On thermodynamically consistent schemes for phase field equations

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Abstract

This paper addresses the issue of thermodynamically consistent derivations of field equations governing nonisothermal processes with diffuse interfaces and their implications for interface conditions in the associated sharp interface theories. We operate within the framework of extended irreversible thermodynamics, allowing gradient terms to be present not only in the free energy and entropy densities but also in the internal energy, for both nonconserved and conserved order parameter theories. These various gradient terms are shown to relate to the splitting of the surface tension into an energetic and an entropic part.

It is shown that the principle of nondecreasing local entropy production does not single out uniquely the form of the governing field equations. Instead it leads naturally to a one-parameter family of alternative theories which do not contradict the Curie principle of irreversible thermodynamics.

The principal applications are to the solidification of a pure material and of a binary alloy. In the case of a pure substance an asymptotic analysis is developed in the vicinity of the solidification front. The main effect of the alternative theories, as well as of the splitting of the surface tension, on the corresponding free boundary problem is manifested in the first order terms in the nonequilibrium contributions to the interface undercooling. We also consider the possibility of assigning from empirical data some specific values to the phenomenological parameters involved in these models.

1 Introduction

Models of phase transformations in continuum mechanics can be divided into two main classes: sharp interface models and models with diffuse interfaces. We begin with a brief historical review of their derivations within the standard scheme of classical irreversible thermodynamics (CIT).

In the case of sharp interface models, one assumes local thermodynamic equilibrium at each point in the bulk phases, so that the Gibbs equation holds at each point:

$$de = Tds - Pd(1/\rho) + \Sigma_a \mu_a dc_a. \tag{1}$$

Here e, s and ρ are specific internal energy, entropy, and mass, and μ_a and c_a are the chemical potential and the mass concentration of component "a".

Following Caroli et al [1], for example, one may now incorporate phase interfaces into this scheme by introducing "two-phase" densities of mass, momentum, energy and entropy. They utilize step functions which are characteristic functions for each phase, and the respective interfacial densities are represented by delta-functions. The evolution equations for such two-phase densities incorporate balance equations both in the bulk and at the phase change front.

A somewhat different approach of Charach and Zemel [2] combines balance equations in each phase with the generalized Reynolds transport theorem, leading to balance equations at the sharp interface. For each phase,

$$\frac{\partial(\rho F_i)}{\partial t} = -\nabla \cdot (\rho \vec{v}_i F_i + \vec{J}_{F_i}) + Q_{F_i}. \tag{2}$$

Here i denotes the phase, F_i stands for an appropriate density (mass, momentum, energy, entropy), $\vec{v}_i$ is the velocity of the i-th phase, $\vec{J}_{F_i}$ is the flux of F_i, and Q_{F_i} is the bulk source of F_i.

The sharp interface balance laws then assume the form

$$\int_\Sigma \{F(\vec{J}\hat{n}) + \vec{J}_F \hat{n}\} d\Sigma = \int_\Sigma Q_{F\Sigma} d\Sigma - \int_{\partial\Sigma} J_{F1} dl, \tag{3}$$

where the symbol $\{...\}$ denotes the magnitude of the jump discontinuity, across the interface, of the quantity inside brackets; i.e. its value with subscript i assigned to one phase minus its value at the other phase. The symbol $\hat{n}$ represents the normal to the interface Σ, $\vec{J}_F$ was defined above, and $\vec{J} = \rho_i(\vec{v}_i - \vec{V})$, with $\vec{V}$ the interface velocity (this expression is independent of i). Finally, $Q_{F\Sigma}$ is the surface source of F at the interface and J_{F1} is the surface flux of F through the boundary of Σ.

The above formulation yields a free boundary problem. The constitutive equations for the J's are chosen to be consistent with an entropy principal stating that the local entropy production has to be nonnegative. In the usual linear approach of CIT, the governing equations in the bulk come out simply to be the standard diffusion equations for heat and mass, and the Navier-Stokes equations for the momentum. The balance of momentum at the interface embodies in itself the capillarity pressure. When applied to the interface, the requirement of nonnegative entropy production at the phase front restricts the interfacial kinetics processes. It yields that the kinetic undercooling at the phase interface is proportional to the interface velocity.

The above is not meant to be a complete survey of sharp interface theories; indeed the literature is substantial. For example a different, more mechanical, approach has been taken by Gurtin; see [3] for a two-dimensional version.

It was realized already in the early studies of Young, Poisson, and others that sharp interface models face difficulties in addressing capillarity phenomena. This was the key argument in the subsequent early works of van der Waals, Rayleigh, and many others, who attempted to replace the surfaces of discontinuity by diffuse interfaces. Van der Waals was the first to account for the fact that the free energy depends both on the local density or composition and on the distribution of these quantities in the immediate environment. His work and some other early theories of diffuse interfaces are discussed in the monograph of Rowlinson and Widom [4].

