

## Conserved-phase field system: Implications for kinetic undercooling

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A model is proposed to study the dynamics of phase boundaries using a conserved order parameter. A relation between the temperature and the curvature, surface tension, and velocity is derived and compared with the analogous system of equations using a nonconserved order parameter. The kinetic-undercooling term is altered, thereby changing the stability properties of an interface.

The statics and dynamics of an interface between two phases has been studied extensively using a Landau-Ginzburg approach (see Refs. 1 and 2 and references contained in Ref. 3) in which  $u$  is the temperature (scaled so that  $u=0$  is the usual melting temperature) and  $\phi$  is a nonconserved order parameter. In their simplest form, the equations can be written as

$$u_t + \frac{l}{2}\phi_t = K\Delta u, \quad (1)$$

$$\tau\phi_t = \xi^2\Delta\phi + \frac{1}{2a}(\phi - \phi^3) + 2u, \quad (2)$$

where  $l$  is the latent heat of fusion,  $K$  is the diffusivity,  $\tau$  is a relaxation time, and  $\xi$  and  $a$  are dimensionless scaled constants which are related to the correlation length. Subject to appropriate initial and boundary conditions, this system has been studied mathematically and an existence and uniqueness theory has been developed.<sup>1</sup> A numerical study, using a convergent scheme,<sup>4</sup> has also been performed. The existence and uniqueness of solutions, in conjunction with the numerical results, provide a perspective for understanding the velocity selection mechanism for dendritic growth. This approach also integrates the microscopic and macroscopic aspects of the problem<sup>5</sup> and can also be used to understand the derivations of various macroscopic interface models from first principles.<sup>6</sup> Additional properties such as anisotropy may be included in the derivation of the model.<sup>3,5</sup>

The issue of the relationship between the temperature at the interface and other variables, particularly the local sum of principal curvatures  $\kappa$  and velocity  $v$  of the interface, has been of interest to physicists and metallurgists for many years.<sup>7-9</sup> With respect to the velocity term,<sup>8</sup> there has not been complete agreement on the power of  $v$  in this relation, and the coefficient is a more difficult question still.

In the model [Eqs. (1) and (2)], the value of the temperature at the interface, which is defined to be the set of points for which  $\phi=0$ , various formal analyses<sup>1-3,5</sup> have led to the relation (for  $a \equiv 1$ )

$$\Delta s u = -\sigma\kappa - \frac{\tau}{\xi^2}\sigma v + O(\xi^2), \quad (3)$$

where  $\Delta s=4$  is the entropy difference between phases. This identity has suitable generalizations in anisotropic situations.<sup>3</sup> In (3), and various analogs, one then has a

calculation of the coefficient of the kinetic undercooling term, i.e.,  $-\tau\sigma/\xi^2$ , which can be related to microscopic and measurable quantities.

In the model which we introduce below, one of the basic aims is to recalculate this coefficient for a system with a conserved order parameter and to examine the differences particularly with respect to the changes in the stability of an interface.

We assume the free energy used to derive (2), i.e.,

$$\mathcal{F}_u\{\phi\} = \int_{\Omega} d^n x \left[ \frac{1}{2}\xi^2(\nabla\phi)^2 + \frac{1}{8a}(\phi^2-1)^2 - 2u\phi \right], \quad (4)$$

where  $\Omega$  is a region in  $\mathbb{R}^n$  and  $(\phi^2-1)^2/8a$  is a prototype double-well potential which may be replaced by any other potential with similar qualitative properties. We note that the free energy in (4) may be derived from the microscopics with anisotropic considerations as in Ref. 5. For simplicity, we assume the material is isotropic. A conserved order parameter  $\phi$  may then be expected to satisfy<sup>10</sup>

$$\tau\phi_t = \xi^2\Delta \left[ \frac{\delta\mathcal{F}}{\delta\phi} \right]. \quad (5)$$

