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Interfacial Dynamics for Thermodynamically Consistent Phase–Field Models with Nonconserved Order Parameter *

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Abstract

We study certain approximate solutions of a system of equations formulated in an earlier paper (Physica D **43** 44–62 (1990)) which in dimensionless form are

$$u_t + \gamma w(\phi)_t = \nabla^2 u,$$

$$\alpha\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + F(\phi, u),$$

where u is (dimensionless) temperature, ϕ is an order parameter, $w(\phi)$ is the temperature–independent part of the energy density, and F involves the ϕ–derivative of the free-energy density. The constants α and γ are of order 1 or smaller, whereas ϵ could be as small as 10^{-8}. Assuming that a solution has two single–phase regions separated by a moving phase boundary $\Gamma(t)$, we obtain the differential equations and boundary conditions satisfied by the 'outer' solution valid in the sense of formal asymptotics away from Γ and the 'inner' solution valid close to Γ. Both first and second order transitions are treated. In the former case, the 'outer' solution obeys a free boundary problem for the heat equations with a Stefan–like condition expressing conservation of energy at the interface and another condition relating the velocity of the interface to its curvature, the surface tension and the local temperature. There are $O(\epsilon)$ effects not present in the standard phase–field model, e.g. a correction to the Stefan condition due to stretching of the interface. For second–order transitions, the main new effect is a term proportional to the temperature gradient in the equation for the interfacial velocity. This effect is related to the dependence of surface tension on temperature.

We also consider some cases in which the temperature u is very small, and possibly γ or α as well; these lead to further free boundary problems,

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which have already been noted for the standard phase–field model, but which are now given a different interpretation and derivation.

Finally, we consider two cases going beyond the formulation in the above equations. In one, the thermal conductivity is enhanced (to order $O(\epsilon^{-1})$) within the interface, leading to an extra term in the Stefan condition proportional (in two dimensions) to the second derivative of curvature with respect to arc length. In the other, the order parameter has m components, leading naturally to anisotropies in the interface conditions.

1 Introduction

In [PF1], the authors gave a thermodynamically consistent formalism for developing models of phase–field type for phase transitions in which the only two field variables are temperature and an order parameter. The present paper develops in some detail the laws governing the motion of phase interfaces which are implied by these models and their generalizations, in the case of both first and second order phase transitions. (The latter are defined here to be those transitions in which the internal energy is the same in the two phases at constant temperature.) These laws are obtained by a formal reduction of the models in [PF1] to free boundary problems. Such a reduction is obtained by the use of systematic formal asymptotics based on the smallness of a parameter ϵ, a dimensionless surface tension. (This identification of ϵ is shown in (24) and Sec. 12, although its definition comes, via the coefficient κ_1 in (3), from the gradient term in a postulated entropy functional introduced in [PF1].) This was the procedure first followed in [CF] for the traditional phase field equations. We consider only models in which the density is constant and the order parameter is not a conserved quantity.

Within these restrictions, our treatment here is in many respects more complete and general than that given in [CF], [C1], [WS] and in other papers. For example, in allowing the thermal diffusivity D to depend on the order parameter, we may include the case when this diffusivity is enhanced within the interfacial region; the interface condition expressing energy balance then includes an extra term involving (in two dimensions) the second derivative of the curvature with respect to arc length along the interface and representing lateral diffusion within that region.

We also explore other implications of the dependence of both D and the heat capacity c on the order parameter, and generalize the procedure to the case when there are several order parameters. This latter case is frequently encountered in modeling phase transitions, and leads naturally to anisotropies in the interface conditions. It leads to some interesting mathematical problems involved with finding a heteroclinic orbit for a special kind of Hamiltonian system.

The contrasting nature of phase interfaces for first and second order transitions is brought out. In the latter case, we derive a forced motion-by-curvature problem.

The conditions leading to a free boundary problem of Mullins–Sekerka type are elucidated and contrasted with those usually postulated within the framework of the traditional phase field model. In particular, the time evolution from Stefan–type motion into Mullins–Sekerka motion is discussed (Sec. 14).

The relation between the interface thickness, the surface tension, and the Gibbs–Thompson law, is discussed, and our viewpoint corroborated by known physical data.

Finally, the asymptotic procedure here used is developed and discussed with great care, and certain first order terms in the interface conditions are derived here for the first time.

The phase field models developed in [PF1] were based on certain postulated forms for the internal energy, free energy, and entropy of the system. These are made precise in Sec. 3 of this paper. Other assumptions, of a mathematical nature, are made in the paper, particularly in Sec. 5. These latter are assumptions about the nature of the layered solutions we are investigating, and are made in order to carry out a matched asymptotic expansion. Assumptions of this type are in fact nearly always made in formal asymptotic treatments of applied problems, but are rarely made explicit. We strive to spell them out completely.

There has been good progress in rigorous justification of the type of formal asymptotics used here, which means proving the existence of solutions for which our assumptions hold. See [CC], [St], [St2] for such a justification in the case of the traditional phase field model. (Such progress has been even more impressive in the case of the Allen-Cahn and Cahn-Hilliard models.)

Other thermodynamically consistent models have been developed in recent years; see [T], [UR], [AP1], [AP2], [WS], and the references given there (note also [K], described from a thermodynamically consistent point of view in [WS]). In many cases they are more complicated than ours, due to the inclusion of effects such as variable density.

2 The main ideas and results

As in [PF1] we start from a Helmholtz free energy function of the form

$$f(\phi, T) = \bar{w}(\phi) - T\bar{s}_0(\phi) - cT\log T,$$

where ϕ is the order parameter, T the absolute temperature, $\bar{w}(\phi)$ and $\bar{s}_0$ are the temperature-independent parts of the energy density and entropy density, and c is the heat capacity at constant ϕ, which for the time being we take to be constant. The internal energy is then

$$\bar{e}(\phi, T) = \frac{\partial(f/T)}{\partial(1/T)} = \bar{w}(\phi) + cT \tag{1}$$

and the kinetic equations, (3.8) and (3.6) of [PF1], can be written in the form of the following equations, the main object of study in this paper:

$$cT_{\bar{t}} + \bar{w}(\phi)_{\bar{t}} = \nabla \cdot D(\phi, T)\nabla T, \tag{2}$$

$$\kappa_0(\phi, T)\phi_{\bar{t}} = \kappa_1 \nabla^2 \phi - \frac{1}{T}\frac{\partial f(\phi, T)}{\partial \phi}. \tag{3}$$

Here $\bar{x} \in R^2$ or R^3 and $\bar{t} \in R$ are space and time variables, ∇ denotes vector differentiation with respect to $\bar{x}$, D is the heat conduction coefficient, κ_1 measures the contribution to the entropy and free energy made by gradients in ϕ, and κ_0 is a relaxation time for ϕ. (The coefficient κ_0 is called K_1^{-1} in [PF1].) Note that $\bar{w}$ and f are related to $\bar{s}_0(\phi)$:

$$-\frac{1}{T}\frac{\partial}{\partial \phi} f(\phi, T) = \bar{s}_0'(\phi) - \frac{1}{T}\bar{w}'(\phi). \tag{4}$$

where the primes indicate differentiation. In Sec. 18, the order parameter ϕ is generalized to have several components, in which case (3) becomes a vector equation, κ_0 becomes a matrix, the first term on the right of (3) becomes a more general second order operator, and the last term becomes $-\frac{1}{T}\nabla_\phi f(\phi, T)$.

As in [PF1], the function $\bar{w}$ will be postulated to be concave (in fact, quadratic), and at fixed T the function of ϕ on the left of (4) has the form of a "seat function" of ϕ with three zeros, at values $\phi = h_-(T), h_0(T)$, and $h_+(T)$ (see Figure 1). Fig. 1(a) illustrates the possibility (used in [WS]), that one or more of these functions 'h' may be constants. Moreover, we postulate the existence of a temperature T_0 (the melting temperature if the transition is of first order) such that $f(h_-(T_0), T_0) = f(h_+(T_0), T_0)$. More specific assumptions on our functions are given in Section 3.

As indicated in [PF1] and (especially) in [PF3], the traditional phase–field model of Langer [L] and Caginalp, in which $\bar{w}$ is linear, can be put into this general framework, but corresponds to cases where $s_0(\phi)$ is a nonconcave function.

The special case of (2), (3) studied in [PF3] for purposes of illustration is revisited here in Section 4. In that section, we relate our parameters to various physical constants in order to gauge their orders of magnitude. In this same vein, we relate the interface thickness ϵ to the surface tension σ. (The parameter ϵ is defined below in Section 3, in terms of κ_0 and κ_1.)

If the parameters κ_0 and κ_1 in (3) are small, in the sense to be explained below in Section 3, then solutions can be constructed (in the manner of formal asymptotics) which depict spatial configurations of two distinct phases. More precisely, at any instant of time, space is divided into regions $\mathcal{D}_+$ and $\mathcal{D}_-$, with a thin mobile layer separating them. In many typical cases, the order parameter ϕ is approximately a constant, say $\phi_\pm$, in $\mathcal{D}_\pm$. In the thin layer between $\mathcal{D}_+$ and $\mathcal{D}_-$, ϕ makes a transition from near ϕ_- to near ϕ_+.

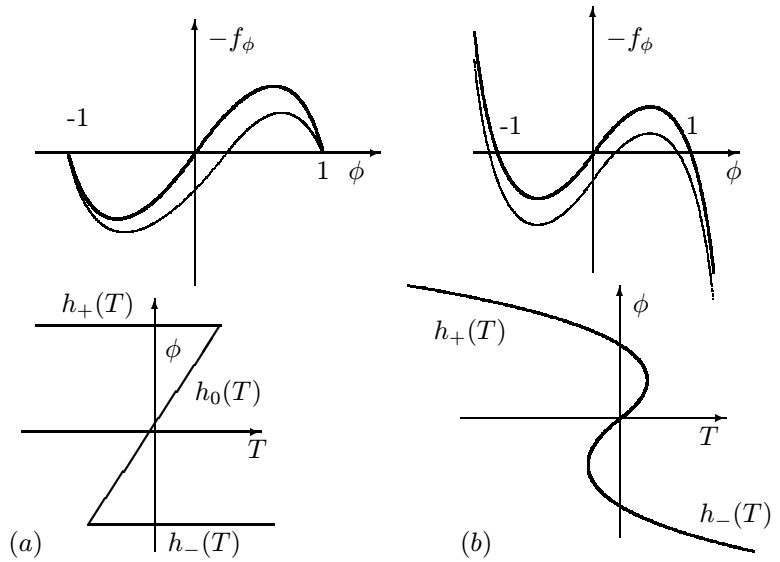

Figure 1: Two possible functions $-f_\phi(\phi, T)$ plotted for $T = T_0$ (thick) and $T > T_0$ (thin), and their null sets (with the functions $h_i(T)$) :
(a) $-f_\phi(\phi, T) = (\phi^2 - 1)(\phi_c(T - T_0) - \phi)$
(b) $-f_\phi(\phi, T) = \phi(1 - \phi^2) - T + T_0$

Our purpose is to study these layered solutions in detail. Our focus is on all solutions of this type, rather than on solutions satisfying specific boundary or initial conditions.

We are mainly concerned with first-order phase transitions. A matched asymptotic analysis for this case is given in Sections 5 – 12. Only the two-dimensional case is considered, but the method is easily extended to three dimensions. Our analysis relies on the smallness of ϵ, a parameter (actually a dimensionless surface tension) related to κ_1 which will be given later. We assume that the dimensionless width of the layers is $O(\epsilon)$) and that their internal structure scales with ϵ in a way to be defined more carefully in Sec. 5. Under these assumptions, the analysis allows one to deduce further information of a detailed nature about the layered solutions. For example, it provides approximate information about how the interphase regions move. It is this property of engendering further information which lends the assumption its credibility.

The result of the analysis is that the layered solutions can be formally approximated at the macroscopic level by the solution of a free boundary problem, the interphase layer being approximated by a sharp interface. The free boundary problem, set out in Section 11, consists of heat equations in each of the two single-phase domains, coupled through their common domain boundary (the interface) by means of two specific relations. One of them is a Stefan–like

condition, and the other is a condition relating the temperature there to the velocity, curvature, and surface tension . These approximations, valid away from the layer, are supplemented by fine structure approximations, valid in the vicinity of the layer, which give information about the phase and temperature profiles within the interphase region.

The analysis reveals some new effects: (a) to order ϵ, the temperature may be discontinuous at the interface; (b) the effect of interface stretching is accounted for by an extra term in the Stefan condition; and (c) there is in general a small extra normal derivative term as well as a curvature term in the other interface condition.

In Section 13, we consider the analogous question of phase boundary motion in the case of second order phase transitions. The previous development is easily adapted to this case, but the results are strikingly different. The model considered by Allen and Cahn [AC] is a particular case.

The basic free boundary problem obtained in Section 11 has many particular limiting cases when certain order of magnitude assumptions are made on the parameters of the problem; a few of these possibilities are explored in Sections 14 and 15. As opposed to previous derivations of similar limiting cases, we show that the various alternative free boundary problems obtained in [CF] and [C2] as formal approximations for small ϵ when certain parameters are taken to depend on ϵ, appear here as corollaries of our basic results. The same is true for the classic motion–by–curvature problem. Thus one general analysis does it all. In the case of curvature–driven free boundary problems of various kinds, we elucidate in Section 15 the physical conditions under which they are valid approximations. These conditions are distinctly different from those which have been suggested in the past, and are motivated by thermodynamic considerations.

In Section 16, the implications of allowing the coefficients to depend on ϕ and T are explored. Section 17 is devoted to the interesting case, not considered before, when the thermal diffusivity is enhanced within the interphase zone. Again, the analysis in Sections 5 – 12 can be adapted. The most significant new feature is the appearance, in the Stefan interface condition, of an extra term representing diffusion within the zone. This term involves the second tangential derivative (or, in three dimensions, the surface Laplacian) of the curvature of the interface. An analogous result has been derived by Cahn, Elliott, and Novick–Cohen [CEN], in the case of Cahn–Hilliard type equations. They show that enhanced mobility within the interfacial zone results in a limiting free boundary problem in which the motion is driven by the Laplacian of the curvature. See [CT] for a materials scientific theory of a class of surface motions depending on the Laplacian of curvature.

In Section 18 the generalization, important in some applications, is made to multi-component order parameters. As we shall see, this provides a possible basis for treating the motion of anisotropic interfaces. Free boundary problems of the same general type as before are obtained, but the coefficients of the curvature and velocity in the free boundary conditions are more complicated.

A systematic matched asymptotic analysis of moving layer problems of this sort was first carried out in [CF]; see also [C2] and [F2]. Similar problems were treated using related techniques in [P] and in [RSK]. To an extent, our conclusions are analogous to those in [CF] and [C2], but there are many important differences, as was mentioned above.

3 The basic model and hypotheses for first order phase transitions; nondimensionalization.

The models considered here consist of field equations (2), (3) for a temperature function $T(\bar{x},\bar{t})$ and an order parameter function $\phi(\bar{x},\bar{t})$. In the main part of the paper we shall assume that c, κ_0, and D are positive constants, and that ϕ is a scalar function. Some assumptions about the function f will also be needed. These depend somewhat on whether the phase transition is of first or second order. We begin with the case of a first order transition (sections 5–12), for which the assumptions are set out below. Second order transitions are treated in Sec. 13.