Introducing gradient terms of order parameters into the free energy functional has the effect of producing diffuse interfaces. Phase field theories incorporate such terms as a simple penalty for spatial nonuniformity, and treat the order parameters on the same footing as those of temperature and concentration. Order parameters in some theories are defined clearly in terms of concentrations or the arrangements of atoms on lattices; however other nonconserved order parameter fields are often defined only in phenomenological terms.

Van der Waals was in effect the first to use gradient terms this way, and the idea was rediscovered and fully appreciated in the pioneering papers of Cahn and Hilliard ([5] and later papers) that started the subject known today as the conserved order parameter theories. Nonconserved order parameter fields were handled this way later by Allen and Cahn ([6] and others; for a related treatment see [7]).

Isotropic isothermal nonuniform systems were the first to be considered.

For them, one postulates a free energy functional

$$F[\Phi] = \int_\Omega [f(\Phi(r)) + \frac{1}{2}\epsilon_F^2 |\nabla\Phi(r)|^2] dv, \tag{4}$$

where f is the local density of the Helmholtz free energy, Φ is the order parameter, and ϵ_F is a small coupling parameter for the gradient term, which may depend on temperature. The dynamical equation for Φ then takes the form

$$\tau \frac{\partial \Phi}{\partial t} = -\frac{\delta F}{\delta \Phi} \quad \text{or} \quad \frac{\partial \Phi}{\partial t} = \nabla \cdot D \nabla \frac{\delta F}{\delta \Phi},$$

according to whether Φ is nonconserved or conserved.

This approach is in accord with the Landau-Ginzburg theory of phase transformations [8]. It has been further extended to nonisothermal solidification processes in pure substances (see e.g. [8, 9, 10, 11, 12, 13]) and to a nonisothermal Cahn-Hilliard theory in [14] and other places. In fact in very recent years, there has been much progress in developing thermodynamically consistent theories of phase transitions in which the free energy and other thermodynamic quantities depend on gradients of order parameters. We mention the notable papers by Alt and Pawlow [15] - [17] as being especially careful and mathematically complete studies. Many applications of these theories exist; see for example the references in [17].

We shall outline the basic features of the simpler temperature-dependent phase field theories for a pure substance, as in [10, 13] and elsewhere. The difference in densities between the phases is disregarded, so that the phase is defined only in terms of a nonconserved order parameter Φ. The order parameter field is phenomenological and relates to "the degree to which the substance is in the liquid phase," or it may represent the degree to which the local material is ordered, in both cases "on a scale from -1 to 1".

The free energy density f in (4) is now taken to depend also on temperature T: $f = f(\Phi, T)$. When $\Phi = \pm 1$, which are taken to be the values of Φ representing the two pure phases, the function f is the free energy function appropriate for that particular phase; it is then continued for all values of Φ between those two extreme values, in such a way that it has local minima with respect to Φ at $\Phi = \pm 1$. (Although the locations of these minima may in principle depend on T, we assume here that they do not.) Thus f is of "double well type". Further restrictions on the choice of free energy density are as follows: (i) at the coexistence temperature T_m (equilibrium freezing point), the values of the local minima corresponding to solid and liquid are equal; and (ii)

$$\frac{d}{dT}[f(1,T) - f(-1,T)] > 0, \tag{5}$$

so that above the temperature T_m the minimum of f corresponding to the liquid has to be lower than that for the solid, and vice versa below the freezing point.

Evolution equations for the order parameter and temperature are now sought. Typically, they do not strictly follow from statistical-mechanical formulations, and refer to coarse grained quantities defined phenomenologically. Hence the derivation of the equations should be in accord with the principles of irreversible thermodynamics. The isothermal theories mentioned above indeed guarantee the monotonic decrease of the free energy during isothermal processes.

The situation is less clear for nonisothermal processes. In the first phase-field models the coupling of order parameter theories with heat diffusion was usually based on intuitive considerations only; an energy balance equation was simply appended to the dynamical equation for Φ which would be obtained in isothermal situations. Penrose and Fife [13], however, proposed a recipe which involves, as starting point, an entropy functional $S\{e,\Phi\}$:

$$S = \int_\Omega \left[s(e(\vec{r}), \Phi(\vec{r})) - \frac{1}{2}\epsilon_S^2 |\nabla\Phi(\vec{r})|^2 \right] dv, \tag{6}$$

where s is the entropy density, a function of the energy density e and the order parameter Φ.

