

## Phase-field methods for interfacial boundaries

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A Landau-Ginzburg approach to an interface with finite thickness incorporates surface tension, anisotropy, curvature, and dynamics of the interface along with supercooling. Various aspects are rigorous.

The behavior of an interface between two phases of a material is of interest in many different contexts in physics. Some of the basic questions involve the shape of the interface, the formation of spatial patterns, and instabilities of phase boundaries.<sup>1-8</sup> The problems involving the shape of the phase boundary have been studied in both the equilibrium and nonequilibrium situations. A central aspect of these questions is the relationship between the temperature at the interface and other variables such as the surface tension, curvature, and normal velocity of the interface, anisotropy, and concentration of impurities, etc. In the simplest case, for an isotropic pure material in equilibrium, this is called the Gibbs-Thompson relation and has the form

$$\Delta s u(\mathbf{x}) = -\sigma \kappa(\mathbf{x}) \quad (1)$$

where  $\mathbf{x}$  is a point on the interface,  $u$  is the temperature (scaled so that  $u=0$  is the usual melting temperature),  $\Delta s$  is the change in entropy density,  $\sigma$  is the surface tension, and  $\kappa$  is the sum of principal curvatures at  $\mathbf{x}$ . For a phase boundary which is not in equilibrium, the analog of (1) would be a relation between the shape, (normal) velocity, and temperature of the interface, thereby determining the motion of the interface.

An important physical problem is the connection between the atomic or molecular physics and the macroscopic behavior of the interface. In this paper, we report on progress toward this goal by means of a pair of differential equations arising from statistical mechanics using a Landau-Ginzburg approximation.<sup>9,10</sup> In the anisotropic case a derivation has been presented in Ref. 11 from a lattice spin model.

In particular, one may begin with the (reduced)  $\phi^4$  Hamiltonian on a Bravais lattice of  $N$  spins in  $d$  dimensions,

$$\bar{\mathcal{H}} = \frac{1}{2k_B T} \sum_{\mathbf{x}, \mathbf{x}'} J(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') - \sum_{\mathbf{x}} w[\phi(\mathbf{x})] \quad (2)$$

where  $J(\mathbf{x} - \mathbf{x}')$  is the coupling between spins located at sites  $\mathbf{x}$  and  $\mathbf{x}'$ .  $\phi(\mathbf{x})$  is a spin variable having the real number line as its range, and  $w$  is an even fourth-order polynomial which maintains a finite internal energy. Assume  $J(\mathbf{x} - \mathbf{x}')$  is a nearest-neighbor coupling of strength  $J_i > 0$  in the  $i$ th direction. Then the continuum equation for  $\phi$  can be derived by (i) rewriting the interaction term in (2) as a sum of the Fourier transforms  $\hat{\phi}$  and  $\hat{J}$  over the dual space as  $N^{-1} \sum_{\mathbf{q}} \hat{J}(\mathbf{q}) \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q})$ , (ii) neglecting wave numbers  $q^4$  and higher, (iii) integrating by parts in discrete derivatives, (iv) taking the continuum limit while maintain-

ing finite volume and internal energy. Adding a term  $-2u\phi$  to the resulting Hamiltonian, one obtains the free energy

$$F\{\phi\} = \int d\mathbf{x} F[\mathbf{x}, \phi(\mathbf{x}), \phi_{x_1}(\mathbf{x}), \dots, \phi_{x_d}(\mathbf{x})] \quad (3)$$

$$F = \sum_{i=1}^d \left[ \frac{\xi_i^2}{2} \left( \frac{\partial \phi(x)}{\partial x_i} \right)^2 \right] + \frac{1}{8} [\phi(x)^2 - 1]^2 - 2u\phi(x) \quad (4)$$

where  $\xi_i$  are proportional to  $J_i$ . In equilibrium  $\phi$  must minimize  $F$ , i.e.,  $\delta F/\delta \phi = 0$ . Nonequilibrium is described by the model  $A$  equation in Landau-Ginzburg theory as  $\tau \phi = \delta F/\delta \phi$ , where  $\tau$  is a relaxation time. One has then the equation

$$\tau \frac{\partial \phi}{\partial t} = \sum_{i=1}^d \xi_i^2 \frac{\partial^2 \phi}{\partial x_i^2} + \frac{1}{2}(\phi - \phi^3) + 2u \quad (5)$$

coupled with the heat diffusion equation

$$\frac{\partial u}{\partial t} + \frac{l}{2} \frac{\partial \phi}{\partial t} = K \Delta u \quad (6)$$

which may be studied subject to suitable initial and boundary conditions.<sup>12-20</sup>