A1. $f(\phi,T)$ is twice continuously differentiable in both variables. Considered as a function of ϕ at fixed T for any T in some interval $T_- < T < T_+$, $f(\phi,T)$ has two local minima $\phi = h_-(T)$ and $\phi = h_+(T)$, which we order so that

$$h_-(T) < h_+(T).$$

It also has a single intermediate local maximum at $\phi = h_0(T) \in (h_-(T), h_+(T))$.

Thus $-f_\phi$ typically has one of the forms shown in Figure 1. The two numbers $h_-(T)$ and $h_+(T)$ are the values of ϕ for which uniform phases can exist at temperature T. In general these two minima correspond to different values of the free energy. If that is the case, one of the phases is stable and the other is metastable, so that they cannot coexist at equilibrium. Only if they correspond to the same free energy density,

$$f(h_-(T),T) = f(h_+(T),T), \tag{5}$$

can the two phases coexist at equilibrium.

Our second assumption (which holds only for first order transitions) will be that phase equilibrium is possible only at a single temperature T_0 (the melting temperature, in the case of solid–liquid transitions):

A2. Equation (5) is satisfied if and only if $T = T_0 \in (T_-, T_+)$.

Our third assumption strengthens the local minimum condition on $f(\phi,T)$ at $\phi = h_\pm(T)$ in A1, to

A3.

$$\frac{\partial^2 f}{\partial \phi^2}(h_\pm(T), T) > 0. \tag{6}$$

Our fourth assumption concerns the latent heat. To write it simply, we denote $\phi_\pm = h_\pm(T_0)$; $\phi_c = h_0(T_0)$. Since we are considering the case of a first order phase transition, the energies of the two phases are different : $w(\phi_+) \neq w(\phi_-)$. The more ordered phase (with the order parameter ϕ near ϕ_+) will have the lower energy, and so the latent heat is

$$\bar{\ell} = \bar{w}(\phi_-) - \bar{w}(\phi_+), \tag{7}$$

satisfying

A4.

$$\bar{\ell} > 0. \tag{8}$$

In view of (1) and (7), A4 is equivalent to the condition

$$\frac{\partial}{\partial T} \int_{\phi_-}^{\phi_+} \frac{\partial f(\phi, T)/\partial \phi}{T} d\phi > 0 \quad \text{at} \quad T = T_0.$$

Using A2, we see that this is equivalent to

$$\frac{d}{dT} \left[f(h_-(T), T) - f(h_+(T), T) \right] |_{T=T_0} > 0, \tag{9}$$

so that if (5) holds for $T = T_0$, it cannot hold for $T \neq T_0$, and hence A4 implies the "only if" part of A2.

It will be convenient to recast our equations (2), (3) in dimensionless form. Recall that $\bar{x}$ and $\bar{t}$ are physical variables. We define dimensionless space and time by

$$x = \bar{x}/L; \quad t = \bar{t}D/cL^2. \tag{10}$$

where L is a characteristic macrolength for our system. For example, we may choose it to be he diameter of the spatial domain of definition of our functions ϕ and T or the minimum radius of curvature of the initial interface, defined to be the curve $\{\phi = \phi_c\}$. Each term of Equation (2) has the dimensions of energy density per unit time, and the terms in (3) have dimensions of energy density per unit temperature. We divide (2) by $\frac{DT_0}{L^2}$ and (3) by c, to make each term dimensionless.

To simplify the notation further, we use a new temperature variable $u = \frac{T}{T_0} - 1$, where T_0 is given in A2 above, and define

$$\begin{aligned} w(\phi) &\equiv \tfrac{\bar{w}(\phi)}{\gamma c T_0}, \quad \ell \equiv \tfrac{\bar{\ell}}{\gamma c T_0}, \\ F(\phi, u) &= -\tfrac{1}{\gamma c T(u)} \tfrac{\partial}{\partial \phi} f(\phi, T(u)), \end{aligned} \tag{11}$$

where γ is a dimensionless parameter chosen so that

$$\frac{\partial F}{\partial \phi}(\phi_c, 0) = 1. \tag{12}$$

(We are assuming that $\phi_+ - \phi_-$ is of order 1.) This is our method of normalizing the seat function F. But we have also incorporated γ into the definitions of the dimensionless w and ℓ above; this is natural since f, $\bar{w}$ and $\bar{\ell}$ are related by (1), (4), and (7) and constitute an important point of departure from previous phase-field models (see Sec. 15). The use of γ allows us to obtain approximate but simpler forms of the laws of interfacial motion when γ is small (Sec. 14).

Clearly, (7) continues to hold with the overbars removed. Since $\bar{w}$ and w are only defined up to an arbitrary additive constant, we are free to choose that constant so that

$$w_\pm \equiv w(\phi_\pm) = \mp \frac{\ell}{2}. \tag{13}$$

With these representations, (2) and (3) become

$$u_t + \gamma w(\phi)_t = \nabla^2 u, \tag{14}$$

$$\alpha \epsilon^2 \phi_t = \epsilon^2 \nabla^2 \phi + F(\phi, u), \tag{15}$$

where ∇ now denotes differentiation with respect to x and we have set $\epsilon^2 = \kappa_1 / L^2 \gamma c$ and $\alpha = \kappa_0 D / \kappa_1 c$. We expect α to be $O(1)$ but, as we shall see in Sec. 4 , ϵ^2 is typically very small. Equations (14) and (15) form the basis of the remainder of the paper.

Our assumptions A1 – A4 can now be reexpressed in terms of the new notation:

Equivalent of A1: For each small enough u, the function $F(\phi, u)$ is bistable in ϕ; that is, it has the form of a seat function of ϕ, as exemplified by the graphs in Fig. 1. (Again, we denote the outer zeros of F by $h_\pm(u)$.)

Equivalent of A2:

$$\int_{h_-(u)}^{h_+(u)} F(\phi, u) d\phi = 0 \quad \text{if and only if} \quad u = 0. \tag{16}$$

Equivalent of A3:

$$\frac{\partial F}{\partial \phi}(h_{\pm}(u), u) < 0. \tag{17}$$

It follows from (1), (5), (7), and (11) that

$$\ell = -\int_{\phi_-}^{\phi_+} F_u(\phi, 0) d\phi. \tag{18}$$

We therefore have:

Equivalent of A4:

$$\frac{d}{du} \int_{h_-(u)}^{h_+(u)} F(\phi, u) d\phi < 0 \quad \text{when} \quad u = 0. \tag{19}$$

Again, note the relation between this and the "only if" part of (16).

As a first consequence of these assumptions, we note the fact, which is guaranteed (see [F1] and its references, for instance) by (16) and (17), that the boundary value problem

$$\psi'' + F(\psi, 0) = 0, \quad z \in (-\infty, \infty); \quad \psi(\pm\infty) = \phi_{\pm}, \quad \psi(0) = \phi_c. \tag{20}$$

has a unique solution $\psi(z)$. Changing the integration variable in (19) from ϕ to z by the relation $\phi = \psi(z)$, we see that (19), and hence A4, is in turn equivalent to

$$\int_{-\infty}^{\infty} F_u(\psi(z), 0) \psi'(z) dz < 0. \tag{21}$$

4 Example; numerical values for the parameters.

A simple free energy function modeling liquid–solid phase transitions was considered in the appendix of [PF3]. In dimensional form, it is

$$f = f_0 \left[\frac{T}{4T_0}(\phi^2 - 1)^2 + \left(\frac{T}{T_0} - 1 \right) a(\phi + 1)^2 \right] + cT \log \frac{T}{T_0}, \tag{22}$$

$$\bar{w}(\phi) = -f_0 a(\phi + 1)^2,$$

where f_0 is a parameter with dimensions of energy density, and a is dimensionless.

To relate some of the constants in (22) to measurable quantities we note first that, by (7), the latent heat is

$$\bar{\ell} = \bar{w}(-1) - \bar{w}(1) = 4af_0.$$

Another measurable quantity giving information about the parameters of the model is the surface tension $\bar{\sigma}$. It is equal to the excess free energy per unit area in a plane interface, which for $T = T_0$ is ([CA])

$$\bar{\sigma} = \int_{-\infty}^{\infty} \left[f(\psi(\bar{r}/\epsilon), T_0) + \frac{1}{2}\kappa_1 T_0 \left(\frac{d\psi}{d\bar{r}} \right)^2 \right] d\bar{r}. \tag{23}$$

According to (22), the function $F(\phi, 0)$ is $-\frac{f_0}{\gamma c T_0}\phi(\phi^2 - 1)$, so that the definition (12) of γ gives $F_\phi(0,0) = \frac{f_0}{\gamma c T_0} = 1$ and

$$f_0 = \gamma c T_0.$$

Since now $F(\phi, 0) = -\phi(\phi^2 - 1)$, we have from (20)

$$\psi(z) = \tanh \frac{z}{\sqrt{2}}.$$

Using the relations $z = r/\epsilon = \bar{r}/\epsilon L$, $\phi(\bar{r}) = \psi(z) = \tanh(z/\sqrt{2})$, and $f(\phi, T_0) = \frac{1}{4}f_0(\phi^2 - 1)^2 = \frac{1}{4}f_0 \mathrm{sech}^4(z/\sqrt{2})$, we can simplify (23) to

$$\begin{aligned} \bar{\sigma} &= \epsilon L \textstyle\int_{-\infty}^{\infty} \left[\frac{1}{4} f_0 \mathrm{sech}^4 \left(\frac{z}{\sqrt{2}} \right) + \frac{\kappa_1 T_0}{4\epsilon^2 L^2} \mathrm{sech}^4 \left(\frac{z}{\sqrt{2}} \right) \right] dz \\ &= \epsilon L \gamma c T_0 \tfrac{2\sqrt{2}}{3} \quad \text{since} \quad f_0 = \gamma c T_0 \quad \text{and} \quad \epsilon^2 = \tfrac{\kappa_1}{\gamma c L^2}. \end{aligned} \tag{24}$$

Therefore we can think of the product $\epsilon\gamma$ as a measure for the magnitude of the surface tension.

The surface tension at a solid–liquid interface can be deduced from the value of the Gibbs–Thompson coefficient

$$G = \frac{\bar{\sigma} T_0}{\bar{\ell}} = \frac{\bar{\sigma} T_0}{4af_0}.$$

From (24) and this we obtain for the width of the interface

$$\epsilon L = \frac{3\bar{\sigma}}{2\sqrt{2}\gamma c T_0} = \frac{3\sqrt{2}aG}{T_0}.$$

The value of a can be estimated as follows: first, if the entropy is to be a concave function of ϕ, then, as shown in [PF3], we must have $a > \frac{1}{2}$; secondly, if the liquid can be supercooled to a temperature T_- then f must have a local minimum at $\phi = -1$ when $T = T_-$, which with (22) implies $T_-/T_0 > a/(1+a)$ i.e. $a < T_-/(T_0 - T_-)$. For example in the case of the ice-water transition we might take $T_0 = 273$K, $T_- = 233$K, giving $a < 5.8$. We shall take the value $a = 1$ to be typical.

Typical values of G and T_0 are 10^{-5} cm-deg and 300K, respectively. Using them, we obtain

$$\epsilon L \approx 1.5 \times 10^{-7} \text{ cm},$$

which is of the order of a few lattice spacings of an ice crystal, a not unreasonable interface thickness. If L equals, say, 10 cm., then ϵ is less than 10^{-7} and the approximations to be developed in this paper should be very accurate.

5 The approximation scheme.

Our procedure is based on assumptions which have been used implicitly in various earlier studies of similar problems ([CF], [RSK], [P], etc.) and have been rigorously justified, under certain conditions, in the analogous cases of the Cahn–Allen equations [MSc], [Chen1] and the Cahn–Hilliard equation [ABC]. We spell them out completely. Their plausibility rests in large part on the fact that they lead to a succession of reasonable formal approximations. For simplicity we consider only the two dimensional case.

The core assumption is that there exist families of solutions $(u(x,t;\epsilon), \phi(x,t;\epsilon))$ of (14), (15), defined for all small $\epsilon > 0$, all x in a domain $\mathcal{D} \subset R^2$, and all t in an interval $[0, t_1]$, with "internal layers." This concept is defined precisely in the form of assumptions $(a) - (e)$ below, as follows.

For such a family, we assume that, for all small $\epsilon \geq 0$, the domain $\mathcal{D}$ can at each time t be divided into two open regions $\mathcal{D}_+(t;\epsilon)$ and $\mathcal{D}_-(t;\epsilon)$, with a curve $\Gamma(t;\epsilon)$ separating them. This curve does not intersect $\partial\mathcal{D}$. It is smooth, and depends smoothly on t and ϵ. In particular, its curvature and its velocity are bounded independently of ϵ. These regions are related to the family of solutions as follows.

(a) Let Ω be any open set of points (x,t) in $\mathcal{D} \times [0,t_1]$ such that $\text{dist}(x, \Gamma(t;0))$ is bounded away from 0. Then for some $\epsilon_0 > 0$, u can, we assume, be extended to be a smooth (say, three times differentiable) function of the three variables x, t, and ϵ uniformly for $0 \leq \epsilon < \epsilon_0$, (x,t) in Ω. The same is assumed true of $\phi(x,t;\epsilon)$.

It follows in particular that the functions $u_k(x,t) \equiv \frac{1}{k!}\partial_\epsilon^k u|_{\epsilon=0}$, $k = 0,1,2,3$, are defined in all of $\mathcal{D} \setminus \Gamma(t;0)$. A similar statement holds for $\partial_\epsilon^k \phi|_{\epsilon=0}$.

It also follows from (15) that for (x,t) in any region Ω as described above, $F(\phi,u) = O(\epsilon^2)$. This implies, by the definition of $h_\pm$, that ϕ is close either to $h_+(u)$ or $h_-(u)$. (The third possibility would be ϕ near $h_0(u)$; but in view of the instability of this constant solution of (15) (for fixed u), we assume there are no extended regions where ϕ is close to this value.)

(b) For Ω in $\mathcal{D}_\pm(t;0) \times [0,t_1]$, we assume that ϕ is close to $h_\pm(u)$. Our interpretation is that the material where ϕ is close to $h_-(u)$ is in "phase I" (the less ordered phase, since $\phi_- < \phi_+$) and that where ϕ is near h_+ is in phase II, the more ordered phase.

Much of our analysis will refer to a local orthogonal spatial coordinate system (r, s) depending parametrically on t and ϵ, defined in a neighborhood of $\Gamma(t;\epsilon)$, which we define precisely as the set where $\phi = \phi_c$. We define $r(x,t;\epsilon)$ to be the signed distance from x to $\Gamma(t;\epsilon)$, positive on the $\mathcal{D}_+$ side of $\Gamma(t;\epsilon)$. Then for small enough δ, in a neighborhood

$$\mathcal{N}(t;\epsilon) = \{x : r(x,t;\epsilon) < \delta\},$$

we can define an orthogonal curvilinear coordinate system (r, s) in $\mathcal{N}$, where $s(x,t;\epsilon)$ is defined so that when $x \in \Gamma(t;\epsilon)$, $s(x,t;\epsilon)$ is the arc length along $\Gamma(t;\epsilon)$ to x from some point $x_1(t;\epsilon) \in \Gamma(t;\epsilon)$ (which always moves normal to Γ as t varies).