The evolution equations for e and Φ, hence for T and Φ, in this and other papers employ the variational derivatives of the entropy functional in accord with thermodynamics, i.e. in such a way as to ensure that the entropy of an isolated system is nondecreasing in time. This approach is close in spirit to the work of Umantsev and Roitburd [23] on nonisothermal relaxation in a nonlocal medium and has been further extended in recent publications [18, 24].

More recently, Umantsev [25], Alt and Pawlow [15] - [17] (in more general settings) and Wheeler, McFadden, and Boettinger (WMB) [26] introduced gradient terms not only in the free energy and entropy functionals but also in the internal energy functional

$$E\{e,\Phi\} = \int_\Omega \left[e(s(\vec{r}), \Phi(\vec{r})) + \frac{1}{2}\epsilon_E^2 |\nabla\Phi(\vec{r})|^2 \right] dv. \tag{7}$$

Thermodynamic consistency now requires

$$\epsilon_F^2 = \epsilon_E^2 + T\epsilon_S^2. \tag{8}$$

These authors derived thermodynamically consistent equations for processes coupling heat diffusion to the dynamics of an order parameter field. Those equations are considerably more complicated than those with $\epsilon_E = 0$.

The gradient theories discussed above are very close in spirit to the relatively new branch of thermodynamics known as Extended Irreversible Thermodynamics (EIT). In this approach, summarized in a recent monograph of Jou, Casas-Vasquez and Lebon [27], the entropy density depends locally not only on the internal energy and the specific volume but also on the dissipative fluxes, and one regards the latter as independent variables. It is also assumed that the local rate of such a generalized entropy production is nonnegative. Closely related to EIT is the theory of fluids of grade N [28], where the internal energy density of the fluid is a function of entropy, mass density and their gradients up to order $N-1$. Falk [29] has recently shown that for a conserved order parameter, the corresponding Cahn-Hilliard theories can be embedded in EIT; in that paper a nonisothermal extension of these theories was developed to allow not only for mass diffusion, but also for heat transfer and fluid motion using the principle of nonnegative local entropy production. Finally, we mention again the general theories of Alt and Pawlow [15] - [17]. In a departure from this approach, Fried and Gurtin [30] constructed a theory based on an order parameter and accretive stresses. In this way, the evolution equations all appear as balance laws. Extensions were also made to deformable materials (see e.g. [31], where a connection to a sharp interface theory was given).

In this paper, we operate within EIT, and the Gibbs relation is assumed at the outset. Our main focus is on the relation between the various possible phase field formulations with quadratic gradient terms and the corresponding sharp interface models. But first, for nonisothermal solidification of pure substances, we demonstrate a rather peculiar coupling between the gradients of Φ and the temperature, which yields an infinite family of field equations incorporating the equations of WMB [26] as a particular case. This coupling is present also for solidification of binary alloys, governed by diffusion of heat, concentration (treated as the conserved order parameter field), and a nonconserved order parameter field. The freedom in selecting the governing equations does not contradict the Curie principle, and represents a new feature of the gradient theories in the nonisothermal regimes.

Secs. 2 - 4 are spent in developing the EIT framework of our models; the family of field equations is exhibited in sec. 3.

In sec. 5 we employ asymptotic analysis of the diffuse interfaces to investigate in detail the effects of the gradient terms and of the alternative forms of the field equations, in the case of the solidification of a pure substance. Essentially, we find that they affect only the kinetic undercooling term in the Gibbs-Thompson relation at the solid-liquid interface, except for higher order terms in the relevant small parameter. Moreover, to this order it suffices to take ϵ_S and ϵ_E to be independent of temperature.

The value of the small parameter ϵ_F in the nonisothermal version of (4) and (8) can, by this asymptotic reduction, be related to the surface tension at the equilibrium freezing point (see [18], for example). This exemplifies many correspondences which can be made between phase field concepts and sharp interface concepts. Theoretical treatments of surface tension generally consider it to consist of an energetic and an entropic part [19, 20, 21, 22]. It can be shown that the parameters ϵ_E and ϵ_S in (6), (7) and (8) are measures of the excess internal energy and entropy at the interface. Therefore this decomposition of the surface tension occurs naturally in the phase field context, and relates directly to the detailed form of the Gibbs–Thompson interface condition.

At the end of sec. 5, a discussion is given of the relevance of the derived form of the undercooling term to quantities which could in principle be measured experimentally. The discussion in the final section also relates our results with previous theoretical treatments of surface tension.