The system of equations describing the interface is then

$$u_t + \frac{1}{2}\phi_t = K\Delta u, \quad (6)$$

$$\tau\phi_t = \xi^2\Delta \left[ \xi^2\Delta\phi + \frac{1}{2a}(\phi - \phi^3) + 2u \right], \quad (7)$$

subject to appropriate initial and boundary conditions. In particular, the boundary conditions must be chosen so that the external boundary on the liquid (or +) side satisfies

$$\phi_{\partial} = \phi_+; \quad u_{\partial} = u_+, \quad (8)$$

where  $\phi_+$  is the largest root of  $(1/2a)(\phi_+ - \phi_+^3) + 2u_+ = 0$ , and analogously, on the solid (or -) side  $\phi_-$  is the smallest root of  $(1/2a)(\phi_- - \phi_-^3) + 2u_- = 0$ . Under normal conditions, one expects an initial profile for  $\phi$  which has a transition-layer behavior such as  $\tanh x/\xi a^{1/2}$ .

In the steady-state situation (i.e., all time derivatives set equal to zero), Eqs. (6) and (7) reduce to

$$0 = \Delta u, \quad (9)$$

$$0 = \Delta \left[ \xi^2\Delta\phi + \frac{1}{2a}(\phi - \phi^3) + 2u \right]. \quad (10)$$

Then  $u$  is determined uniquely by the boundary condition  $u_0$  so that the system is described essentially by Eq. (10). A similar situation had been observed for (1) and (2). In fact, it is clear that any steady-state solution to (1) and (2) must be a solution to (9) and (10). However, (9) and (10) admit other solutions such as (depending on the other boundary conditions)

$$\xi^2 \Delta^2 \phi + \frac{1}{2a} \Delta(\phi - \phi^3) = g, \quad (11)$$

where  $g$  is any harmonic function. In one-dimensional space a solution to (9) and (10) is given by any linear function for  $u$  and any  $\phi$  satisfying

$$\xi^2 \phi_{xxxx} + \frac{1}{2a} (1 - 3\phi^2) \phi_{xx} - \frac{3}{a} \phi \phi_x = 0. \quad (12)$$

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$$-v\tau a^{3/2} \xi^{-1} [\phi(\rho) - \phi_-] = \frac{d}{d\rho} \left[ \frac{d^2 \phi}{d\rho^2} + \frac{1}{2} (\phi - \phi^3) + 2ua \right] (\rho). \quad (14)$$

Defining  $\phi_0(\rho) = \tanh \rho/2$  we note that it solves

$$\frac{d^2 \phi_0}{d\rho^2} + \frac{1}{2} (\phi_0 - \phi_0^3) = 0, \quad (15)$$

while the derivative solves

$$\frac{d^2}{d\rho^2} \phi'_0 + \frac{1}{2} (1 - 3\phi_0^2) \phi'_0 = 0. \quad (16)$$

Assuming an expansion of  $\phi$  of the form  $\phi = \phi_0 + \xi a^{1/2} \phi_1$  one may write the term in brackets in (14) as (with  $\epsilon \equiv \xi a^{1/2}$ )

$$\frac{d^2 \phi}{d\rho^2} + \frac{1}{2} (\phi - \phi^3) + 2ua = \frac{d^2}{d\rho^2} \epsilon \phi_1 + \frac{1}{2} (1 - 3\phi_0^2) \epsilon \phi_1 + 2ua + \text{higher order}. \quad (17)$$

Using (17) and integrating (14) again between  $-\infty$  and  $\rho$ , one has

$$-v\tau a^{3/2} \xi^{-1} \tau \int_{-\infty}^{\rho} [\phi(\tilde{\rho}) - \phi_-] d\tilde{\rho} = \left[ \epsilon \frac{d^2 \phi_1}{d\rho^2} + \frac{1}{2} (1 - 3\phi_0^2) \epsilon \phi_1 + 2ua \right]_{-\infty}^{\rho}. \quad (18)$$

The contribution to the right-hand side from  $-\infty$  is zero. This follows from the fact that the boundary conditions at  $-\infty$  imply

$$\frac{1}{2} [(\phi_0 + \epsilon \phi_1) - (\phi_0 + \epsilon \phi_1)^3] + 2ua = 0 \quad (\text{at } -\infty). \quad (19)$$