Transforming u and ϕ to such a coordinate system, we obtain the functions

$$\hat{u}(r,s,t;\epsilon) = u(x,t;\epsilon), \quad \hat{\phi}(r,s,t;\epsilon) = \phi(x,t;\epsilon).$$

Let $\hat{u}_k(r,s,t)$, $\hat{\phi}_k(r,s,t)$ be defined in the same way as u_k and ϕ_k above, in terms of derivatives at $\epsilon = 0$. They exist, by virtue of (a) above.

(c) For each $t \in [0, t_1]$, we assume that the ϵ-derivatives u_k, $k \le 3$, restricted to the open domain $\mathcal{D} \cap \{r > 0\}$, can be extended to be smooth functions on the closure $\bar{\mathcal{D}} \cap \{r \ge 0\}$ (on Γ, they no longer signify the derivatives indicated above). Similarly, we assume that the restrictions to $\mathcal{D} \cap \{r < 0\}$ can be extended to be smooth functions on $\bar{\mathcal{D}} \cap \{r \le 0\}$ and that the analogous statements are true of the ϵ-derivatives of ϕ.

(d) Let $z = r/\epsilon$, and let $U(z,s,t;\epsilon) = \hat{u}(r,s,t;\epsilon)$ in the neighborhood of Γ introduced above. Then for any positive ϵ_0 and z_0, we assume that $U(z,s,t;\epsilon)$ can be extended to be a smooth function of the variables $(z,s,t;\epsilon)$, uniformly for $0 \le \epsilon < \epsilon_0$, $|z| < z_0$, $0 \le t \le t_1$, all s. The analogous statements for $\hat{\phi}$ in place of $\hat{u}$ are also assumed to hold.

It follows that the functions $U_k(z,s,t) = \frac{1}{k!}\partial_\epsilon^k U(z,s,t;\epsilon)|_{\epsilon=0}$ are well defined.

We now have that for any $r_0 > 0$, $z_0 > 0$, the Taylor series approximations

$$u(x,t;\epsilon) = u_0(x,t) + \epsilon u_1(x,t) + o(\epsilon), \tag{25a}$$

$$\hat{u}(r,s,t;\epsilon) = \hat{u}_0(x,t) + \epsilon \hat{u}_1(x,t) + o(\epsilon), \tag{25b}$$

$$U(z,s,t;\epsilon) = U_0(z,s,t) + \epsilon U_1(z,s,t) + o(\epsilon), \tag{25c}$$

together with their differentiated versions, are valid for all sufficiently small ϵ : in the case of (25a,b), uniformly for $\mathrm{dist}(x, \Gamma(t;0)) > r_0 > 0$ and in the case of (25c), for $\mathrm{dist}(x, \Gamma(t;\epsilon)) < \epsilon z_0$. Similar statements hold for ϕ, $\hat{\phi}$, Φ. Truncated series as in (25a) and (25b) will constitute our 'outer' approximation; ones like those in (25c) will constitute the 'inner' approximation.

(e) The approximations in (25b,c) above are assumed to hold simultaneously in a suitable region: for some $0 < \nu < 1$, we assume that (25b) holds for

$$\text{dist}(x, \Gamma(t;\epsilon) > \epsilon^{\nu},$$

and (25c) holds for

$$\text{dist}(x, \Gamma(t;\epsilon) < 2\epsilon^{\nu}.$$

Differential equations for the functions u_k, ϕ_k, etc. can be obtained by substituting (25a) and its analog into (14) and (15) and equating coefficients of powers of ϵ. For this purpose, the only conclusion from (15) which will be needed is the relation

$$F(\phi, u) = 0(\epsilon^2), \tag{26}$$

which provides algebraic equations relating u_k and ϕ_k, $k \leq 1$. For example,

$$\phi_0 = h_{\pm}(u_0) \text{ in } \mathcal{D}_{\pm}. \tag{27}$$

In the same way, we get from (14) that

$$\begin{aligned} &\partial_t e_0 = \nabla^2 u_0 \text{ in } \mathcal{D}_{\pm}, \\ &e_0 = u_0 + \gamma w(\phi_0). \end{aligned} \tag{28}$$

Our object will be to find free boundary problems satisfied by the outer functions u_k, ϕ_k. For this, we need not only differential equations and algebraic relations such as (27) and (28) holding in $\mathcal{D}_{\pm}$, but also extra conditions on Γ. These extra conditions will be obtained by finding the inner functions U_k, Φ_k and using assumption (e) to obtain matching conditions relating them to the outer functions u, ϕ. And to find these inner functions, we shall in turn need to relate the surface $\Gamma(t;\epsilon)$ to the family ϕ precisely and to specify a curvilinear coordinate system near Γ. This will be done in the next section.

6 The r, s and z, s coordinate systems; matching relations.

Recall that our definition of Γ will be the level surface

$$\Gamma(t;\epsilon) = \{x : \phi(x, t;\epsilon) = \phi_c\}, \tag{29}$$

and the (r, s) coordinate system is attached to Γ.

To go from Cartesian to (r, s) coordinates we transform derivatives as follows:

$$\begin{aligned} &\partial_t \ \text{ is replaced by } \ \partial_t + r_t\partial_r + s_t\partial_s; \\ &\nabla^2 \ \text{ is replaced by } \ \partial_{rr} + |\nabla s|^2\partial_{ss} + \nabla^2 r\partial_r + \nabla^2 s\partial_s. \end{aligned} \tag{30}$$

Here, we have used the fact that $|\nabla r| \equiv 1$.

The derivatives of r and s in these expressions can be written in terms of kinematic and geometric properties of the interface Γ. The details of the calculation are given in the Appendix; we quote only the results here. Let $v(s,t;\epsilon)$ denote the normal velocity of Γ in the direction of $\mathcal{D}_+$ at the point s, and let κ denote its curvature, defined by $\kappa(s,t;\epsilon) = \nabla^2 r(x,t;\epsilon)|_\Gamma$. Then the time derivatives of r and s can be written

$$r_t(x,t;\epsilon) = -v(s,t;\epsilon), \quad s_t = -\frac{rv_s}{1+r\kappa}, \tag{31a}$$

where, here and below, the arguments of v and κ are $(s(x,t;\epsilon),t;\epsilon)$, and subscripts on v and κ denote differentiation. The corresponding expression for the space derivatives of r and s are

$$\nabla^2 r(x,t;\epsilon) = \frac{\kappa}{1+r\kappa}, \tag{31b}$$

$$\nabla^2 s(x,t;\epsilon) = \frac{r\kappa_s}{(1+r\kappa)^3}, \quad |\nabla s|^2 = \frac{1}{(1+r\kappa)^2}. \tag{31c}$$

To obtain the equations for the inner approximation we first define, in accordance with (1) and (11), the nondimensional internal energy

$$e = u + \gamma w(\phi). \tag{32}$$

As in (25b), we shall denote by $\hat{e}$ the same quantity e expressed as a function of r,s,t,ϵ. In view of (30) and (31), our basic equations (14) and (15) then become

$$\begin{aligned} &\partial_t\hat{e} - v\partial_r\hat{e} - \tfrac{rv_s}{1+r\kappa}\partial_s\hat{e} = \\ &\hat{u}_{rr} + \tfrac{\kappa}{1+r\kappa}\hat{u}_r + \tfrac{1}{(1+r\kappa)^2}\hat{u}_{ss} + \tfrac{r\kappa_s}{(1-r\kappa)^3}\hat{u}_s, \end{aligned} \tag{33}$$

$$\begin{aligned} &\alpha\epsilon^2(\hat{\phi}_t - v\hat{\phi}_r - \tfrac{rv_s}{1+r\kappa}\hat{\phi}_s) = \\ &\epsilon^2\left(\hat{\phi}_{rr} + \frac{\kappa}{1+\kappa r}\hat{\phi}_r + \frac{1}{(1+r\kappa)^2}\hat{\phi}_{ss} + \frac{r\kappa_s}{(1+r\kappa)^3}\hat{\phi}_s\right) + F(\hat{\phi},\hat{u}). \end{aligned} \tag{34}$$

To obtain the inner expansion we follow the procedure set out in Sec. 5(d), defining in $\mathcal{N}(t;\epsilon)$ the stretched normal coordinate

$$z = r/\epsilon \tag{35}$$

and the functions

$$U(z,s,t;\epsilon)=\hat{u}(r,s,t;\epsilon),\ \Phi(z,s,t;\epsilon)=\hat{\phi}(r,s,t;\epsilon),\ E(z,s,t;\epsilon)=\hat{e}(r,s,t;\epsilon).$$

To obtain differential equations for U and Φ, we substitute (35) into (33), (34), obtaining :

$$U_{zz}+\epsilon\kappa U_z+v\epsilon E_z-\epsilon^2\kappa^2U_z+\epsilon^2U_{ss}-\epsilon^2E_t=O(\epsilon^3), \tag{36}$$

$$\Phi_{zz}+F(\Phi,U)+\epsilon\kappa\Phi_z+\alpha\epsilon v\Phi_z=O(\epsilon^2), \tag{37}$$

$$E=U+\gamma w(\Phi). \tag{38}$$

The functions U,Φ,E can be expanded in powers of ϵ as in (25c) :

$$\left.\begin{array}{l} U(z,s,t;\epsilon)=U_0(z,s,t)+\epsilon U_1(z,s,t)+o(\epsilon)\quad(\epsilon\to 0),\\ \Phi=\Phi_0+\epsilon\Phi+o(\epsilon)\end{array}\right\} \tag{39}$$

and so on. By the regularity assumptions in Sec. 4, $v(s,t;\epsilon)$ and $\kappa(s,t;\epsilon)$ can also be expanded in series like (39). The differential equations satisfied by the functions U_0, Φ_0, etc. are obtained by substituting (39) into (36) and (37). This will be done in the next section, but first we formulate the matching conditions (e.g. [F2]) obtained by requiring that the inner and outer expansions represent the same function in their common domain of validity (which exists by Assumption (e) of the previous section). They are the following, where we have omitted the carets from the symbols u and ϕ.

$$\lim_{r\to 0\pm}u_0(r,s,t)=\lim_{z\to\pm\infty}U_0(z,s,t); \tag{40}$$

$$\lim_{r\to 0\pm}\partial_r u_0(r,s,t)=\lim_{z\to\pm\infty}\partial_z U_1(z,s,t). \tag{41}$$

If $U_1(z,s,t)=A_\pm(s,t)+B_\pm(s,t)z+o(1)$ as $z\to\pm\infty$, then

$$A_\pm(s,t)=u_1(0\pm,s,t);\quad B_\pm=\partial_r u_0(0\pm,s,t), \tag{42}$$

and so on. Similar relations apply, connecting $\phi_0,\ \phi_1$ to $\Phi_0,\ \Phi_1$, etc. Finally if $\partial_z U_2=A^*_\pm(s,t)+B^*_\pm(s,t)z+o(1)$, then

$$A^*_\pm(s,t)=\partial_r u_1(0\pm,s,t). \tag{43}$$

7 The zero-order inner approximation.

We substitute (35) and (39) into (36) and (37) to obtain a series expansion in powers of ϵ for each side of the latter. By equating the coefficients of each power of ϵ we obtain a sequence of equations for the various terms U_i and Φ_i . The first couple of them are analyzed as follows :

$O(1)$ in (36):

$$U_{0zz} = 0.$$

We want U_0 to be bounded as $z \to \pm\infty$, because of (40); so U_0 is independent of z :

$$U_0 = U_0(s,t).$$

$O(1)$ in (37):

$$\Phi_{0zz} + F(\Phi_0, U_0) = 0. \tag{44}$$

By (29), we have $\Phi_0(0,s,t) = \phi_c$. By the equation for Φ analogous to (40), we seek a solution Φ_0 which approaches distinct finite limits as $z \to \pm\infty$, and it is clear from (44) that these limits must be roots Φ of $F(\Phi, U_0) = 0$. Moreover, it can be seen by multiplying (44) by Φ_{0z} and integrating from $-\infty$ to $+\infty$ that the integral in (16) with u replaced by U_0 must vanish. By A2 (16), this implies

$$U_0 \equiv 0. \tag{45}$$

Therefore Φ_0 must satisfy the differential equation in (20), and by the definition of r it satisfies the other conditions in (20) as well, so that it must actually be the function defined in (20):

$$\Phi_0(z,s,t) \equiv \psi(z). \tag{46}$$

satisfying the condition

$$\psi(\pm\infty) = h_\pm(0) \equiv \phi_\pm. \tag{47}$$

(Notice that Φ_0 does not depend on s or t.)

The matching condition (40) now gives, by (45), (46) and (47), the following boundary condition on the lowest-order outer solution :

$$u_0\,|_{r=\pm 0} = 0; \quad \phi_0|_{r=\pm 0} = \phi_\pm. \tag{48}$$

At this point, we are in a position to define and evaluate, to lowest order, interfacial free energy and entropy densities at $T = T_0$. The total free energy in the system is ([PF1, eqs. 3.9 and 3.12])

$$\bar{\mathcal{F}}[\phi, T(u)] = \int_{\bar{\Omega}} (f(\phi, T(u)) + \frac{1}{2}\kappa_1 T(u)|\nabla\phi|^2) d\bar{x},$$

$T(u) = (u+1)T_0$. Its dimensionless form follows from our previous nondimensionalization procedure:

$$\mathcal{F}[\phi, u] = \bar{\mathcal{F}}[\phi, T]/\gamma c T_0 L^2 = \int_\Omega \left(\frac{f(\phi,T)}{\gamma c T_0} + \frac{T(u)}{2T_0}\epsilon^2 |\nabla\phi|^2 \right) dx.$$

The (dimensionless) surface tension σ is the interfacial free energy per unit length of interface. It can be calculated, at $T = T_0$ ($u = 0$) by subtracting the free energy density of a uniform phase, which is $f(\phi_\pm, T_0)$, from the function f in the integrand and then integrating with respect to $z = r/\epsilon$ from $-\infty$ to ∞. To lowest order in ϵ we may use the approximation $\phi = \psi(r/\epsilon),\ T = T_0$ in this integral, obtaining

$$\sigma = \epsilon \int_{-\infty}^{\infty} \left(\hat{f}(\psi(z)) + \frac{1}{2}(\psi'(z))^2 \right) dz, \tag{49}$$

where we have set

$$\hat{f}(\psi) = \frac{f(\psi, T_0) - f(\phi_\pm, T_0)}{\gamma c T_0}, \tag{50}$$

the dimensionless bulk free energy density. But since from (44), (45), and (46)

$$\psi'' = -F(\psi, 0) = \frac{d}{d\psi}\hat{f}(\psi),$$

it follows that $(\psi')^2 = 2\hat{f}(\psi)$, so that the contributions of the two terms in the integral for σ are equal. We therefore have

$$\sigma = \epsilon \int_{-\infty}^{\infty} (\psi'(z))^2 dz = \epsilon \int_{-1}^{1} \sqrt{2[\hat{f}(\phi) - \hat{f}(\phi_\pm)]}\, d\phi \equiv \epsilon\sigma_1. \tag{51}$$

This is a standard formula (see e.g. [AC]). We shall call σ_1 the scaled dimensionless surface tension.

8 The jump condition at the interface.

In this section, we show how the energy balance equation (33), applied to the inner approximation, leads to a jump condition for the outer solution at the interface, from which the velocity of the interface can be determined once the outer solution is known. We first calculate this to lowest order, and then to order ϵ.