2 The Gibbs relation for gradient theories

Let us consider a two-phase binary alloy (solid and liquid). The volume of the system is fixed. We also assume, following WMB [26], that the energy density e is a function of the entropy density s, the concentration c, and the phase field Φ. Then the Gibbs equation referred to a unit volume reads

$$de = Tds + \mu dc + \frac{\partial e}{\partial \Phi}_{(s,c)} d\Phi. \tag{9}$$

Consequently

$$ds = \frac{1}{T}de - \frac{\mu}{T}dc - \frac{1}{T}\frac{\partial e}{\partial \Phi}_{(s,c)} d\Phi \tag{10}$$

and introducing the free energy density $f = e - Ts$, one obtains

$$df = -sdT + \mu dc + \frac{\partial f}{\partial \Phi}_{(T,c)} d\Phi. \tag{11}$$

Here

$$\frac{\partial f}{\partial \Phi}_{(c,T)} = \frac{\partial e}{\partial \Phi}_{(s,c)}, \quad s = -\frac{\partial f}{\partial T}_{(c,\Phi)}, \quad e = f - T\frac{\partial f}{\partial T}_{(c,\Phi)}. \tag{12}$$

Note for future reference that at $T = T_m$, the quantity in (5) can now be identified as

$$\frac{d}{dT}\left[f(1,T) - f(-1,T)\right]_{(T=T_m)} = \Delta s(T_m) = \frac{L}{T_m}, \tag{13}$$

where Δs is the increment in entropy from solid to liquid, and L is the latent heat at freezing temperature.

In the spirit of (6) and (7), we now introduce the densities

$$\begin{array}{rcl} e'(s,c,\Phi,\nabla\Phi) & = & e(s,c,\Phi) + \frac{1}{2}\epsilon_E^2|\nabla\Phi|^2 \\ s'(e,c,\Phi,\nabla\Phi) & = & s(e,c,\Phi) - \frac{1}{2}\epsilon_S^2|\nabla\Phi|^2 \end{array} \tag{14}$$

We shall make the simplifying assumption that ϵ_S and ϵ_E are constant parameters. This assumption will be clarified and justified at the end of sec. 5 in view of the corresponding sharp interface conditions derived there.

We shall also define the corresponding free energy density $f' = e' - Ts'$. Assuming (8) to be valid, we have

$$f'(T,c,\Phi,\nabla\Phi) = f(T,c,\Phi) + \frac{1}{2}\epsilon_F^2|\nabla\Phi|^2 \tag{15}$$

(alternatively, if we assume (15), then (8) holds).

Then

$$de' = Tds' + \mu dc + \frac{\partial e}{\partial \Phi}d\Phi + \epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi), \tag{16}$$

$$ds' = \frac{1}{T}de' - \frac{\mu}{T}dc - \frac{1}{T}\frac{\partial e}{\partial \Phi}d\Phi - \frac{1}{T}\epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi), \tag{17}$$

and

$$df' = -s'dT + \mu dc + \frac{\partial e}{\partial \Phi}d\Phi + \epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi). \tag{18}$$

Notice that the Gibbs relation (16) is now expressed in terms of e' and s' and treats the gradient terms on an equal footing with variations of c and Φ. This is the natural formalism of EIT and we adopt it as the starting point for further discussion. In this form the variational derivatives of the functionals are replaced by ordinary derivatives of the integrands.

The appearance of gradient terms in the internal energy and entropy densities can be clarified if, following Umantsev [25], one starts with the free energy functional (4) with a temperature-dependent coupling parameter ϵ_F and defines the densities s' and e' as

$$s' = -\frac{\partial f'}{\partial T}_{(\Phi,\nabla\Phi)}, \quad e' = f' - T\frac{\partial f'}{\partial T}_{(\Phi,\nabla\Phi)}. \tag{19}$$

It then follows that $\epsilon_S^2 = \frac{d(\epsilon_F^2)}{dT}$, and

$$\epsilon_E^2 = \epsilon_F^2 - T\frac{d(\epsilon_F^2)}{dT}, \tag{20}$$

in accordance with (8). The assumption that ϵ_S and ϵ_E are constant now implies that ϵ_F^2 is a linear function of T.