By definition one has  $\phi_0(-\infty) = -1$ , so that

$$-\epsilon \phi_1 + 2ua = 0 \quad (\text{at } -\infty). \quad (20)$$

Using (20) and noting that the derivatives of  $\phi$  vanish at  $-\infty$ , one may rewrite (18) in the form

$$\begin{aligned} L\phi_1 &\equiv \epsilon \left[ \frac{\partial^2 \phi_1}{\partial \rho^2} + \frac{1}{2} (1 - 3\phi_0^2) \phi_1 \right] \\ &= -2ua - v\tau a^{3/2} \xi^{-1} \tau \int_{-\infty}^{\rho} [\phi(\tilde{\rho}) - \phi_-] d\tilde{\rho} \\ &\equiv F. \end{aligned} \quad (21)$$

The homogeneous equation  $L\psi = 0$  has a solution  $\phi'_0$  by (16). Thus, a necessary condition for the solvability of (21) is  $(\phi'_0, F) \equiv \int_{-\infty}^{\infty} \phi'_0 F = 0$ . To leading order, then, one

We consider next the dynamical problem and initially make the restriction to one-dimensional space. In particular, we are interested in determining the temperature at the interface of a planar wave moving at constant velocity and comparing the result with (3). Thus, we consider a traveling wave solution of the form  $\phi(x - vt)$  on the real line with  $\phi(\pm\infty) = \phi_{\pm}$ ,  $u(\pm\infty) = u_{\pm}$  such that  $\phi_{\pm}$  satisfies the relations after (8). Using the stretched variable  $\rho \equiv x/\xi a^{1/2}$ , one may rewrite (7) as

$$-v\tau a^{3/2} \xi^{-1} \tau \frac{d\phi}{d\rho} = \frac{d^2}{d\rho^2} \left[ \frac{d^2 \phi}{d\rho^2} + \frac{1}{2} (\phi - \phi^3) + 2ua \right]. \quad (13)$$

After integration of this equation from  $-\infty$  to  $\rho$ , one has

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has the interfacial temperature relation

$$\begin{aligned} 4u &= -(a^{1/2} \xi^{-1} \tau) v \int_{-\infty}^{\infty} \phi'_0(\rho) \int_{-\infty}^{\rho} [\phi_0(\tilde{\rho}) - \phi_-] d\tilde{\rho} \\ &= -(a^{1/2} \xi^{-1} \tau) v \int_{-\infty}^{\infty} (\text{sech}^2 \rho / 2) \ln(e^{\rho} + 1) d\rho. \end{aligned} \quad (22)$$

Equation (22) may be compared with the analogous result from the nonconserved order parameter, i.e., Eqs. (1) and (2). In particular, a similar treatment of (2) results in<sup>1,2</sup>

$$4u = -(a^{-1/2} \xi^{-1} \tau) v \int_{-\infty}^{\infty} (\text{sech}^4 \rho / 2) d\rho. \quad (23)$$

The main difference between (22) and (23), then, is the exponent of the parameter  $a$  which strongly influences the size of the dynamical undercooling term. Within the scaling exhibited in (6) and (7), this term is much less significant since  $a^{1/2} \xi^{-1} \tau \ll a^{-1/2} \xi^{-1} \tau$ . Note that the scaling of (5) in the form

$$\tau \phi_t = \xi^2 a \Delta (\delta \mathcal{F} / \delta \phi) \quad (24)$$

would result in a dynamical undercooling term which is of

the same order as the nonconserved system. The coefficient however would be larger by a factor of about 5.

The size of the coefficient has important implications for the stability of the interface. We defer this discussion until the full interfacial relation and the limiting cases have been obtained.

If the curvature of a moving interface is considered, then a similar analysis leads to the relation on the interface  $\Gamma$ ,

$$\Delta s u = -\frac{2}{3} \xi a^{-1/2} \kappa - c_0 a^{1/2} \xi^{-1} \tau v + \text{higher order},$$

$$c_0 \equiv \int_{-\infty}^{\infty} (\text{sech}^2 \rho / 2) \ln(e^\rho + 1) d\rho. \quad (25)$$

With  $\phi_0(\rho) \equiv \tanh \rho / 2$  as the leading order solution, it is clear formally that (6) approaches the heat equation in both the liquid and solid as  $\xi$  and  $a$  approach zero. The latent heat condition across the interface is also satisfied in an appropriate weak sense. These issues are discussed in the context of nonconservative phase-field equations in Ref. 6.