In view of (39), (45), and (46), we may set

$$U = \epsilon\tilde{U}, \quad \Phi = \psi + \epsilon\tilde{\Phi},$$

where $\tilde{U},\ \tilde{\Phi} = O(1)$. We then have by (38)

$$E = \epsilon\tilde{U} + \gamma w(\psi + \epsilon\tilde{\Phi}).$$

Since ψ does not depend on t, it follows that $E_t = O(\epsilon)$, and hence from (36) that

$$\tilde{U}_{zz} + vE_z + \epsilon\kappa\tilde{U}_z = O(\epsilon^2). \tag{52}$$

Integrating (52), we get

$$\tilde{U}_z + vE + \epsilon\kappa\tilde{U} + C_1(s,t,\epsilon) = O(\epsilon^2) \tag{53}$$

for some integration constant $C_1 = C_{11} + \epsilon C_{12}$.

Since by (39a) $\tilde{U} = U_1 + \epsilon U_2 + O(\epsilon^2)$, the lowest order approximation in (53) yields

$$U_{1z} = -(vE)_0 - C_{11} = -\gamma v_0 w(\psi(z)) - C_{11}, \tag{54}$$

where in the second equation we have used the fact that the expansions of U, v, and Φ induce an expansion of vE in powers of ϵ, with $(vE)_0 = \gamma v_0 w(\psi)$ being the lowest order term. Similarly induced expansions will be used below.

To obtain the lowest order jump condition for the outer approximation, we apply (40) and (41) to the left and right sides of (54). We thus obtain

$$\partial_r u_0\,|_{r=0\pm} = -v_0 e_0|_{r=0\pm} - C_{11} = \pm\gamma v_0 \ell/2 - C_{11}, \tag{55}$$

using (48) and (13). By subtraction we get the jump relation

$$[\partial_r u_0] = -v_0\,[e_0] = \gamma v_0 \ell, \tag{56}$$

where the square brackets indicate the limit from the right ($r = 0+$) minus the limit from the left ($r = 0-$).

We now derive the jump condition to order ϵ analogous to (56). Consider the terms of order ϵ in (53). Since $\tilde{U}_1 = U_2$, these terms are

$$U_{2z} = -(vE)_1 - \kappa_0 U_1 - C_{12}. \tag{57}$$

To evaluate U_1, we integrate (54):

$$U_1 = -\gamma v_0 p(z) - C_{11} z + C_2, \tag{58}$$

where

$$p(z) = \int_{z_0}^{z} w(\psi(s))ds, \tag{59}$$

z_0 will be chosen later, and C_2 is another integration constant, unknown at this stage, but depending on z_0. Hence from (57), we have

$$U_{2z} = -(vE)_1 + \gamma\kappa_0 v_0 p(z) - C_{12} + \kappa_0 C_{11} z - \kappa_0 C_2.$$

Applying the matching relations (43) and (40), we obtain:

$$\partial_r u_1|_{r=0\pm} = -(ve)_1|_{r=0\pm} + \gamma\kappa_0 v_0 P_\pm - C_{12} - \kappa_0 C_2, \tag{60}$$

where the P's are defined by the relation

$$p(z) = w(\phi_\pm)z + P_\pm + o(1) \quad (z \to \pm\infty), \tag{61}$$

i.e.

$$P_\pm = \int_{z_0}^{\pm\infty} (w(\psi(z)) - w(\phi_\pm))\, dz.$$

For the sake of symmetry in notation, we choose the lower limit z_0 so that $P_+ = -P_- \equiv P$. Thus we obtain (60) with $P_\pm = \pm P$. Subtracting, we obtain

$$[\partial_r u_1] = -[(ve)_1] + 2\gamma\kappa_0 v_0 P. \tag{62}$$

Combining (56) with (62), we get, to order ϵ,

$$[\partial_r u] = -[ve] + 2\epsilon\gamma\kappa v P + O(\epsilon^2). \tag{63}$$

This relation can be used to determine v to order ϵ once the outer solution is known to this order.

Physically, eqn (63) expresses the conservation of energy at the interface. The left side represents the net flux of energy into Γ per unit length; the first term on the right represents the portion of that energy which is taken up with phase change. The second term on the right of (63), which is a higher order term not usually displayed, represents the effect of Γ stretching or contracting as it evolves; its presence is necessary to ensure conservation of energy to this order.

9 The zero-order outer approximation.

The zero-order outer approximation to our layered family of solutions consists of a curve $\Gamma_0(t)$ dividing $\mathcal{D}$ into two subregions $\mathcal{D}_+(t)$ and $\mathcal{D}_-(t)$, and functions $u_0,\ \phi_0$, continuous in each of $\mathcal{D}_\pm$. These can now be determined: we obtain u_0 and Γ_0 by solving a Stefan problem $\mathcal{S}_0$, defined below, and then we obtain ϕ_0 from (27) by taking $\phi_0 = h_\pm(u_0)$.

(a) In $\mathcal{D}_\pm$, u_0 is to satisfy (27), (28)

$$\partial_t e_0^\pm = \nabla^2 u_0, \tag{64}$$

where

$$e_0^\pm = u_0 + \gamma w(h_\pm(u_0)). \tag{65}$$

Note that in the case where $h_\pm(u)$ are independent of u, (64) is the usual linear heat equation for u_0. This was the case for the liquid phase in the density functional model in [PF1], and for both phases in [WS].

(b) On $\Gamma_0(t)$ we have the interface condition (48)

$$u_0 = 0 \tag{66}$$

and the Stefan condition (56)

$$[\partial_r u_0] = \gamma v_0 \ell. \tag{67}$$

(*c*) Our focus has been on the properties of layered solutions in general, without reference to initial or boundary conditions. But we are now led to a free boundary problem for which it is natural to specify these extra conditions. In fact, there may be boundary conditions for the temperature u, and hence for u_0, at $\partial\mathcal{D}$ (exclusive of Γ_0), and initial conditions $u_0(x,0)$, $\Gamma_0(0)$.

If $u_0(x,0)$ is nonpositive in $\mathcal{D}_+$ (the solid) and nonnegative in $\mathcal{D}_-$ (liquid), $\mathcal{S}_0$ is the classical Stefan problem, and for smooth initial conditions has a unique classical solution for a small time interval. Our basic assumptions about the families (u,ϕ) in Sec. 5 imply that in fact this is true for all $t \in [0,t_1]$, the interval mentioned in Sec. 5.

If $u_0(x,0)$ has signs opposite from those, however, then it is generally believed that $\mathcal{S}_0$ is an ill-posed problem, in which case our assumptions in Sec. 5 will hold only in very special circumstances, such as when the domain and all data have radial symmetry. This ill-posed problem would correspond to a model for crystal growth into a supersaturated liquid with no account taken of curvature or surface tension effects. We shall see in Sec. 14 that if $u_0(x,0)$ is very small in magnitude, then the assumptions in Sec. 5 become reasonable again; in fact the lowest-order free boundary problem then contains regularizing curvature terms.

10 The first-order interface condition.

To obtain a more accurate outer solution we must calculate u_1, and for this we need expressions for u_1 on the interface Γ.

First, we apply the matching condition (42) to (58), taking into account (61) and the fact that $P_\pm = \pm P$, to obtain

$$u_1|_{\Gamma\pm} = \mp\gamma v_0 P + C_2. \tag{68}$$

Here the subscript $\Gamma_\pm$ means the limit as Γ is approached from the + side or the − side. To determine these limits, we must now find the constant C_2. It turns out that this can be done by examining the $O(\epsilon)$ terms in (37). By using (46), one can put those terms into the form

$$L\Phi_1 = -F_u(\psi(z),0)U_1 - \kappa_0\psi'(z) - \alpha v_0\psi'(z), \tag{69}$$

where L is the operator defined by $L\Phi \equiv \Phi_{zz} + F_\phi(\psi(z),0)\Phi$.

We know that the operator L has a nullfunction $\psi'(z)$ which decays exponentially as $z\to\pm\infty$, obtained by differentiating (44) with respect to z and setting $\Phi_0 = \psi$. We are seeking a solution of (69) which grows at most as fast

as a polynomial at ∞. Multiplying (69) by ψ' and integrating, we see that the equation (69) has such a solution only if the right side is orthogonal to ψ':

$$\int_{-\infty}^{\infty} F_u(\psi(z),0)U_1(z,s,t)\psi'(z)dz + \kappa_0(s,t)\sigma_1 + \alpha v_0(s,t)\sigma_1 = 0,$$

where (recall (51))

$$\sigma_1 = \int_{-\infty}^{\infty} (\psi'(z))^2 dz.$$

Substituting from (58), we obtain

$$\int_{-\infty}^{\infty} F_u(\psi(z),0)(-\gamma v_0 p(z) - C_{11}z + C_2)\psi'(z)dz + (\kappa_0 + \alpha v_0)\sigma_1 = 0. \tag{70}$$

¿From (18) and (20), the coefficient of C_2 here is seen to be $-\ell$. On the basis of Assumption A4, we may therefore solve (70) for C_2 as

$$C_2(s,t) = (\alpha\tilde{\sigma} + \gamma\tilde{p})\, v_0(s,t) + \tilde{\sigma}\kappa_0(s,t) + \tilde{q}C_{11}, \tag{71}$$

where

$$\tilde{p} = -\frac{\int p(z)\rho(z)dz}{\ell}, \quad \tilde{q} = -\frac{\int z\rho(z)dz}{\ell}, \quad \tilde{\sigma} = \frac{\sigma_1}{\ell}, \tag{72a}$$

with

$$\rho(z) = F_u(\psi(z),0)\psi'(z). \tag{72b}$$

Substituting (71) into (68), we find

$$u_1|_{\Gamma\pm} = (\alpha\tilde{\sigma} + \gamma\tilde{p} \mp \gamma P)\, v_0 + \tilde{\sigma}\kappa_0 + \tilde{q}C_{11}. \tag{73}$$

Finally, the constant C_{11} may be found from (55):

$$C_{11}(s,t) = -\partial_r u_0|_{r=\pm 0} \pm \frac{1}{2}\gamma\ell v_0(s,t). \tag{74}$$

In the classical case when the Stefan problem (64) - (67) is well posed, it can be used to determine the quantities on the right of (73) from the initial and boundary conditions for u_0 and Γ_0. In (74), either sign may be chosen; the right side is independent of the choice. We shall use the upper sign in $\mathcal{D}_+$ and the lower one in $\mathcal{D}_-$.

Set $(\partial_r u_0)_\pm \equiv \partial_r u_0|_{r=\pm 0}$. Then substituting (74) into (73), we have

$$u_1|_{\Gamma\pm} + \tilde{q}(\partial_r u_0)_\pm = m_\pm v_0 + \tilde{\sigma}\kappa_0, \tag{75}$$

where

$$m_\pm = \alpha\tilde{\sigma} + \gamma(\tilde{p} \mp P) \pm \frac{1}{2}\gamma\ell\tilde{q}. \tag{76}$$

If $m_+ \neq m_-$, it is clear from (75) that the outer temperature distribution u will undergo a discontinuity of the order ϵ across the interface.

Example: Consider the particular case when $F_u(\phi, 0)$ is an even function of ϕ, and $\psi'(z)$ is even. Then from the above, we have $\tilde{q} = 0$, so that (75) becomes

$$u_1|_{\Gamma\pm} = (\alpha\tilde{\sigma} + \gamma(\tilde{p} \mp P))\, v_0 + \tilde{\sigma}\kappa_0.$$

If, in addition, (as in [PF1])

$$w(\phi) = A\phi - B\phi^2 + const,$$

then P vanishes whenever B does. In this case, then, the possibility that u_1 is discontinuous across Γ is associated with the presence of quadratic terms in w. The case when they are absent is the one treated, in the context of the traditional phase field model, in [CF] and [F2].

11 The first-order outer solution.

We can now formulate the procedure for determining the first order approximation to the outer solution. This approximation can be determined by solving the following modified Stefan problem $\mathcal{S}_\epsilon$, which generalizes the problem $\mathcal{S}_0$ defined in section 9:

(a) In $\mathcal{D}_\pm$, u is to satisfy (14)

$$\partial_t e = \nabla^2 u, \tag{77}$$

where

$$e = u + \gamma w(\phi),$$

$$\phi = h_\pm(u) \ \text{ in } \ \mathcal{D}_\pm \ \text{ by (26).} \tag{78}$$

(b) On $\Gamma_\pm$ we have, from (66), (75), and (63), the conditions

$$(u + \epsilon\tilde{q}(\partial_r u))|_{\Gamma\pm} = \epsilon m_\pm v + \epsilon\tilde{\sigma}\kappa; \tag{79}$$

$$[\partial_r u] = -v[e] + \epsilon\gamma\kappa v P, \tag{80}$$

where the coefficients are given by (72a), (76).

(c) In addition, boundary conditions, to hold on $\partial\mathcal{D}$, and initial data are to be prescribed.

The coefficients in (79), (80) are the same as in (75) and (62). As mentioned before, when $h_\pm$ are constants, (77) is the heat equation with constant coefficients. Even when $h_\pm$ are not constants, the heat equation is a reasonable approximation in typical cases (see Sec. 14).

The term in $\partial_r u$ in (79) appears to introduce a singular perturbation into the problem, but this is not likely to be true. We consider a model problem consisting of (77) and (79) on the half line $\{r > 0\}$ with the right side of (79) taken to be a known constant. The potential effect of such a singular perturbation can be ascertained from the inner equations associated with stretching the variable r. In the model problem it is readily seen to be a regular perturbation.

What we have shown so far is that under the assumptions in Sec. 5 , the exact solution family $(u(x,t;\epsilon), \phi(x,t;\epsilon))$ satisfies (77) - (80) except for error terms of the order ϵ^2. Let us now suppose that $\mathcal{S}_\epsilon$ is a well-posed problem, and let $(\tilde{u}(x,t;\epsilon), \tilde{\phi}(x,t;\epsilon), \tilde{\Gamma}(t;\epsilon))$ denote its solution when the conditions in (c) are the same as those of the exact family. Thus $(\tilde{u}, \tilde{\phi}, \tilde{\Gamma})$ satisfy the same equations and initial conditions as (u, ϕ, Γ), except that the $O(\epsilon^2)$ terms are discarded. It is natural to expect the following assertion, which is basic to the paper, to hold:

Expectation: $|u(x,t;\epsilon) - \tilde{u}(x,t;\epsilon)|$, $|\phi(...) - \tilde{\phi}(...)|$, $|\Gamma(t;\epsilon) - \tilde{\Gamma}(t;\epsilon)| = O(\epsilon^2)$ $(\epsilon \to 0)$, uniformly in $\mathcal{D} \times [0, t_1]$.

12 Discussion; surface tension.

As in previous phase field models, a Gibbs–Thompson term $\epsilon\tilde{\sigma}\kappa$ and a kinetic undercooling term $\epsilon m_\pm v$ appear on the right of (79). In addition, there appears an $O(\epsilon)$ normal derivative term on the left, which can be important for second order transitions, as we shall discover.

The last term in (79) may be compared with the thermodynamic formula for the Gibbs–Thompson effect, which can be written

$$(T - T_0)\,|_\Gamma = \frac{\bar{\sigma} T_0}{\bar{\ell}} \bar{\kappa}$$

where $\bar{\sigma}$ is the surface tension, $\bar{\ell}$ the latent heat and $\bar{\kappa}$ the curvature in physical units. The corresponding formula in our dimensionless units is

$$u|_\Gamma = \frac{\sigma\kappa}{\ell} \tag{81}$$

where $\sigma = \bar{\sigma}/\gamma c T_0 L$. From (51) and (72a),

$$\sigma = \epsilon \int_{-\infty}^{\infty} \psi'(z)^2 dz = \epsilon\sigma_1 = \epsilon\ell\tilde{\sigma}.$$

Thus (81) simplifies to $u|_\Gamma = \epsilon\tilde{\sigma}\kappa$, which indeed agrees with the relevant terms in (79).