We can now extend the formalism by allowing gradient terms related to the concentration to appear in each of the functionals F, S and E. (A free energy functional incorporating gradient terms both for the phase field and the concentration was used in [32] and [33] in addressing rapid solidification of binary alloys.) Denoting the corresponding gradient parameters by δ_F^2, δ_E^2 and δ_S^2 with

$$\delta_F^2 = \delta_E^2 + T\delta_S^2 \tag{21}$$

and requiring δ_E and δ_S to be constants, we have for $e'(s', c, \nabla c, \Phi, \nabla\Phi)$, $s'(...)$, $f'(...)$ the relations

$$de' = Tds' + \mu dc + \frac{\partial e}{\partial \Phi}d\Phi + \epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi) + \delta_F^2\nabla c\cdot d(\nabla c), \tag{22}$$

$$ds' = \frac{1}{T}de' - \frac{\mu}{T}dc - \frac{1}{T}\frac{\partial e}{\partial\Phi}d\Phi - \frac{1}{T}\epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi) - \frac{\delta_F^2}{T}\nabla c\cdot d(\nabla c), \tag{23}$$

$$df' = -s'dT + \mu dc + \frac{\partial e}{\partial\Phi}d\Phi + \epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi) + \delta_F^2\nabla c\cdot d(\nabla c). \tag{24}$$

3 Field equations for solidification of a pure substance

Let us consider first a pure substance, for which (17) reduces to

$$ds' = \frac{1}{T}de' - \frac{1}{T}\frac{\partial e}{\partial\Phi}d\Phi - \frac{1}{T}\epsilon_F^2\nabla\Phi\cdot d(\nabla\Phi). \tag{25}$$

The first and second laws are now written in the following form:

$$\frac{\partial e'}{\partial t} = -\nabla \cdot \vec{J}_E, \tag{26}$$

$$\frac{\partial s'}{\partial t} = \sigma - \nabla \cdot \vec{J}_S, \quad \sigma \geq 0. \tag{27}$$

Here $\vec{J}_E$ is the energy flux, which reduces for a uniform system to the heat flux, but might be modified when the order parameter field is varying in space and time. The term σ denotes the local rate of entropy production and has to be nonnegative. On the basis of (25) and (26), the quantities σ and $\vec{J}_S$ can be written in terms of $\vec{J}_E$, $\frac{\partial \Phi}{\partial t}$, and spatial derivatives of Φ and T. And most importantly for our procedure, σ is a linear combination of $\vec{J}_E$ and $\frac{\partial \Phi}{\partial t}$, the coefficients depending on Φ, T, and their spatial derivatives. Feasible evolution equations can therefore be constructed by simply requiring that $\vec{J}_E$ and $\frac{\partial \Phi}{\partial t}$ be proportional to the appropriate coefficient, so that $\sigma \geq 0$.

Such expressions yield an evolution equation for Φ directly, and one for e by means of (26). This pair of equations will be our desired phase field system.

We now carry out that program. Let us denote

$$\sigma_\Phi = -\frac{1}{T}\frac{\partial \Phi}{\partial t}\left[\frac{\partial e}{\partial \Phi} - \epsilon_F^2 \nabla^2 \Phi\right] \tag{28}$$

Then from (25) - (27) it follows that

$$\frac{\partial s'}{\partial t} = -\nabla \cdot (\vec{J}_E/T) + \vec{J}_E \nabla(1/T) + \sigma_\Phi - \frac{\epsilon_F^2}{T}\nabla \cdot \left[\frac{\partial \Phi}{\partial t}\nabla \Phi\right]. \tag{29}$$

Using the fact that $\nabla\left(\frac{\epsilon_F^2}{T}\right) = \epsilon_E^2 \nabla\left(\frac{1}{T}\right)$ and the identity

$$-\frac{\epsilon_F^2}{T}\nabla \cdot \left[\frac{\partial \Phi}{\partial t}\nabla \Phi\right] = -\nabla \cdot \left[\frac{\epsilon_F^2}{T}\frac{\partial \Phi}{\partial t}\nabla \Phi\right] + \epsilon_E^2 \frac{\partial \Phi}{\partial t}\nabla \Phi \cdot \nabla(1/T), \tag{30}$$

one obtains

$$\begin{aligned} \frac{\partial s'}{\partial t} &= \sigma_\Phi + \vec{J}_E \cdot \nabla(1/T) - \nabla \cdot \vec{J}_S + \epsilon_E^2 \frac{\partial \Phi}{\partial t}\nabla \Phi \cdot \nabla(1/T) && (31) \\ &= \sigma - \nabla \cdot \vec{J}_S. && (32) \end{aligned}$$

Here the entropy current $\vec{J}_S$ is identified as

$$\vec{J}_S = \frac{1}{T}\left[\vec{J}_E + \epsilon_F^2 \frac{\partial \Phi}{\partial t} \nabla \Phi\right]. \tag{33}$$

The local entropy production σ defined in (31) involves the scalar contribution σ_Φ, the dissipation caused by the energy flux vector, and an additional term which involves the product of $\frac{\partial \Phi}{\partial t}\nabla\Phi$ with the gradient of $(1/T)$. The latter can be treated either as a part of the vector energy flux conjugated to the vector thermodynamic force $\nabla(1/T)$ or as a part of the scalar "phase field flux" conjugated to the scalar thermodynamic force $\nabla(1/T)\cdot\nabla\Phi$. We therefore have two basic options, referred to below as Models A and B, respectively. Neither of them violate the Curie principle, which prohibits coupling of dissipation due to thermodynamic forces of different tensorial properties.