The phase-field equations (5) and (6) thereby incorporate the physics of supercooling in a physically realistic manner. The thermal and geometric properties of the interface are also depicted accurately. In particular, the nonzero thickness of the interface and the nonzero surface tension are consequences of a finite correlation length. In fact, each of these quantities is proportional to  $\xi = \xi_i$  in the isotropic case (see Theorems 3.4 and 7.3 of Ref. 12). Furthermore, the finite thickness of the interface means the latent heat is released throughout the interface. This feature would be absent in a modified Stefan approach that would stipulate a Gibbs-Thompson-type condition on a sharp interface.

We consider briefly the relationship between this phase-field model (5) and (6) and the Stefan model<sup>21</sup> which incorporates the physics of heat diffusion and latent heat, but neglects surface tension and precludes supercooling. Formally, the Stefan model is a limiting case of the phase-field model as the parameters  $\tau$  and  $\xi$  approach zero and the double well, e.g.,  $\alpha^{-1}(\phi - \phi^3)$ , approaches  $\delta(\phi^2 - 1)$ , i.e.,  $\alpha \rightarrow 0$ . This has not yet been analyzed rigorously but it seems a scaling such as  $\tau = \xi^2$  and  $\alpha = \xi$  would imply this limit. There is an analogy between this limit case and the Ising limit of  $\phi^4$  theory<sup>22,23</sup> for lattice spin systems.

The phase-field model described above may be used to

determine a Gibbs-Thompson-type relationship between the temperature at the phase boundary and other variables. In particular, formal asymptotics have been used to derive<sup>11</sup> the relation

$$\Delta s u = -[\sigma + \sigma'']\kappa - \frac{\tau v}{\xi_A^2} \sigma + O(\xi^2), \quad (7)$$

where  $\sigma$  is now dependent on orientation angle,  $\xi_A$  is a measure of the thickness of the interface which is also dependent on orientation, and  $v$  is the speed of the interface toward the liquid. The relaxation time,  $\tau$ , may depend on orientation without affecting the calculations. The formal asymptotic analysis may be performed for arbitrary dimension. Anisotropy which depends on two or more angles leads to other second derivatives of the surface tension and to a modification of  $\xi_A$  in (7). The  $\sigma''$  term, often called a surface stiffener, generally appears in anisotropic systems (e.g., see Ref. 24 and other references in Ref. 11).

The asymptotics procedure leading to (7) has been proved rigorously under various conditions. In equilibrium, Eq. (6) reduces to Laplace's equation  $\Delta u = 0$ . Hence, the value of  $u$  in the spatial region,  $\Omega$ , is determined entirely by the boundary conditions (either Dirichlet or Neumann). The basic idea involved in the asymptotic analysis is to consider Eq. (5) with the left-hand side set equal to zero and to examine orders of  $\xi$ . The  $O(1)$  solution (e.g., in the isotropic case) is  $\phi_0 = \tanh \frac{1}{2}\rho$ , where  $\rho$  is the variable in the normal direction to the interface divided by  $\xi$ . Subtracting the  $O(1)$  equation

$$\frac{\partial^2 \phi_0}{\partial \rho^2} + \frac{1}{2}(\phi_0 - \phi_0^3) = 0$$

from the full equation results in the remainder problem for  $\phi_1 \equiv \xi^{-1}(\phi - \phi_0)$ :

$$\frac{\partial^2 \phi_1}{\partial \rho^2} + \frac{1}{2}[1 - 3\phi_0^2]\phi_1 = \xi^{-1} \left[ -2u - \xi\kappa \frac{\partial \phi_0}{\partial \rho} \right] + \text{higher order}. \quad (8)$$

Since  $\partial \phi_0 / \partial \rho$  satisfies the homogeneous equation for (8), a solution  $\phi_1$  will exist only if the right-hand side of (8) is orthogonal to the homogeneous solution,  $\partial \phi_0 / \partial \rho$ , i.e.,

$$0 = \int \frac{\partial \phi_0}{\partial \rho} \left[ -2u - \xi\kappa \frac{\partial \phi_0}{\partial \rho} \right] d\rho + \text{higher order}, \quad (9)$$

which leads to (1). Note that  $\Delta s = 4$  and  $\sigma = \frac{2}{3}\xi$  in this model. It is clear from (8) that if  $\kappa$  is  $O(1)$  then  $u$  must be  $O(\xi)$  on the interface. If the gradient of  $u$  is  $O(1)$  then this forces the interface to be close to the curve on which  $u = 0$ . However, if  $u = O(1)$  everywhere (this can be guaranteed by the boundary conditions) then it is possible for the interface to deviate substantially from the curve  $u = 0$ .