The problem (77)–(80) differs from the modifications of the Stefan problem obtained in [CF] in three respects:

(a) The $O(\epsilon)$ correction to the value of the temperature at the interface involves a flux term (on the left of (79)), so that it is perturbed into a Robin boundary condition. In the example given in section 10, of course, $\tilde{q}$ vanishes, making this correction zero.

(b) The value of u will in general be discontinuous at the interface because of the first term on the right of (79) if $m_+ \neq m_-$. Again in the above example, when $B = 0$, the discontinuity disappears. The amount of the discontinuity will be $O(\epsilon)$.

(c) the Stefan condition (80) involves a small correction term due to the stretching of the interface. A term like this was noted in [UR]; otherwise, all these effects were absent in previous models of phase field type.

It will be shown in Sec. 14 that there are circumstances when the free boundary problem (77)–(80) can be approximated, in a formal sense, by other (generally simpler) free boundary problems. There are a number of possibilities here; they include different types of curvature-driven interfacial motion.

13 Second-order transitions.

By a second-order transition we mean one where the internal energy is the same in the two phases, for each fixed value of the temperature in the interval $[T_-, T_+]$. A good example is the case when w is an even function of ϕ and F is odd in ϕ. For second order transitions, there is no unique transition temperature T_0, contrary to postulate A2. Instead, we define T_0 to be some other characteristic temperature of the problem, for example the average of the system's initial temperature distribution.

In the notation of (1), we have $\bar{e}(h_+(T), T) = \bar{e}(h_-(T), T)$, and in that of (65),

$$e_0^+(u) = e_0^-(u) \text{ for each } u. \tag{82}$$

In view of (1), this implies that the quantity $\frac{d}{dT}\left[\frac{1}{T} f(h_\pm(T), T)\right]$ is the same for either choice of sign. Thus $\frac{d}{dT}\int_{h_-(T)}^{h_+(T)} \left[\frac{1}{T} f_\phi(\phi, T)\right] d\phi = 0$. In nondimensional terms (11), we have

$$\frac{d}{du}\int_{h_-(u)}^{h_+(u)} F(\phi, u) d\phi = 0. \tag{83}$$

Therefore in place of Assumption A4, the inequality sign in (19) becomes an equality for all u, hence the latent heat $\ell = 0$, and similarly (21) becomes

$$\int_{-\infty}^{\infty} F_u(\psi(z), u)\psi'(z) dz = 0 \quad \text{for all} \quad u \quad \text{in the range of interest.} \tag{84}$$

In dealing with second order transitions, our formal assumptions will simply be A1 and (84).

Following the asymptotic development in sections 4–11, we see that the following changes are necessary.

The conclusion (45), hence also the left part of (48), no longer hold. In fact, the value of u_0 on the interface is no longer determined a priori. Therefore in the lowest order outer problem (64)–(67), (66) is to be replaced by $[u_0] = 0$, and the right side of (67) is replaced by zero. Thus u_0 and its derivative are continuous across Γ_0. In view of (82), we see that u_0 is determined as the solution of the heat equation (64) in all of $\mathcal{D}$, *with no reference to* Γ (appropriate boundary and initial conditions may be prescribed). The interface's location is found independently, as we now describe.

We pass to (70), which by virtue of (84) and (74) with $\ell = 0$ becomes

$$m_1 v_0 + \kappa_0 = m_2 \partial_r u_0, \tag{85}$$

where

$$m_1 = \alpha - \frac{\gamma}{\sigma_1} \int_{-\infty}^{\infty} p(z)\rho(z)dz, \quad m_2 = -\frac{1}{\sigma_1} \int_{-\infty}^{\infty} z\rho(z)dz,$$

the functions p and ρ being defined in (59) and (72b).

To find the interface $\Gamma(t)$, then, u_0 is first determined by (64), and then Γ is found from the "forced" motion–by–curvature problem (85), with known forcing term $m_2 \partial_r u_0$ dependent on position and on time.

In Sec. 16 , we shall examine the more realistic case when the thermal diffusivity D is different in the two phases; then it can be checked that the problem for u_0 can no longer be decoupled from that for Γ.

The interface condition (85) is similar to the motion-by-curvature law given by the Cahn–Allen theory of isothermal phase transitions ([AC], [MSc]), but there is now an extra term proportional to the temperature gradient (which is continuous across the interface). For a physical interpretation of this term, suppose that the surface tension (excess free energy of the interface) decreases with temperature. Then the interface will tend to move so as to increase its temperature. This tendency is borne out by (85) in the typical case that m_1 and m_2 are positive. There is an analogous forcing term in the corresponding equation (79) for first–order transitions, but in that context its effect is relatively small.

When the temperature deviation u is small ($\delta << 1$ in the context of Sec. 14), then the forcing term can be neglected, and the interfacial motion follows the classical motion–by–curvature law. This case was noted in [C3], and is the law of motion found for a simpler model in [CA] and [AC]. (In [C3], it was erroneously implied that our model gives only second order transitions; see [PF2].)

14 The transition from Stefan to Mullins-Sekerka evolution. Other free boundary problems.

There are several special circumstances in which our basic free boundary problem (77) - (80) can be approximated formally by simpler free boundary problems.

For example, the nonlinear diffusion equation (77) can typically be approximated by a linear one. In fact, the left side can be written as

$$\hat{c}_\pm(u)u_t, \text{ where } \hat{c}_\pm(u) \equiv 1 + w'(h_\pm(u))h'_\pm(u),$$

and the specific heat functions $\hat{c}_\pm(u)$ can be approximated by constants when the functions $h_\pm(u)$ are constants (as in [WS] and for one case in [PF1]), nearly constant, and/or when u is small enough. In such cases, they may by replaced by $\hat{c}_\pm(0)$. In the following, we shall assume that this approximation is valid. It should be noted that the assumption $u \ll 1$ is entirely reasonable in many cases. It simply says

$$|T - T_0| \ll T_0. \tag{86}$$

In the case of water, for example, it means that the temperature range (in Centigrade degrees) in the phenomenon under consideration is much smaller than 273.

Anticipating that the simpler problems to be examined may involve dynamics on a longer time scale and hence slower speed, we proceed formally by rescaling u and t. We set

$$u = \delta\bar{u}, \quad t' = \beta t, \quad v = \beta\bar{v},$$

where the parameters δ and β are ≤ 1 and may be small. We make these substitutions in (77) - (80) with the error terms $O(\epsilon^2)$ appended, and divide by δ to obtain

$$\beta\hat{c}_\pm\bar{u}_{t'} = \nabla^2\bar{u} + O(\epsilon^2/\delta) \text{ in } \mathcal{D}_\pm, \tag{87a}$$

$$(\bar{u} + \epsilon\bar{q}(\partial_r\bar{u}))|_{\Gamma\pm} = \frac{\epsilon\beta}{\delta}m_\pm\bar{v} + \frac{\epsilon}{\delta}\tilde{\sigma}\kappa + O(\epsilon^2/\delta) \text{ on } \Gamma, \tag{87b}$$

$$[\partial_r\bar{u}] = \frac{\beta}{\delta}\bar{v}\gamma\ell + \frac{\epsilon\beta}{\delta}\gamma\kappa\bar{v}P + O(\epsilon^2/\delta) \text{ on } \Gamma. \tag{87c}$$

To show how one kind of evolution may develop into a different kind at large times, we consider first the "normal" case when $\delta = 1$. Then if we set $\beta = 1$ as well (so no rescaling actually occurs) and disregard terms of orders ϵ and higher order in (87), we get the classical Stefan problem

$$\hat{c}_\pm u_t = \nabla^2 u \text{ in } \mathcal{D}_\pm, \tag{88a}$$

$$u = 0 \text{ on } \Gamma, \tag{88b}$$

$$[\partial_r u] = v\gamma\ell \text{ on } \Gamma. \tag{88c}$$

Let $\mathcal{D}$ represent a bounded vessel containing the material under consideration, and suppose it is thermally insulated, so that the normal derivative $\partial_r u = \partial_\nu u = 0$ on $\partial\mathcal{D}$. Suppose that $u > 0$ in the liquid phase, $u < 0$ in the solid. Consider layered solutions with interface $\Gamma(t)$ evolving according to (88). Then it can be checked that

$$\frac{d}{dt}\left[\hat{c}_+ \int_{\mathcal{D}_+} u^2 dx + \hat{c}_- \int_{\mathcal{D}_-} u^2 dx\right] = -2\int_{\mathcal{D}} |\nabla u|^2 dx$$

which in view of (88b) is strictly negative as long as u does not vanish identically. Suppose that $\Gamma(t)$, the solution of (88), exists for all t and does not intersect $\partial\mathcal{D}$. Then it is natural to conjecture that as $t\to\infty$, $u(x,t)\to 0$ uniformly in $\mathcal{D}$ and that $\Gamma(t)$ approaches a limiting configuration Γ_∞.

Eventually, then, $u = O(\epsilon)$ and the quantity $\epsilon\tilde{\sigma}\kappa$ on the right of (79) and (87b) can no longer be neglected on Γ relative to u. (This term indicates, in fact, that the temperature u can in general never achieve smaller orders of magnitude than ϵ.) When u achieves this order of smallness, we set $\delta = \epsilon$ in (87) and observe that if we select $\beta = \epsilon$ as well, and drop higher order terms, we obtain a reasonable problem of "Mullins-Sekerka" type [MS]:

$$\nabla^2 \bar{u} = 0 \text{ in } \mathcal{D}_\pm, \tag{89a}$$

$$\bar{u} = \tilde{\sigma}\kappa \text{ on } \Gamma, \tag{89b}$$

$$[\partial_r \bar{u}] = \gamma\bar{v}\ell \text{ on } \Gamma. \tag{89c}$$

An existence theory for the solution $(\bar{u}, \Gamma)$ of (89) has recently been given by Chen [Ch2]; for the Hele-Shaw problem, which bears some similarity, see [CP].

In short, when the temperature becomes small enough, the evolution according to (88) is conceptually replaced by the much slower evolution according to (89). The evolution (89) is well known to decrease the length of $\Gamma(t)$ and to preserve the area inside it, so it is expected that under the slow process, Γ will typically evolve from Γ_∞ (or something near it) into a circle with the same area.

Other free boundary problems can be obtained by assuming γ and/or α are small, i.e. that the latent heat is small or the relaxation process for ϕ is quick. For example, if $\epsilon^2 \ll \delta = \gamma \ll \epsilon$, we may set $\beta = 1$ to obtain the classical motion-by-curvature law

$$\alpha v = -\kappa \text{ on } \Gamma, \tag{90}$$

coupled to a heat equation with prescribed jump condition (88c) on Γ (known from solving (90)).

A number of other possibilities can occur; we leave them for the reader to discover.

15 Comparison with other models and limiting arguments.

The free boundary problem (89) and its companion with (89a) replaced by

$$\bar{u}_t = \nabla^2 \bar{u},$$

have been derived by asymptotic methods from other phase field models, most notably in [C2] and [WS]. Here we compare both the model in [WS] and its asymptotic development with ours; similar considerations hold for the Langer model in [C2].

The model in [WS] has the property that our functions introduced in A1 are constant: $h_-(T) \equiv 0,\ h_+(T) \equiv 1$. Thus the order parameter in the purely liquid or solid phase does not depend on T. On the other hand, the latent heat $\bar{\ell}(T)$ may depend on T. To compare the model in [WS] to ours, we must replace ϕ by $1-\phi$ (distinguishing "order" from "disorder" parameters). In our notation, their evolution problem (their eqns. 40, 41) corresponds to our (14), (15) with

$$F(\phi, u(T)) = \frac{1}{\gamma c}\left(\frac{1}{T_0} - \frac{1}{T}\right)\bar{w}'(\phi) - 4\phi(\phi-1)(\phi-\frac{1}{2}) \tag{91}$$

and $\bar{w}(\phi) = \bar{\ell}p(\psi)|_{\psi=1-\phi}$, where $p(\psi)$ is a function with $p(0) = 0,\ p(1) = 1$, whose first and second derivatives vanish at $\phi = 0$ and 1.

Note that this model provides no theoretical limit to the extent of supercooling of the liquid or superheating of a solid, unlike the equations depicted in our Fig. 1 and the example in Sec. 4 . In fact, at each value of T the free energy F has local minima (in ϕ) at $\phi = 0$ and 1, representing stable liquid and solid phases. If the temperatures under consideration are kept fairly near to T_0, this should not be an important deficiency.

The temperature-independent part of the correponding dimensionless bulk entropy density given by (4), $s_0' = \frac{1}{\gamma c}\bar{s}_0'$, satisfies

$$s_0'(\phi) = -4\phi(\phi-1)(\phi-\frac{1}{2}) + \frac{\bar{w}'(\phi)}{\gamma c T_0},$$

and since $\bar{w}''(\frac{1}{2}) = 0$, we have $s_0''(\frac{1}{2}) = 1$, showing that the entropy in this model is not a concave function of ϕ.

Further notational comparisons are the following: the parameters $\tilde{\epsilon},\ m$, and a in [WS] correspond to our parameters $\epsilon/2, \alpha^{-1}$, and $1/4\gamma c$, respectively.

Their asymptotics is based on the assumption that the first term in (91) is $O(\epsilon)$. We rewrite the assumption as:

$$\frac{\bar{\ell}}{\gamma c T_0}\left(1-\frac{T_0}{T}\right)p'(1-\phi)=O(\epsilon).$$

Let us assume that the dimensionless quantity $\frac{\bar{\ell}}{cT_0}=O(1)$; this is reasonable in typical scenarios. Since $p'(\phi)$ is also $O(1)$, this implies that

$$\frac{1}{\gamma}\left|1-\frac{T_0}{T}\right|=O(\epsilon).$$

This relation can be guaranteed, for example, by requiring either
(a) $\gamma=O(\epsilon^{-1})$, or
(b) $\frac{T-T_0}{T_0}=O(\epsilon)$.
Physical meaning can be given to both of these cases. In case (a), the implication is that

$$T\frac{\partial F}{\partial T}\approx\frac{\bar{\ell}}{\gamma c T_0}p(1-\phi)=O(\gamma^{-1})=O(\epsilon),$$

whereas

$$\frac{\partial F}{\partial \phi}=O(1).$$

The meaning is that the free energy depends much more (by a factor ϵ^{-1}) sensitively on ϕ than on the temperature T.

In case (b), we have, in our notation, $u=O(\epsilon)$, which is exactly the assumption ($\delta=\epsilon$) under which we have derived (89). This says simply that the temperature is close, as measured by ϵ, to the melting temperature T_0.

16 Variable c, D, and α.

All of the preceding can be extended in a straightforward way to the case when c, D, and α are given functions of ϕ and T, and w depends on T as well as on ϕ. This allows these first three physical parameters to differ in the different phases. It was observed by Chen [Chen3] that if c differs in the two phases, then ℓ must depend on T. It is often the case that the temperature variation in the problem under consideration is small enough that it does not by itself induce a significant variation in the values of these physical constants. For simplicity, we assume this is the case, i.e. that c and D depend on ϕ but not on D.

The results under this generalization are quite analogous to those obtained before, and so are not surprising. We record them here for the sake of completeness.