Model A:

In this case we decompose the entropy production as follows:

$$\sigma = \sigma_\Phi + \sigma_E, \tag{34}$$

where σ_Φ is defined by (28) and σ_E is defined by

$$\sigma_E = \left[\vec{J}_E + \epsilon_E^2 \frac{\partial \Phi}{\partial t}\nabla\Phi\right]\cdot\nabla(1/T). \tag{35}$$

The condition $\sigma_\Phi \geq 0$ can be satisfied in the simplest way if Φ obeys the field equation

$$\frac{\partial \Phi}{\partial t} = -M_\Phi\left[\frac{\partial f}{\partial \Phi} - \epsilon_F^2 \nabla^2\Phi\right] \tag{36}$$

for some positive function M_Φ. This equation has a standard form and in the isothermal case reduces to the Landau-Ginzburg (Allen-Cahn) equation for a proper choice of f.

The second condition, $\sigma_E \geq 0$, can be satisfied if

$$\vec{J}_E + \epsilon_E^2 \frac{\partial \Phi}{\partial t}\nabla\Phi = M_T \nabla(1/T), \quad M_T > 0. \tag{37}$$

Taking into account that

$$\frac{\partial e'}{\partial t} = \frac{\partial e}{\partial t} + \epsilon_E^2 \nabla\Phi\cdot\nabla\left(\frac{\partial \Phi}{\partial t}\right) \tag{38}$$

yields

$$\frac{\partial e}{\partial t} = -\nabla \cdot [M_T \nabla(1/T)] + \epsilon_E^2 (\nabla^2 \Phi) \frac{\partial \Phi}{\partial t}. \tag{39}$$

Equations (36) and (39) are the basic equations in this scheme and are essentially those of WMB [26]. Notice that for the present model the energy flux $\vec{J}_E$ is modified in such a way that in addition to the heat flux, it accounts for the contribution due to the space and time derivatives of the phase field Φ.

Model B:

We now introduce an alternative decomposition of σ:

$$\sigma = \sigma'_\Phi + \sigma'_E, \tag{40}$$

where

$$\sigma'_\Phi = \sigma_\Phi + \epsilon_E^2 \frac{\partial \Phi}{\partial t} \nabla \Phi \cdot \nabla(1/T) \tag{41}$$

and

$$\sigma'_E = \vec{J}_E \cdot \nabla(1/T). \tag{42}$$

This decomposition yields

$$\frac{\partial \Phi}{\partial t} = -M'_\Phi \left\{ \frac{\partial f}{\partial \Phi} - \epsilon_F^2 \nabla^2 \Phi - \epsilon_E^2 T \nabla \Phi \cdot \nabla(1/T) \right\}, \quad M'_\Phi > 0, \tag{43}$$

$$\vec{J}_E = M'_T \nabla(1/T), \quad M'_T > 0, \tag{44}$$

$$\frac{\partial e}{\partial t} = -\nabla \cdot [M'_T \nabla(1/T)] - \epsilon_E^2 \nabla \Phi \cdot \nabla \frac{\partial \Phi}{\partial t}. \tag{45}$$

For the present model the energy flux $\vec{J}_E$ involves only the gradient of the temperature, but the phase field diffusion is affected by a new source term, proportional to the product of the gradients of the temperature and the order parameter field. The above definition of the energy flux affects also the entropy flux $\vec{J}_S$, defined by (33).

Combinations of A and B:

We can combine the above models by splitting σ as follows:

$$\sigma = \sigma''_\Phi + \sigma''_E, \tag{46}$$

where

$$\sigma''_\Phi = \sigma_\Phi + \alpha\epsilon_E^2 \frac{\partial \Phi}{\partial t} \nabla\Phi \cdot \nabla(1/T), \tag{47}$$

$$\sigma''_E = \left[\vec{J}_E + (1-\alpha)\epsilon_E^2 \frac{\partial \Phi}{\partial t} \nabla\Phi\right] \cdot \nabla(1/T), \tag{48}$$

and α is an arbitrary number. This yields a one-parameter family of thermodynamically consistent field equations:

$$\frac{\partial \Phi}{\partial t} = -M_1 \left\{ \frac{\partial f}{\partial \Phi} - \epsilon_F^2 \nabla^2 \Phi - \alpha \epsilon_E^2 T \nabla\Phi \cdot \nabla(1/T) \right\}, \tag{49}$$

$$\frac{\partial e}{\partial t} = -\nabla \cdot [M_2 \nabla(1/T)] + \epsilon_E^2 \left(\frac{\partial \Phi}{\partial t} \nabla^2 \Phi - \alpha \nabla \cdot (\nabla\Phi \frac{\partial \Phi}{\partial t}) \right). \tag{50}$$

Thus Model A is achieved with $\alpha = 0$ and B with $\alpha = 1$.