The asymptotics is similar in the nonequilibrium and anisotropic cases. The main differences are that the  $\tau\phi_t$  term leads to another term in (9) which is proportional to the velocity, and the anisotropy modifies both the surface tension and the interfacial thickness.

A formal, i.e., nonrigorous argument such as the one presented above is not complete in that a number of mathematical issues are left unresolved. These are the following:

(a) The "matching" of inner and outer solutions by the

usual asymptotic methods does not always lead to the correct solution for nonlinear problems. For linear problems there are general results which indicate that the formal asymptotics will be correct.

(b) In this problem there is an unusual nonlinearity (besides the  $\phi^3$  term) which is implicit in the equations, i.e., the relationship between the temperature and curvature at the interface.

(c) Since the interface itself is not fixed *a priori*, the variation of the interface as  $\xi$  approaches zero creates an additional difficulty.

(d) With an interface which is not fixed, the question of whether there exists a curve whose curvature is given by a particular function must be investigated.

(e) In the nonequilibrium problem the formal analysis is contingent upon the existence of appropriate traveling wave solutions, i.e.,  $(u, \phi)$  in the form  $u(z - vt)$ ,  $\phi(z - vt)$  for a suitable variable  $z$ .

A number of these issues have been resolved in the past few years and some are currently being studied. In particular, the problem raised in (a) was resolved in Ref. 12, and a rigorous proof was presented based on a mathematically fixed boundary. Physically, this means that given a sequence of materials with surface tension (i.e.,  $\frac{2}{3}\xi$ ) approaching zero and having identical phase boundaries, the Gibbs-Thompson condition is necessarily satisfied. The issue raised in (b) is thereby also resolved to some extent in this controlled situation. The problem discussed in (c) has been explicitly considered in Refs. 13 and 17 under spherically symmetric conditions. It was shown that there exist solutions which satisfy the Gibbs-Thompson relation and that any solution must satisfy it. The question of uniqueness is open except in the one-dimensional case where an exact calculation is possible. In two-dimensions the most satisfying resolution of (a)-(d) has been presented in Refs. 18 and 19 without assumptions on symmetry. (See also Ref. 25 for related mathematical problems.) In this case, (d) becomes a nontrivial problem and must be addressed prior to the asymptotic analysis. We prove that there exists a function  $u$  and a curve  $\Gamma$  such that  $\Delta u = 0$  and  $u$  satisfies (1) on  $\Gamma$ . The analysis involves writing the curvature in terms of derivatives of  $\Gamma$  so that (1) itself is a nonlinear differential equation. The conclusion is obtained by considering differential inequalities related to (1), and using theorems from nonlinear analysis. Using this result, we analyze (5) (with  $\phi_t \equiv 0$ ). Constructing solutions to differential inequalities related to (5) we prove there will be three (or more) solutions, with two of them being one-phase solutions and the third a two-phase solution with an interface  $\Gamma$ . The temperature at the interface is then shown to satisfy the Gibbs-Thompson relation.

The issues involved in (c) and (d) may be expressed physically as the extent to which a global problem is approximated by a local analysis. For example, if a particular analysis is performed for a sphere, is it valid near a point on a surface with the same local curvature? For many nonlinear problems this cannot be taken for granted.

In nonequilibrium the role of  $u$  is more complicated, and a plane wave solution with constant velocity is possible only if there exists a solution to the system of equations:

$$-\tau v \phi_x = \xi^2 \phi_{xx} + \frac{1}{2}(\phi - \phi^3) + 2u, \quad (10)$$

$$-v u_x + \frac{1}{2} l v \phi_x = K u_{xx}, \quad (11)$$

subject to appropriate boundary conditions.

These equations are currently being studied with the aim of resolving (e). Under some conditions on the parameters and boundary conditions it appears that there is no solution to (10) and (11). The formal analysis<sup>11</sup> which leads to (7) is contingent on the velocity being locally constant at least to  $O(1)$ . Formally, there is a decoupling between the velocity-related terms. A rigorous analysis is necessary to resolve this problem.