The first observation is that the expression (4) for a term in the right side of (3) must be supplemented by the extra term $-c'(\phi)\log T$.

By way of notation, we set

$$D(\phi) = D_1 d(\phi), \quad c(\phi) = c_1 k(\phi),$$

where D_1 and c_1 are defined to be the minimal values of D and c, respectively. We assume that the dimensionless functions d and k are $O(1)$.

In the definitions of dimensionless variables given in (10) and (11), we now replace the symbols D and c by D_1 and c_1. The basic equations (14) and (15) now become

$$\partial_t(k(\phi)u + \gamma w(\phi)) = \nabla \cdot d(\phi)\nabla u, \tag{92}$$

$$\alpha(\phi)\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + F(\phi, u). \tag{93}$$

All of the analysis in the previous sections has its analog in the present more general context. The resulting free boundary problem (77)–(80) takes the following form:
In $\mathcal{D}_\pm$,

$$\partial_t e_\pm(u) = \nabla \cdot d_\pm(u)\nabla u, \tag{77)' = (94}$$

$$\begin{gathered} e_\pm(u) = k(h_\pm(u))u + \gamma w(h_\pm(u)), \quad d_\pm(u) = d(h_\pm(u)), \\ \phi = h_\pm(u) \ \text{ in } \ \mathcal{D}_\pm. \end{gathered} \tag{78)' = (95}$$

On $\Gamma_\pm$,

$$u + \epsilon n_\pm(d\partial_r u)|_{\Gamma\pm} = \epsilon m_\pm v + \epsilon\tilde{\sigma}\kappa; \tag{79)' = (96}$$

$$[d(u)\partial_r u] = -[ve] + \epsilon\gamma\kappa v P. \tag{80)' = (97}$$

Here the constants $m_\pm$ and $n_\pm$ have to be defined as follows. Let

$$d_0(z) = d(\psi(z)), \quad p(z) = \int (w(\psi(z))/d_0(z))dz, \quad q(z) = \int (1/d_0(z))dz, \tag{98}$$

and let the constants P and Q be such that

$$\begin{aligned} p(z) &= \tfrac{w_\pm}{d(\phi_\pm)} z \pm P + o(1), \quad z \to \pm\infty, \\ q(z) &= \tfrac{1}{d(\phi_\pm)} z \pm Q + o(1). \end{aligned}$$

In the following, ρ, ℓ are the same as before. Let

$$m_1 = \int \alpha(\psi(z),0)(\psi'(z))^2 dz > 0,$$

$$\tilde{p} = \frac{\int p(z)\rho(z)dz}{\ell}, \quad \tilde{q} = \frac{\int q(z)\rho(z)dz}{\ell}.$$

Then

$$m_\pm = -m_1 + \gamma(\tilde{p} \mp P) \pm \frac{1}{2}\gamma\ell(\tilde{q} \mp Q),$$

$$n_\pm = \tilde{q} \mp Q.$$

For future reference, we give here the modified versions of relations (33) and (52):

$$\partial_t \hat{e} - v\partial_r \hat{e} - \tfrac{rv_s}{1+r\kappa}\partial_s \hat{e} = (d\hat{u}_r)_r + d\tfrac{\kappa}{1+r\kappa}\hat{u}_r + \tfrac{1}{(1+r\kappa)^2}(d\hat{u}_s)_s + d\tfrac{r\kappa_s}{(1+r\kappa)^3}\hat{u}_s, \qquad (33)' = (99)$$

$$(d\tilde{U}_z)_z + vE_z + \epsilon\kappa d\tilde{U}_z = O(\epsilon^2). \qquad (52)' = (100)$$

Referring to Sec. 14 , we obtain the following generalizations of the examples in (88)–(90).

The "normal" case (88):

$$\hat{c}_\pm \partial_t u = \nabla \cdot d_\pm(u)\nabla u \qquad (88a)' = (101a)$$

$$u = 0 \quad \text{on} \quad \Gamma, \qquad (88b)' = (101b)$$

$$[d\partial_r u] = v\gamma\ell \quad \text{on} \quad \Gamma, \qquad (88c)' = (101c)$$

where a different but obvious definition is given for $\hat{c}_\pm$.

Motion by curvature (90) $(\delta = \gamma \ll \epsilon, \quad \beta = 1)$.

$$m_1 v = -\sigma_1 \kappa \quad \text{on} \quad \Gamma. \qquad (90)' = (102)$$

The "Mullins-Sekerka" case (89) $(\beta = \delta = \epsilon)$.

$$\nabla \cdot d_\pm \nabla \bar{u} = 0 \quad \text{in} \quad \mathcal{D}_\pm, \qquad (89a)' = (103a)$$

$$\bar{u} = \tilde{\sigma}\kappa \quad \text{on} \quad \Gamma, \qquad (89b)' = (103b)$$

$$[d_\pm \partial_r \bar{u}] = \gamma\bar{v}\ell \quad \text{on} \quad \Gamma. \qquad (89c)' = (103c)$$

Similar considerations hold for second order transitions. The coupling of the generalization of (85) with that of (64) is particularly interesting.

17 Enhanced diffusion in the interface.

In some materials science connections ([CT], and references therein), it is important to take into account increased material diffusivity in surfaces. In our models it is heat rather than material which is diffusing. Nevertheless, there is clearly an analogy with material diffusion, and so it may be interesting to adapt our results to the case when diffusivity is much greater in the interfacial region than it is elsewhere. Specifically, we treat the case when this ratio is of the order ϵ^{-1}. We show, among other things, that an effect of this is the presence, in (89c) or (103c), of an extra term on the right taking the form of the second derivative of the curvature κ with respect to arc length along the interface. A similar result was obtained by a different route for a Cahn-Hilliard model in [CFN].

Our basic assumption is that the function D can be written as the sum of two terms as follows. Let $D_1 = \text{ Min}\,[D(\phi_+), D(\phi_-)]$. Then

$$D = D(\phi;\epsilon) = D_1\left(\epsilon^{-1}\hat{D}(\phi) + \tilde{D}(\phi)\right) \equiv D_1 d(\phi;\epsilon), \tag{104}$$

where $\hat{D}$ and $\tilde{D}$ are $O(1)$ functions, and $\hat{D}(\phi)$ vanishes when $\phi = \phi_\pm$. In fact, we assume that for some positive number ω,

$$\hat{D}(\phi) > 0 \ \text{ for } \ \phi_- + \omega < \phi < \phi_+ - \omega; \ \ \hat{D}(\phi) = 0 \ \text{ otherwise.} \tag{105}$$

The function $d(\phi;\epsilon)$ is analogous to the function $d(\phi)$ used in Sec. 16 , so in particular D_1 is used again in the definitions of the nondimensional variables.

We shall direct attention to the modifications in the previous treatment occasioned by (104). They begin in Sec. 6 . Concentrating on the first term in (36), we see that it must be replaced by $\left[(\epsilon^{-1}\hat{D} + \tilde{D})(U_0 + \epsilon U_1 + ...)_z\right]_z$. Therefore the terms of orders $O(\epsilon^{-1})$ and $O(1)$ in the revised version of (36) (analog of (100)) are:

$$\partial_z\left[(\epsilon^{-1}\hat{D}(\Phi_0(z)) + \tilde{D}(\Phi_0(z)) + \hat{D}'(\Phi_0(z))\Phi_1)U_{0z} + \hat{D}(\Phi_0(z))U_{1z}\right] = 0.$$

Integrating this with use of the fact that $U_{0z}(z) = \hat{D}(\Phi_0(z)) = 0$ at $z = \pm\infty$, we obtain

$$(\epsilon^{-1}\hat{D}(\Phi_0(z)) + \tilde{D}(\Phi_0(z)) + \hat{D}'(\Phi_0(z))\Phi_1)U_{0z} + \hat{D}U_{1z} = 0. \tag{106}$$

The $O(\epsilon^{-1})$ term in this equation tells us that

$$\hat{D}(\Phi_0(z))U_{0z} = 0. \tag{107}$$

Now let $I = \{z : \Phi_0(z) \in [\phi_- + \omega, \phi_+ - \omega]\}$. It follows from (105) and (107) that

$$U_{0z} = 0, \quad z \in I.$$

Moreover since $\hat{D}'(\Phi_0(z)) = 0$ for $z \notin I$, we see that the third term in (106) vanishes. Hence

$$\tilde{D}(\Phi_0(z))U_{0z} + \hat{D}(\Phi_0(z))U_{1z} = 0.$$

This tells us (a) that for $z \notin I$, $U_{0z} = 0$, so that in fact for all z,

$$U_{0z} \equiv 0;$$

and therefore (b) that

$$U_{1z} = 0, \quad z \in I. \tag{108}$$

In Sec. 7 , (44)–(48) remain unchanged. In particular, $\Phi_0(z) = \psi(z)$ as before.

Recall (99), which shows the way that our d enters into the energy balance equation. In view of that and (104), equation (52)' = (100) must be corrected to

$$\partial_z \left(d\tilde{U}_z \right) + vE_z + \epsilon\kappa d\tilde{U}_z - \epsilon\kappa^2 \hat{D} z \tilde{U}_z + \epsilon \partial_s \left(\hat{D}\tilde{U}_s \right) = O(\epsilon^2), \quad (52)'' = (109)$$

and the new version of (53) is

$$\begin{aligned} d\tilde{U}_z + vE + \epsilon\kappa \int d\tilde{U}_z dz - \epsilon\kappa^2 \int \hat{D} z \tilde{U}_z dz + \epsilon \int \partial_s \left(\hat{D}\tilde{U}_s \right) dz \\ + C_1(s,t,\epsilon) = O(\epsilon^2). \end{aligned} \qquad (53)' = (110)$$

Here $C_1 = C_{11} + \epsilon C_{12}$. As before (54), $(vE)_0 = \gamma v_0 w(\psi(z))$. Therefore the $O(\epsilon^{-1})$ and $O(1)$ terms in (110) are

$$\left(\epsilon^{-1} \hat{D}(\psi(z)) + \hat{D}'(\psi(z))\Phi_1 + \tilde{D}(\psi(z)) \right) U_{1z} + \hat{D}(\psi(z))U_{2z} = -\gamma v_0 w(\psi(z)) - C_{11}.$$

But we know from (108) that $\hat{D}U_{1z} = \hat{D}'U_{1z} = 0$, so in fact our alternate version of (54) is:

$$\hat{D}(\psi(z))U_{2z} + \tilde{D}(\psi(z))U_{1z} = -\gamma v_0 w(\psi(z)) - C_{11}. \qquad (54)' = (111)$$

Let $\chi(z)$ be the characteristic function of I', i.e. $\chi(z) = 0$ for $z \in I$, and $= 1$ otherwise. In view of (108), multiplying (111) by $\chi(z)$ does nothing to the term in U_{1z}, but annihilates the term in $\hat{D}$. We so obtain

$$U_{1z} = -\gamma v_0 \frac{\chi(z) w(\psi(z))}{\tilde{D}(\psi(z))} - C_{11} \frac{\chi}{\tilde{D}}, \tag{112}$$

$$U_1 = -\gamma v_0 \int (\chi w/\tilde{D}) dz - C_{11} \int (\chi/\tilde{D}) dz + C_2, \tag{113}$$

C_2 being an integration constant and the arguments of w and $\tilde{D}$ being $\psi(z)$.

¿From (69), which continues to hold as written, and (113), we have the other condition

$$\begin{aligned} 0 &= \int_{-\infty}^{\infty} F_u(\psi(z),0)\psi'(z)U_1(z) + (\kappa_0 + \alpha v_0)\sigma_1 \\ &= \int F_u \psi'(z) \left[-\gamma v_0 \int \tfrac{\chi w}{\tilde{D}} dz - C_{11} \int \tfrac{\chi}{\tilde{D}} dz + C_2 \right] + (\kappa_0 + \alpha v_0)\sigma_1, \end{aligned}$$

hence solving for C_2, we get

$$C_2 = (\alpha\tilde{\sigma} + \gamma\bar{p}^*)v_0 + \tilde{\sigma}\kappa_0 + \bar{q}^* C_{11},$$

where now

$$\begin{aligned} p^*(z) &= \int_{z_0}^{z} \tfrac{\chi w}{\tilde{D}} dz = \tfrac{w_\pm}{\tilde{D}_\pm} z \pm P^*/2 + o(1) \quad (z \to \pm\infty), \\ q^*(z) &= \int_{z_1}^{z} \tfrac{\chi}{\tilde{D}} dz = \tfrac{1}{\tilde{D}_\pm} z \pm Q^*/2 + o(1) \quad (z \to \pm\infty), \\ \bar{p}^* &= -\frac{\int p^* \rho dz}{\ell}, \\ \bar{q}^* &= -\frac{\int q^* \rho dz}{\ell}, \end{aligned}$$

and $\rho, \tilde{\sigma}, \ell$ are the same as before (see (72a), (72b), (18)).

¿From (113), (42), we have

$$\begin{aligned} u_1|_{\Gamma\pm} &= \mp\gamma v_0 P^*/2 \mp C_{11} Q^*/2 + C_2 \\ &= \mp\gamma v_0 P^*/2 \mp C_{11} Q^*/2 + (\alpha\tilde{\sigma} + \gamma\bar{p}^*)v_0 + \tilde{\sigma}\kappa_0 + \bar{q}^* C_{11} \\ &= {}_0(\alpha\tilde{\sigma} + \gamma\bar{p}^* \mp \gamma P^*/2) + \tilde{\sigma}\kappa_0 + (\bar{q}^* \mp Q^*/2)C_{11}. \end{aligned}$$

Also from (112), (41), we have

$$\tilde{D}\partial_r u_0|_{\Gamma\pm} = \pm\frac{\gamma v_0 \ell}{2} - C_{11},$$

$$C_{11} = \pm\frac{\gamma v_0 \ell}{2} - \tilde{D}\partial_r u_0|_{\Gamma\pm}.$$

Hence

$$u_1|_\pm + n_\pm(\tilde{D}\partial_r u_0)|_{\Gamma\pm} = m_\pm^* v_0 + \tilde{\sigma}\kappa_0,$$

$$m^*_\pm = \alpha\tilde{\sigma} + \gamma(\bar{p}^* \mp P^*/2) \pm \frac{1}{2}\gamma\ell(\bar{q}^* \mp Q^*/2), n_\pm = \bar{q}^* \mp Q^*/2.$$

This equation provides the interface condition on Γ analogous to (75). Hence the analog of (79) is

$$u + \epsilon n_\pm(\tilde{D}\partial_r u)_\pm = \epsilon m^*_\pm v + \epsilon\tilde{\sigma}\kappa.$$

We now construct the analog of (80). For this purpose, we write down the $O(\epsilon)$ terms in (110) (recall $\tilde{D}U_{1z} = 0$):

$$(dU_z)_2 + (vE)_1 + \kappa_0 \int \left(\hat{D}U_{2z} + \tilde{D}U_{1z}\right) dz + \int \partial_s \left(\hat{D}U_{1s}\right) dz + C_{12} = 0. \quad (114)$$