The degree of freedom α is a new feature of the gradient theories with $\epsilon_E^2 > 0$. The modified heat and phase field equations are hereby thermodynamically consistent, satisfying the requirement of nonnegative local entropy production, and do not violate the Curie principle stated above. In the limit $\epsilon_E = 0$ adopted by Penrose and Fife [13], all the models discussed above yield the same result:

$$\vec{J}_S = (1/T)\vec{J}_E, \quad \vec{J}_E = M_T \nabla(1/T), \quad M_T > 0, \tag{51}$$

$$\frac{\partial \Phi}{\partial t} = -M_\Phi \left[\frac{\partial f}{\partial \Phi} - \epsilon_F^2 \nabla^2 \Phi \right], \tag{52}$$

$$\frac{\partial e}{\partial t} = -\nabla \cdot [M_T \nabla(1/T)]. \tag{53}$$

In comparison with these equations, it is worth noting that the extra terms in the above models all involve spatial gradients of the order parameter. As we shall see, the implication is that those terms are relevant only in regions of rapid variation of the order parameter. In fact, it is seen from (49) and (50) that when ϵ_E and ϵ_F are small (which we assume), the terms with either of these parameters are small in regions away from the interface, where we expect $\nabla\Phi \leq O(1)$.

In sec. 5, we perform an asymptotic analysis of solutions of (49) and (50) within the diffuse interface, in order to gauge the effects there of the two small parameters ϵ_F and ϵ_E, as well as of the parameter α. It will be shown explicitly how the dynamics in the interfacial region is affected by those numbers.

4 Field equations for solidification of a binary alloy

We consider now a binary system for which the differential of the entropy density is given by (22). In addition to the energy and entropy balance equations given by (26) and (27), there is now the mass balance equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}_C. \tag{54}$$

Here $\vec{J}_C$ is the diffusion current to be defined below via the entropy production σ. Using (23), (54), (26), and (27), we may state the time rate of change of the entropy density as

$$\frac{\partial s'}{\partial t} = -\nabla \cdot (\vec{J}_E/T) + \vec{J}_E \cdot \nabla(1/T) + \sigma_\Phi - \frac{\epsilon_F^2}{T}\nabla \cdot \left[\frac{\partial \Phi}{\partial t}\nabla\Phi\right] +$$

$$+\nabla \cdot \frac{\mu \vec{J}_C}{T} - \vec{J}_C \cdot \nabla(\mu/T) - \frac{\delta_F^2}{T}\nabla c \cdot \nabla\frac{\partial c}{\partial t}, \tag{55}$$

where σ_Φ is defined by (28). Using (30) and the identity

$$-\frac{\delta_F^2}{T}\nabla\frac{\partial c}{\partial t} \cdot \nabla c = -\nabla \cdot \left[\frac{\delta_F^2}{T}\frac{\partial c}{\partial t}\nabla c\right] + \frac{\delta_F^2}{T}\frac{\partial c}{\partial t}\nabla^2 c + \delta_E^2\frac{\partial c}{\partial t}\nabla c \cdot \nabla(1/T), \tag{56}$$

one may rewrite (55) as follows:

$$\frac{\partial s'}{\partial t} = -\nabla \cdot \frac{1}{T}\left[\vec{J}_E - \mu\vec{J}_C + \epsilon_F^2\frac{\partial \Phi}{\partial t}\nabla\Phi + \delta_F^2\frac{\partial c}{\partial t}\nabla c\right] +$$

$$+\vec{J}_E\nabla(1/T) - \vec{J}_C\nabla(\mu/T) + \sigma_\Phi + \frac{\delta_F^2}{T}\frac{\partial c}{\partial t}\nabla^2 c +$$

$$+\epsilon_E^2\frac{\partial \Phi}{\partial t}\nabla\Phi \cdot \nabla(1/T) + \delta_E^2\frac{\partial c}{\partial t}\nabla c \cdot \nabla(1/T). \tag{57}$$

