Scientific, Singapore, 1992), pp. 121–128, and associated videotape.
 [19] A. A. Wheeler, B. T. Murray, and R. J. Schaefer, *Physica D* **66**, 243 (1993).
 [20] M. E. Glicksman, *Mater. Sci. Eng.* **65**, 45 (1984).
 [21] J. S. Langer, in *Le Hesard et la Matiere/Chance and Matter*, Les Houches, Session XLVI (North-Holland, Amsterdam, 1987), Course 10, p. 629.
 [22] G. Caginalp and P. Fife, *Phys. Rev. B* **34**, 4940 (1986).
 [23] G. Caginalp, *Ann. Phys. (N.Y.)* **172**, 136 (1986).
 [24] J. W. Cahn and R. Kikuchi, *Phys. Rev. B* **31**, 4300 (1985).
 [25] P. R. Harrowell and D. W. Oxtoby, *J. Chem. Phys.* **86**, 2932 (1987).
 [26] J. E. Hilliard, *Phase Transformations* (American Society for Metals, Metals Park, OH, 1970), pp. 497–560.
 [27] J. B. Smith, *J. Comput. Phys.* **39**, 112 (1981).
 [28] A. R. Umantsev, V. V. Vinograd, and V. T. Borisov, *Sov. Phys. Crystallogr.* **30**, 262 (1986); **31**, 596 (1986).
 [29] G. Caginalp, *Phys. Rev. A* **39**, 5887 (1989).
 [30] P. C. Fife, *Dynamics of Internal Layers and Diffusive Interfaces*, CBMS-NSF Regional Conference Series in Applied Mathematics Vol. 53 (SIAM, Philadelphia, 1988), pp. 11–15.
 [31] R. Pego, *Proc. R. Soc. London, Ser. A* **422**, 261 (1989).
 [32] J. Rubenstein, P. Sternberg, and J. B. Keller, *SIAM J. Appl. Math.* **49**, 116 (1989).
 [33] C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C. S. Smith (University of Chicago, Chicago, 1952).
 [34] S-L. Wang, R. F. Sekerka, A. A. Wheeler, B. T. Murray, S. R. Coriell, R. J. Braun, and G. B. McFadden, *Physica D* (to be published).
 [35] O. Penrose and P. C. Fife, *Physica D* **43**, 44 (1990).
 [36] G. Caginalp and X. Chen, in *On the Evolution of Phase Boundaries*, edited by M. E. Gurtin and G. B. McFadden, The IMA Series in Mathematics and Its Applications Vol. 43 (Springer-Verlag, New York, 1992), pp. 1–27.
 [37] A. Umantsev, *J. Chem. Phys.* **96**, 605 (1992).