We apply (43) to obtain an equation for $\left(\tilde{D}\partial_r u\right)_1 |_{\Gamma\pm}$, which is given in terms of the asymptotic behavior of the first term in (114) according to (43). For this, we have to write each of the other 4 terms in (114) in the form $A^*_\pm(s,t) + B^*_\pm(s,t)z + o(1) \quad (z \to \pm\infty)$. Only the terms $A^*_\pm$ will be relevant (see (43)). The contribution of $(vE)_1$, by (42), is $(ve)_1|_{\Gamma\pm}$, and the last integral in (114) is bounded by virtue of the compact support of $\hat{D}$. By (111), the first integral can be expressed by means of (59) and (61) as

$$-\gamma v_0 \int w(\psi(z))dz - C_{11}z = -\gamma v_0 \left(w_\pm z \pm P/2\right) - C_{11}z + o(1) \quad (z \to \pm\infty).$$

Using all of these facts, we obtain

$$\left(\tilde{D}\partial_r u\right)_1 |_{\Gamma\pm} + (ve)_{1\pm} \mp \gamma\kappa_0 v_0 P/2 + \int_{z_0}^{\pm\infty} \partial_s \hat{D}(\psi(z))\partial_s U_1(z,s,t)dz + C_{12} = 0.$$

We take the difference between the upper and the lower signs and recall that $\hat{D}(\psi(z))$ does not depend on s, to obtain

$$\left[(\tilde{D}\partial_r u)_1\right] + [(ve)_1] - \gamma\kappa_0 v_0 P + \int_{-\infty}^{\infty} \hat{D}(\psi(z))\partial_s^2 U_1(z,s,t)dz = 0. \quad (115)$$

¿From (113) and the definitions of p^*, q^*, we may write

$$U_1 = v_0 M_{1\pm}(z;\gamma,\ell,\alpha) + \tilde{\sigma}\kappa_0 + M_3(z)(\tilde{D}\partial_r u_0)|_{\Gamma\pm},$$

$$M_{1\pm}(z) = -\gamma(p^*(z) - \bar{p}^*) \mp \frac{1}{2}\gamma\ell(q^*(z) - \bar{q}^*) + \alpha\tilde{\sigma},$$

$$M_3(z) = q^*(z) - \bar{q}^*.$$

Bear in mind that the M's do not depend on s, but that $v_0,\ \kappa_0,$ and u_0 do. We therefore have, from this and (115)

$$\left[\left(\tilde{D}\partial_r u\right)_1\right] = -\left[(ve)_1\right] + \gamma\kappa v P - a_\pm v_{ss} - b\kappa_{ss} - c\partial_s^2\left(\tilde{D}\partial_r u\right)|_{\pm 0}, \qquad (116)$$

where

$$a_\pm = \int_{-\infty}^{\infty} \hat{D}(\psi(z))M_{1\pm}(z)dz, \quad b = \tilde{\sigma}\int_{-\infty}^{\infty}\hat{D}(\psi(z))dz, \quad c = \int_{-\infty}^{\infty}\tilde{D}M_3 dz,$$

and we have dropped the subscripts "0" on the right of (116). On the right side of (116), either sign may be chosen.

The corrections to the next order Stefan problem due to enhanced diffusion, therefore, are as follows. Equations (77)'=(94) and (79)'=(96) are unchanged except for replacing d by $\tilde{D}$ and a slightly different definition of $m_\pm$. But (80)'=(97) becomes

$$\left[\tilde{D}\partial_r u\right] = -[ve] + \epsilon\left(\gamma\kappa v P - a_\pm v_{ss} - b\kappa_{ss} - c\partial_s^2\left(\tilde{D}\partial_r u_0\right)|_{\pm 0}\right) \ (80)" = (117)$$

Thus, $O(\epsilon)$ corrections to the Stefan condition are found, depending on the second derivatives of the velocity and curvature.

The new form of the special limit Mullins-Sekerka problem in Sec. 14 is perhaps more interesting, and constitutes the main point of this section. The interface condition (89c) is changed to

$$\left[\tilde{D}\partial_r \bar{u}\right] = \gamma\bar{v}\ell - b\kappa_{ss} \ \text{ on } \ \Gamma. \qquad (89c)" = (118)$$

As mentioned before, the extra term represents the diffusion of heat within the interface itself. Thus the Mullins-Sekerka problem (89) is now modified by this additional term in the Stefan condition.

A comment about the qualitative behavior of this free boundary problem is in order. It is well known that solutions of (89) or (89)'=(103) for which the interface encloses a region $\mathcal{D}_-$ whose closure is contained in a bounded domain $\mathcal{D}$, and for which $\bar{u}$ satisfies zero Neuman conditions on the outer boundary $\partial\mathcal{D}$, have the curve–shortening and area–preserving properties. Thus if $L(t)$ is the length of $\Gamma(t)$ and $A(t)$ is the area of $\mathcal{D}_-(t)$, we have

$$\frac{dL}{dt} \le 0; \quad A(t) = const. \qquad (119)$$

It is easily shown that our present revision of this problem with (118) replacing (103c) has the same properties (119). In fact

$$0 = \int_{\mathcal{D}} \bar{u}\nabla\cdot\tilde{D}_{\pm}\nabla\bar{u} = -\int_{\mathcal{D}} \tilde{D}_{\pm}\left|\nabla\bar{u}\right|^2 - \int_{\Gamma}\bar{u}\left[\tilde{D}\partial_r\bar{u}\right]$$

$$\leq \int_{\Gamma}\bar{u}\left(\gamma v\bar{\ell}+b\kappa_{ss}\right) = \tilde{\sigma}\int_{\Gamma}\kappa\left(\gamma v\bar{\ell}+b\kappa_{ss}\right)$$

$$= \tilde{\sigma}\gamma\bar{\ell}\int_{\Gamma}\kappa v + \tilde{\sigma}b\int_{\Gamma}\kappa\kappa_{ss} = \tilde{\sigma}\gamma\bar{\ell}\frac{dL}{dt} - \tilde{\sigma}b\int_{\Gamma}(\kappa_s)^2$$

$$\leq \tilde{\sigma}\gamma\bar{\ell}\frac{dL}{dt},$$

hence

$$\frac{dL}{dt} \leq 0.$$

The other relation in (119) is derived in the same manner.

18 Multicomponent order parameter.

It is commonplace to describe the local microscopic or macroscopic state of a crystalline material by means of a multicomponent order parameter (see, e.g., [IS] and recent papers [Lai], [BB]).

Going further, we remark that in some density–functional theories (e.g. [Ha]), the microscopic probability distribution of atoms at any location is described by a number density function. This function provides detailed information about the degree to which, and sense in which, the material is ordered at that location. It is therefore an infinite–dimensional generalization of a scalar order parameter. One way to extract a scalar order parameter ϕ from such a theory was described in [PF1], namely artificially to restrict the allowed density functions to a one–dimensional subspace of function space. Then the scalar ϕ serves to designate locations on that 1–D subspace, which can be pictured as a straight line. In the resulting phase–field model, the transition from liquid to solid across an interface corresponds to the density function changing while restricted to that line, whereas in the unrestricted model, it may change along some other curve in function space. In principle, this discrepancy could be partially remedied by restricting to a higher dimensional subspace, in which case we would be dealing with several order parameters.

We sketch now how our analysis of interfacial motion can be extended to the case when the order parameter has m components,

$$\phi = (\phi_1, \cdots \phi_m). \tag{120}$$

To avoid compounding complications, we treat D, c, and α as constants, and continue to operate in 2-dimensional physical space. We consider only first order transitions.

As mentioned in Sec. 1 , the system (2), (3) was derived in [PF1] as a gradient system with respect to the entropy functional displayed following (3). Thus, the right side of (3) is $\frac{\delta S}{\delta \phi}$. $\Big($Note that $-\frac{1}{T}\frac{\partial f(\phi,T)}{\partial \phi} = \frac{\partial \bar{s}(\phi,\bar{e})}{\partial \phi}$.$\Big)$

The gradient term $-\frac{1}{2}\kappa_1|\nabla\phi|^2$ in that functional was chosen as the simplest negative definite quadratic function of $\nabla\phi \equiv (\partial\phi/\partial x_1, \partial\phi/\partial x_2)$. In the case when ϕ has several components, the analogous term must still be a negative definite function of $\nabla\phi$, and we still choose it to be a quadratic form. We denote it by $-\frac{1}{2}Q(\nabla\phi)$. Thus the more general entropy functional is

$$S\,[\phi,\bar{e}] = \int_\Omega \left\{ s(\phi(x),\bar{e}(x)) - \frac{1}{2}Q(\nabla\phi) \right\} dx. \tag{121}$$

We have considerable latitude in choosing Q, including the possibility of making it anisotropic. Even with one order parameter, anisotropy can alternatively be modelled [MW] by making κ_1 depend on the direction θ of $\nabla\phi$, but if this dependence is not such that $\kappa_1(\theta)|\nabla\phi|^2$ continues to be a quadratic form, the Laplacian in (3) is replaced by a quasi-linear second order partial differential operator whose coefficients depend discontinuously on $\nabla\phi$ at places where $\nabla\phi = 0$.

The most general form Q, in the case of m components, is

$$Q(\nabla\phi) = \kappa_1 \Sigma_{ijk\ell} a_{ijk\ell} \partial_i\phi_k \partial_j\phi_\ell,$$

where $\partial_i = \partial/\partial x_i$ and the a's form a positive definite array and are symmetric in the pair (i,j) (which run from 1 to 2) as well as the pair (k,ℓ) (which run from 1 to m). The normalizing parameter κ_1 is chosen so that

$$\mathrm{Min}_X \Sigma a_{ijk\ell}\xi_i^k\xi_j^\ell = 1,$$

where $X = \Big\{\xi_i^k : \sum_{k,i}|\xi_i^k|^2 = 1\Big\}$.

Our new assumptions A1 – A4 are analogous to those given before in section 2:

A1'. As before, $f(\phi,T)$ has two and only two local minima with respect to ϕ, which are now m-tuples ϕ denoted as before by $h_\pm(T)$. We can no longer order them or speak of a single intermediate maximum. (The following can be partially extended to the case when there are more than two minima; we do not pursue this.)

A2'. Again, for a first–order transition, equation (5) holds if and only if $T = T_0 \in (T_-, T_+)$.

Set $\phi_\pm = h_\pm(T_0)$.

The "inner layer" equation generalizing (20) and (44) is the system of equations

$$A\frac{d^2\phi}{\partial z^2} - \frac{1}{\gamma c T_0}\nabla_\phi f(\phi, T_0) = 0, \tag{122}$$

where A is a positive definite symmetric $m \times m$ matrix obtainable from Q, which in general depends on the orientation of the interface (see the definition of A below), and ∇_ϕ means $(\partial/\partial\phi_1, \ldots, \partial/\partial\phi_m)$.

A3'. For all such matrices A, (122) has a solution $\psi(z)$ satisfying

$$\psi(\pm\infty) = \phi_\pm, \tag{123}$$

which is unique except for translation. Moreover, we assume the solution $\psi(z)$ approaches its limits exponentially. (There are important and interesting cases then uniqueness fails; our analysis can be partly extended to many of those cases.)

Note (a) in case $m = 1$, A3' is known to be guaranteed if (5) and (6) hold. Also (b) by taking the L_2^m inner product of (122) with the vector $\partial\psi/\partial z$, it is seen that (5) is a necessary condition for A3' to hold. Existence theorems for boundary value problems such as (122), (123) have been proved in [S] and [Chm]; in the latter paper examples were given in which uniqueness does not hold.

A4'. the same as before.

We nondimensionalize as before, except that γ in (11) is chosen so that

$$\mathrm{Max}_\phi |\nabla_\phi F(\phi, 0)| = 1,$$

which replaces (12).

The changes in the previous analysis are as follows.

In the generalization of (15), α becomes a positive diagonal matrix, $F(\phi, u)$ is now defined to be $-\frac{1}{\gamma c T}\nabla_\phi f(\phi, T(u))$, and $\nabla^2\phi$ is replaced by the partial differential operator $E\phi$ defined by

$$(E\phi)_k = \sum_{ij\ell} a_{ijk\ell}\partial_i\partial_j\phi_\ell.$$

The equation analogous to (37) is

$$\left[A\phi_{zz} + \epsilon B\kappa\phi_z + \epsilon C\phi_{zs} + \epsilon\alpha v\phi_z + O(\epsilon^2)\right] + F(\phi, u) = 0, \tag{124}$$

where the matrices A, B, and C depend on the angle θ of orientation of Γ at the point s as follows. We represent the unit normal to Γ pointing into $\mathcal{D}_+$ by $\nu = (\cos\theta, \sin\theta)$, and the unit tangent vector obtained by rotating it through an angle $\pi/2$ in the positive direction by $\tau = (-\sin\theta, cos\theta)$. Then

$$(A(\theta))_{k\ell} = \sum_{ij} a_{ijk\ell}\nu_i\nu_j,$$

$$(B(\theta))_{k\ell} = \sum_{ij} a_{ijk\ell}\tau_i\tau_j,$$

$$(C(\theta))_{k\ell} = \sum_{ij} a_{ijk\ell}\left(\nu_i\tau_j + \nu_j\tau_i\right).$$

Notice that

$$dA(\theta)/d\theta = C(\theta), \quad dC(\theta)/d\theta = 2(B(\theta) - A(\theta)) \tag{125}$$

From (124), we see that the inner profile is governed by the following system of differential equations to replace (44):

$$A(\theta)\Phi_{0zz} + F(\Phi_0, 0) = 0, \quad \Phi_0(\pm\infty) = \phi_\pm. \tag{126}$$

This is (122), (123) with A depending on θ; we again denote the solution by $\psi(z,\theta)$.

Also, in place of (69), we obtain the following system from the $O(\epsilon)$ terms in (124); here we use the fact that $\partial_s = \kappa\partial_\theta$, and let primes denote $\partial/\partial z$:

$$L\Phi_1 = -F_u(\psi(z,\theta),0)U_1 - \kappa_0 B(\theta)\psi'(z,\theta) - \kappa_0 C(\theta)\partial_\theta\psi'(z,\theta) - v_0\alpha\psi'(z,\theta), \tag{127}$$

L is the self-adjoint ordinary differential operator defined by

$$L\Phi \;\equiv\; A(\theta)\Phi'' - G(z,\theta)\Phi,$$

and the symmetric matrix function $G(z,\theta)$ is the Hessian of the function $-\frac{1}{\gamma c T_0}f(\phi, T_0)$ with respect to ϕ, evaluated at $\phi = \psi(z,\theta)$.

Differentiating (126) with respect to z, we find that

$$L\psi' = 0; \tag{128}$$

taking the $(L_2)^m$ scalar product of (127) with ψ', we find a necessary condition for solvability:

$$\langle F_u(\psi(z,\theta),0)U_1, \psi'\rangle + \omega(\theta)\kappa + v\langle\alpha\psi', \psi'\rangle = 0, \tag{129}$$

where

$$\omega(\theta) = \langle B\psi', \psi'\rangle - \langle C\partial_\theta\psi, \psi''\rangle. \tag{130}$$

From this point on the analysis proceeds as before. The basic first order outer approximation satisfies a free boundary problem like (77) - (80) with different coefficients of κ and v in the $O(\epsilon)$ terms. These coefficients depend on θ. For example, in place of $\tilde{\sigma}$ in (79), we have $-\frac{\omega(\theta)}{\ell}$, and in place of α, we have $\langle\alpha\psi', \psi'\rangle/\sigma_1 \equiv \tilde{\alpha}(\theta)$, where now

$$\sigma_1 = \sigma_1(\theta) = \langle A(\theta)\psi', \psi' \rangle. \tag{131}$$

The various limiting problems are obtained as before. Of special interest is the Mullins-Sekerka problem (89), in which the coefficient $\tilde{\sigma}$ of κ in (89b) is replaced by the θ-dependent coefficient given above. A similar statement is true of the motion-by-curvature problem (90), in which the present analog will have a coefficient of κ proportional to ω. Very probably the sign of this coefficient, which is governed by the sign of ω, determines whether these problems are well posed. For this reason, it is of some interest to obtain a simpler expression for ω.