A feature which makes the study of anisotropy difficult is the necessity of retaining higher wave numbers and consequently higher-order differential equations for more detailed anisotropy. Nevertheless, we believe this theory provides a sound basis for understanding the communication between the microscopic and macroscopic levels. This idea is crucial to understanding problems such as the tendency for dendri-

tic growth to occur in the crystallographic directions. One may ask how such regular growth could be the result of instability. The analysis leading to (7) indicates a preference in direction of growth, with or without instabilities. Qualitatively, the interaction between anisotropy and instability may be understood as follows. The growth of a perturbation depends strongly on the surface tension, interfacial thickness, and the extent of supercooling. Since the surface tension and interfacial thickness both depend on orientation,<sup>11</sup> the instabilities are suppressed except in selected directions. Numerical calculations involving anisotropy confirm these expectations.<sup>26</sup> A mathematical analysis of these questions is currently underway.

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- <sup>1</sup>B. Chalmers, *Principles of Solidification* (Krieger, New York, 1977).  
<sup>2</sup>P. Hartman, *Crystal Growth: An Introduction* (North-Holland, Amsterdam, 1973).  
<sup>3</sup>J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).  
<sup>4</sup>D. W. Hoffman and J. W. Cahn, *Surf. Sci.* **31**, 368 (1972).  
<sup>5</sup>J. W. Cahn and D. W. Hoffman, *Acta Metall.* **22**, 1205 (1974).  
<sup>6</sup>W. W. Mullins, *J. Chem. Phys.* **81**, 1436 (1984).  
<sup>7</sup>E. Ben-Jacob, N. Goldenfeld, B. G. Kotliar, and J. S. Langer, *Phys. Rev. Lett.* **53**, 2110 (1984).  
<sup>8</sup>R. Brower, D. Kessler, J. Koplik, and H. Levine, *Phys. Rev. Lett.* **51**, 1111 (1983).  
<sup>9</sup>P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).  
<sup>10</sup>D. Jasnow, *Rep. Prog. Phys.* **47**, 1059 (1984).  
<sup>11</sup>G. Caginalp (unpublished).  
<sup>12</sup>G. Caginalp, *Arch. Ration. Mech. Anal.* **92**, 205 (1986).  
<sup>13</sup>G. Caginalp and S. Hastings (unpublished).  
<sup>14</sup>G. Caginalp, in *Applications of Field Theory to Statistical Mechanics, Proceedings, Sitges, Spain, June 1984*, edited by L. Garrido, Lecture Notes in Physics, Vol. 216 (Springer, Berlin, 1984), p. 216.  
<sup>15</sup>G. Caginalp, in *Problemes à Frontières Libre*, edited by A. Bossavit

- et al.* (Pitman, New York, 1985), p. 107.  
<sup>16</sup>G. Caginalp, in *Lectures in Applied Mathematics*, proceedings of the Nonlinear Problems Conference, Santa Fe, July 1984, edited by B. Nikolaenko (American Mathematical Society, Providence, RI, 1985), Vol. 23, Part 2, p. 347.  
<sup>17</sup>G. Caginalp and B. McLeod, *Quart. App. Math.* (to be published).  
<sup>18</sup>G. Caginalp and P. Fife (unpublished).  
<sup>19</sup>G. Caginalp and P. Fife, in *Nonlinear Parabolic Equations: Qualitative Properties of Solutions, Pitman Research Notes* (Pitman, New York, in press).  
<sup>20</sup>J. T. Lin and G. Fix (unpublished).  
<sup>21</sup>L. I. Rubinstein, *The Stefan Problem*, American Mathematical Society Translations, No. 27 (American Mathematical Society, Providence, RI, 1971).  
<sup>22</sup>G. Caginalp, *Ann. Phys. (N.Y.)* **124**, 189 (1980).  
<sup>23</sup>G. Caginalp, *Ann. Phys. (N.Y.)* **126**, 500 (1980).  
<sup>24</sup>M. P. A. Fisher, D. S. Fisher, and J. D. Weeks, *Phys. Rev. Lett.* **48**, 368 (1982).  
<sup>25</sup>P. C. Fife and W. M. Greenlee, *Russian Math. Surveys* **29**, 103 (1974).  
<sup>26</sup>G. Caginalp and J. T. Lin (unpublished).