The particular manner in which  $\xi$ ,  $\tau$ , and  $a$  approach zero determines the precise sharp interface model which is the limit of the conservative phase-field model. Most significantly, if  $\xi a^{1/2}$  is kept constant, then the surface tension and curvature term remains constant as the interfacial thickness vanishes. If  $\xi a^{1/2}$  and  $\xi^{-1} a^{1/2} \tau$  both vanish in the limit, then the classical Stefan limit is attained with the temperature at the interface maintenance at zero. These limits are displayed in Fig. 1.

An alternative limit is obtained by simply taking  $K \rightarrow \infty$  in (6). The system of equations then reduces to the single equation

$$\tau \phi_t = \xi^2 \Delta \left( \xi^2 \Delta \phi + \frac{1}{2a} (\phi - \phi^3) \right), \quad (26)$$

since (6) now implies that  $\Delta u = 0$ . Hence, (26) is the limiting case in which heat diffuses infinitely rapidly, so that temperature becomes an irrelevant (or decoupled) variable. It is clear that, if  $\phi_t = 0$ ,

$$\phi = \pm 1, 0 \text{ or } \phi_0(x; x_0) = \tanh[(x - x_0)/2\xi a^{1/2}], \quad (27)$$

are all solutions to (26) for any value of  $x_0$ . Furthermore, one can obtain solutions essentially by "superposing"

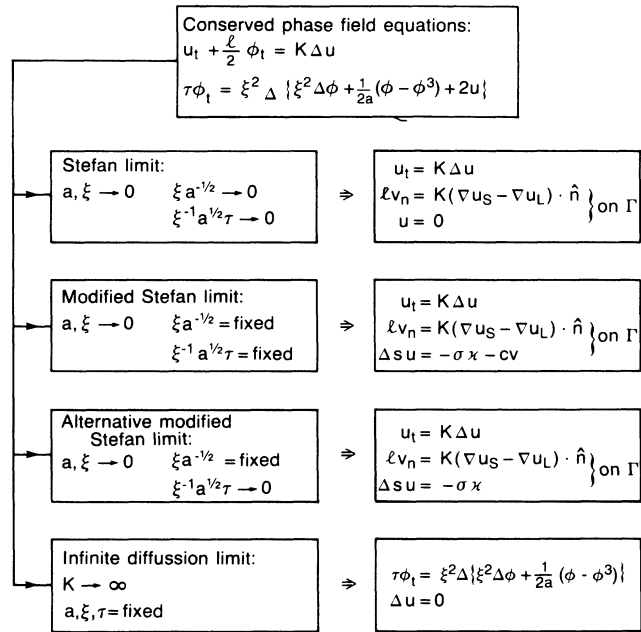


FIG. 1. The sharp interface limits of the conserved phase field equations in various scaling limits, with  $\tau = O(1)$ .

$\phi_0(x; x_0)$ ,  $\phi_0(x; x_1)$ , etc., if  $|x_1 - x_0| \gg \xi a^{1/2}$ . Since  $u$  vanishes in (26), one expects that there will be very little preference between distinct solutions. A recent numerical study of the one-dimensional equation shows metastable states with rapid transitions from one state into another.<sup>11</sup>

We consider now the question of linear stability of a planar interface and make a preliminary comparison of the conserved [(6) and (7)] and nonconserved [(1) and (2)] systems. This comparison is based on proximity to the modified Stefan limit (with kinetic undercooling) and a recent analysis<sup>12</sup> of the stability of a moving planar front. It was observed that the kinetic undercooling term has a stabilizing effect in that a wave mode which is unstable will grow with a smaller exponent. Since both Eqs. (1) and (2) and Eqs. (6) and (7) are close to this model within the appropriate scaling regime, a comparison of the coefficients of the velocity term leads to the expectation that Eqs. (6) and (7) are less stable than Eqs. (1) and (2) in terms of the growth rate.

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