In their treatment of a different phase-field model with scalar order parameter but interfacial energy a given arbitrary function of θ, McFadden et al [MW] obtained an expression, which in our notation would be

$$\omega(\theta) = \sigma_1(\theta) + \sigma_1''(\theta). \tag{132}$$

This also holds in our framework, of course, when $m = 1$, as can be verified by a calculation based on our notation. However, this calculation depends very much on the matrices $A,\ B,\ C$ being able to commute with one another. It appears doubtful that the expression (132) will continue to hold in the multi-component case.

Appendix. Derivation of (31)

Let us represent points on the curve $\Gamma(t)$ by the position vector $R(\xi, t)$, where ξ is a parameter on Γ defined as follows. When $t = 0$ it is arc length from some chosen point. When t increases, the point $R(\xi, t)$ (for fixed ξ) has trajectory normal to $\Gamma(t)$ at each t. We will denote the unit tangent to $\Gamma(t)$ by $T(\xi, t)$ and the unit normal in the direction of increasing r by $N(\xi, t)$.

The normal velocity $v(\xi, t)$ is defined by

$$R_t = v(\xi, t)N(\xi, t). \tag{133}$$

Let σ be arc length on Γ, and

$$\alpha(\xi, t) = \frac{\partial \sigma}{\partial \xi}(\xi, t). \tag{134}$$

At $t = 0$, we have chosen $\xi = \sigma$, so that

$$\alpha(\xi, 0) = 1. \tag{135}$$

In all of the following, we suppose $\Gamma(t)$ is regular; and in particular that its radius at curvature is bounded away from zero.

Consider the point $x(r, \xi, t)$ represented by

$$x(r, \xi, t) = R(\xi, t) + rN(\xi, t). \tag{136}$$

For fixed r and t the curve $x(r,\xi,t)$ will be "parallel" to $\Gamma(t)$ at a distance r. On this new curve, we can find the relation between arc length (which we continue to denote by σ) and the parameter ξ. First, taking the differential of (136) with t and r fixed, we obtain:

$$dx = (R_\xi + rN_\xi)d\xi.$$

But by definition we also have $dx = Td\sigma$. Therefore

$$Td\sigma = (R_\xi + rN_\xi)d\xi. \tag{137}$$

We also have from (134)

$$R_\xi = \alpha T, \tag{138}$$

and since $T \cdot N = 0$,

$$T_\xi \cdot N + T \cdot N_\xi = 0. \tag{139}$$

The curvature $\kappa(\xi,t)$ of $\Gamma(t)$ is given by

$$\kappa N = -T_\sigma = -T_\xi \frac{\partial \xi}{\partial \sigma}(\xi,t) - -\alpha^{-1}T_\xi. \tag{140}$$

Hence from (139), (140) and the fact that N_ξ is in the direction of T (note that $\frac{\partial}{\partial\xi}|N|^2 = N_\xi \cdot N$), we have

$$N_\xi = \alpha\kappa T. \tag{141}$$

From (137), (138), and (141) we now obtain

$$\frac{\partial\sigma}{\partial\xi} = \alpha(2 + r\kappa). \tag{142}$$

Since R_t and R_ξ are in the directions N and T respectively, we have

$$R_t(\xi,t) \cdot R_\xi(\xi,t) = 0.$$

Differentiating this equation with respect to t, we obtain

$$R_{tt} \cdot R_\xi + R_t \cdot R_{\xi t} = 0. \tag{143}$$

But from (133)

$$R_{tt} = v_t N + vN_t, \tag{144}$$

$$R_{\xi t} = v_\xi N + vN_\xi; \tag{145}$$

So from (143)–(145), (133), (138), we have

$$N_t = -\alpha^{-1}v_\xi T. \tag{146}$$

If we set $dx = 0$ in (136) and use (138), (133), (141), (146), we find:

$$\frac{\partial r}{\partial t} = -v, \tag{147}$$

and

$$\frac{\partial \xi}{\partial t} = \frac{r v_\xi}{\alpha^2(2 + r\kappa)}. \tag{148}$$

Now recall the coordinate system $r(x,t)$, $s(x,t)$ defined in section 4 (we suppress ϵ–dependence). This $r(x,t)$ is that in (136). At $t = 0$, this s coincides with the previous ξ. So at $t = 0$, we may replace ξ with s in (142), set $\alpha = 1$, and obtain

$$|\nabla s(x,0)| = \frac{\partial s}{\partial \sigma} = (2 + r\kappa(s,0))^{-1}.$$

Howerver, if $t = t_0$ is any other value of t, we can reset the clock in the original coordinate system (r, ξ, t) so that time starts at t_0, and make the same conclusion. Therefore in general we will have

$$|\nabla_x s(x,t)| = (2 + r\kappa(s,t))^{-1}. \tag{149}$$

In the same way, we find from (147), (148)

$$\frac{\partial r}{\partial t}(x,t) = -v(s(x,t),t), \tag{150}$$

$$\frac{\partial s}{\partial t}(x,t) = \frac{r v_s(s,t)}{1 + r\kappa(s,t)}. \tag{151}$$

In these expressions, we have taken $\alpha = 1$ because of (135) and the change of time setting.

Along with (149), we also have the obvious relation

$$|\nabla_x r(x,t)| = 1. \tag{152}$$

We have established (31a) and part of (31c). Let us now calculate $\nabla^2 r$ and $\nabla^2 s$. We have, for any domain Ω,

$$\int_\Omega \nabla_x^2 r(x,t)dx = \int_{\partial\Omega} \partial_n r(x,t) d\ell, \tag{153}$$

where ∂_n is the normal derivative and $d\ell$ is arc length on $\partial\Omega$.

Let Ω be the curvilinear rectangle (in the r, s coordinate system) shown in the diagram, bounded by sides $L_1 - L_4$.

As $\partial_n r = 0$ on L_2 and L_4, we get:

$$\int_{L_1 \cup L_3} \partial_n r d\ell = |L_3| - |L_1|.$$

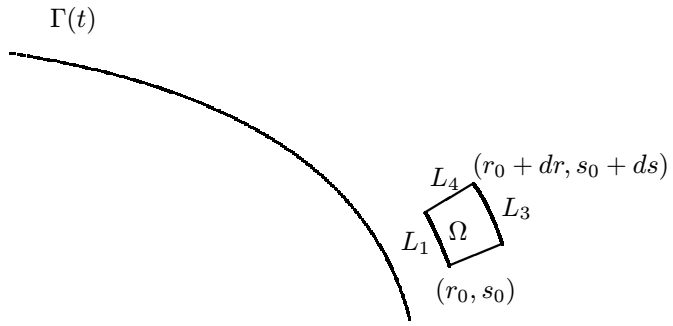

Figure 2: The domain Ω

On L_1 and L_3 we have (149), so that

$$|L_1| \simeq (2 + r_0\kappa(s_0, t))ds,$$

$$|L_3| \simeq (2 + (r_0 + dr)\kappa(s_0, t))ds,$$

so that

$$\int_\Omega \nabla_x^2 r(x, t)dx \simeq \kappa(s_0, t)drds.$$

But the left side of this equation, to lowest order is $\nabla^2 r(s_0, t)$ times the area of Ω, and this area is approximately

$$|\Omega| \simeq |L_1|dr = (2 + r_0\kappa(s_0, t))drds.$$

Thus

$$\nabla^2 r(x, t) = \frac{\kappa(s, t)}{1 + r\kappa(s, t)}. \tag{154}$$

In a similar way, we have

$$\int_\Omega \nabla_x^2 s(x, t)dx = \int_{L_4} (2 + r\kappa(s_0 + ds, t))^{-1}dr - \int_{L^2} (2 + r\kappa(s_0, t))^{-1}dr.$$

Now writing $\kappa(s_0 + ds, t) = \kappa(s_0, t) + d\kappa$ and integrating between r_0 and $r_0 + dr$, we obtain to lowest order,

$$\nabla^2 s(x, t) = \frac{r\kappa_s}{(2 + r\kappa)^3}.$$

This establishes (31b,c).

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References

[ABC] N. Alikakos, P. Bates, and X. Chen, Convergence of the Cahn–Hilliard equation to the Hele–Shaw model, Arch. Rat. Mech. Anal. **128**, 165-205 (1994).

[AC] S.M. Allen and J.W. Cahn, A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening, Acta Metallurgica **27**, 1085–1095 (1970).

[AP1] H.W. Alt and I. Pawlow, A mathematical model of dynamics of non–isothermal phase separation, Physica D, in press.

[AP2] H. W. Alt and I. Pawlow, Models of non–isothermal phase transitions in multicomponent systems, Part I: Theory. preprint.

[BB] B. Boettinger, R. Braun, J. Cahn, J. McFadden, and A. Wheeler, Phase-field model of order-disorder transitions in an FCC crystal, preprint.

[Cahn] Personal communication.

[C1] G. Caginalp, An analysis of a phase field model of a free boundary, Arch. Rat. Mech. Anal. **92**, 205–245 (1986).

[C2] G. Caginalp, Stefan and Hele–Shaw type models as asymptotic limits of the phase field equations, Phys. Rev. A **39**, 5887–5896 (1989).

[C3] G. Caginalp, Penrose–Fife modification of solidification equations has no freezing or melting, Appl. Math. letters **5**, 93–96 (1992).

[CC] G. Caginalp and X. Chen, Phase field equations in the singular limit of sharp interface problems, in On the Evolution of Phase Boundaries, IMA Vol. of Mathematics and its Applications, Springer-Verlag, 1992.

[CF] G. Caginalp and P.C. Fife, Dynamics of layered interfaces arising from phase boundaries, SIAM J. Appl. Math. **48**, 506–518 (1988).

[CA] J.W. Cahn and S.M. Allen, A microscopic theory for antiphase boundary motion and its experimental verification in Fe-Al alloy domain growth kinetics, Jour. de Physique, Colloque C–7, **54** (1977).

[CEN] J.W. Cahn, C.N. Elliott, and A. Novick–Cohen, The Cahn-Hilliard equation with a concentration dependent mobility: motion by minus the Laplacian of the mean curvature, preprint.

[CT] J.W. Cahn and J.E. Taylor, Surface motion by surface diffusion, Acta Metall, in press.

[Chen1] Xinfu Chen, Generation and propagation of interface in reaction–diffusion equations, J. Diff. Equations **96**, 116–141 (1992).

[Chen2] Xinfu Chen, Hele-Shaw problem and area preserving curve shortening motion, Arch. Rat. Mech. Anal. **123**, 117-151 (1993).

[Chen3] Xinfu Chen, Personal communication.

[Chm] A. Chmaj, On the existence of a heteroclinic solution of a 'phase transition' Hamiltonian system: a variational approach, preprint.

[CP] P. Constantin and M. Pugh, Global solutions for small data to the Hele-Shaw problem, preprint.

[F1] P. C. Fife, Mathematical Aspects of Reacting and Diffusing Systems, Lecture Notes in Biomathematics 28, Springer–Verlag, New York, 1978.

[F2] P. C. Fife, Dynamics of Internal Layers and Diffusive Interfaces, CBMS–NSF Regional Conference Series in Applied Mathematics #53, Soc. Ind. Appl. Math, Philadelphia (1988).

[F3] P.C. Fife, Pattern dynamics for parabolic P.D.E.'s, preprint.

[F4] P. C. Fife, Models for phase separation and their mathematics, in Nonlinear Partial Differential Equations with Applications to Patterns, Waves, and Interfaces, M. Mimura and T. Nishida, eds., pp. 183-212, KTK Sci. Pubs., Tokyo (1992).

[Fix] G. Fix, Phase field methods for free boundary problems, in: Free Boundary Problems, A. Fasano and M. Primicerio, eds., 589–589, Pitman, London (1983).

[Ha] A.D.J. Haymet, Theory of the equilibrium liquid–solid transition, Ann. Rev. Phys. Chem **38**, 89–108 (1987).

[He] C. Herring, in Structure and Properties of Solid Surfaces, R. Gomer and C. S. Smith, eds., Univ. of Chicago Press, Chicago (1952).

[IS] Yu. A. Izyumov and V. N. Syromyatnikov, Phase Transitions and Crystal Symmetry, Kluwer Acad. Pubs., Dordrecht, 1990.

[K] R. Kobayashi, Bull. Japan Soc. Ind. Appl. Math. 1, 22 (1991).

[L] J. S. Langer, Models of pattern formation in first–order phase transitions, pp. 164–186 in Directions in Condensed Matter Physics, World Science Publishers (1986).

[Lai] Theory of ordering dynamics for Cu_3Au, Phys. Rev. B **41**, 9239-9256 (1990).

[MW] G. B. McFadden, A. A. Wheeler, R. J. Braun, S. R. Coriell, and R. F. Sekerka, Phase-field models for anisotropic interfaces, Phys. Rev. E, **48**, 2016-2024 (1993).

[MS] W.W. Mullins and R. F. Sekerka, Morphological stability of a particle growing by diffusion or heat flow, J. Appl. Phys. **34**, 323–329 (1963).

[MSc] P. de Mottoni, and M. Schatzmann, Geometrical evolution of developed interfaces, Trans. Amer. Math. Soc., in press.

[P] R.L. Pego, Front migration in the nonlinear Cahn–Hilliard euqation, Proc. Roy. Soc. London A **422**, 261–278 (1989).

[PF1] O. Penrose and P.C. Fife, Thermodynamically consistent models of phase–field type for the kinetics of phase transitions, Physica D **43**, 44–62 (1990).

[PF2] O. Penrose and P.C. Fife, Comment on Caginalp's paper "Penrose–Fife modification of the solidification equations has no freezing or melting", App. Math. Letter **5**, 99 (1992).

[PF3] O. Penrose and P.C. Fife, On the relation between the standard phase–field model and a "thermodynamically consistent" phase–field model, Physica D **69**, 107–113 (1993).

[RSK] J. Rubinstein, P. Sternberg, and J.B. Keller, Fast reaction, slow diffusion and curve shortening, SIAM J. Appl. Math. **49**, 116–133 (1989).

[S] P. Sternberg, The effect of a singular perturbation on nonconvex variational problems, Arch. Rat. Mech. Ana. **101**, 209-260 (1988).

[St] B. Stoth, A model with sharp interface as limit of phase-field equations in one space dimension, preprint.

[St2] B. Stoth, The Stefan problem coupled with the Gibbs-Thompson law as a singular limit of the phase-field equations in the radial case, preprint.

[T] L. Truskinovsky, Kinks versus shocks, in Shock Induced Phase Transitions and Phase Structures in General Media (R. Fosdick et al, eds.) Springer–Verlag, Berlin (1992).

[UR] A.P. Umantsev and A.L. Roitburd, Nonisothermal relaxation in nonlocal media, Sov. Phys. Solid State **30**, 651 (1988).

[WS] S–L. Wang, R.F. Sekerka, A.A.Wheeler, B.T. Murray, S.R. Coriell, R.J. Braun, and G.B. McFadden, Thermodynamically–consistent phase–field models for solidification, Physica D **69**, 189-200 (1993).

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