Using (54), one now obtains

$$\frac{\delta_F^2}{T}\frac{\partial c}{\partial t}\nabla^2 c = -\nabla \cdot [(\vec{J}_C\delta_F^2\nabla^2 c)/T] + \vec{J}_C \cdot \nabla[(\delta_F^2\nabla^2 c)/T] \tag{58}$$

and

$$\delta_E^2\frac{\partial c}{\partial t}\nabla c \cdot \nabla(1/T) = \delta_E^2\nabla \cdot \{\vec{J}_C[\nabla c \cdot \nabla(1/T)]\} + \delta_E^2\vec{J}_C \cdot \nabla[\nabla c \cdot \nabla(1/T)]. \tag{59}$$

Substituting (58) and (59) into (57), one obtains

$$\frac{\partial s'}{\partial t} = -\nabla\cdot\vec{J}_S + \vec{J}_E\cdot\nabla(1/T) - \vec{J}_C\cdot\nabla(\mu'/T) + \sigma_\Phi + \epsilon_E^2\frac{\partial\Phi}{\partial t}\nabla\Phi\cdot\nabla(1/T). \quad (60)$$

Here the generalized chemical potential μ' is defined as

$$\mu' = \mu - \delta_F^2\nabla^2 c - \delta_E^2\nabla c\cdot\nabla(1/T) \quad (61)$$

and the entropy flux vector $\vec{J}_S$ is given by

$$\vec{J}_S = \frac{1}{T}\left[\vec{J}_E - \mu'\vec{J}_C + \epsilon_F^2\frac{\partial\Phi}{\partial t}\nabla\Phi + \delta_F^2\frac{\partial c}{\partial t}\nabla c\right]. \quad (62)$$

As in the previous section, one might allocate the last term in (60) either to the vector part or to the scalar part of the entropy production.

<u>Model A:</u>

We split the entropy production as follows:

$$\sigma = \sigma_\Phi + \sigma_{EC} \quad (63)$$

where

$$\sigma_{EC} = \left\{\vec{J}_E + \epsilon_E^2\frac{\partial\Phi}{\partial t}\nabla\Phi\right\}\cdot\nabla(1/T) - \vec{J}_C\cdot\nabla\left(\frac{\mu'}{T}\right). \quad (64)$$

If we identify $\nabla(1/T)$ and $\nabla(\mu'/T)$ as the generalized vector thermodynamic forces and assume the linear "force-flux" relations, this yields

$$\begin{aligned}\vec{J}_E + \epsilon_E^2\frac{\partial\Phi}{\partial t}\nabla\Phi &= L_{EE}\nabla(1/T) - L_{EC}\nabla(\mu'/T), & (65)\\ \vec{J}_C &= L_{CE}\nabla(1/T) - L_{CC}\nabla(\mu'/T). & (66)\end{aligned}$$

Here L_{EE}, $L_{CE} = L_{EC}$, and L_{CC} are the Onsager coefficients, which satisfy the conditions $L_{EE} > 0$, $L_{CC} > 0$, and $L_{EE}L_{CC} > L_{EC}^2$, needed to ensure that $\sigma_{EC} \geq 0$. Another possible option is to identify as thermodynamic forces $\nabla(1/T)$ and $\nabla\mu'$.

The field equations corresponding to (65) and (66) follow from the conservation of energy and mass, whereas the phase-field equation remains unchanged and is given by (36). Neglecting the cross terms in (65) and (66), one obtains (36), (39), and

$$\frac{\partial c}{\partial t} = \nabla\cdot\{L_{CC}\nabla(\mu'/T)\} \quad (67)$$

as the governing equations of the problem. In the isothermal case, (67) reduces to the Cahn-Hilliard equation.

Combined models:

These models are obtained by modifying the decomposition of the entropy production following the recipes of the previous section. The derivation of the governing equations is straightforward.

5 The effect of the gradient terms in the internal energy functional on the corresponding sharp interface model

In the present section we will demonstrate how the gradient terms in the energy, and the freedom of selecting the parameter α, affect the approximating free boundary problem obtained through layer asymptotics. We shall work within the setting of the combined models, since they are the most general, but restrict attention to the case of a pure substance. We therefore proceed on the basis of the evolution equations (49) and (50). However, it is appropriate to put them into a dimensionless form for purposes of the asymptotics.

Our nondimensionalization procedure will use the following characteristic physical quantities:

X is a characteristic length associated with the geometry of the system.

L is the latent heat at the equilibrium freezing temperature T_m (the difference in values of e between the two phases at that temperature).

$\hat{c}_{ap}$ is the value of the heat capacity $\frac{\partial e}{\partial T}$ in the liquid at temperature T_m.

$\hat{K}$ is the value of the thermal conductivity (see the function K below), again in the liquid at temperature T_m.

We then define dimensionless variables (with bars) by

$$x = X\bar{x}, \;\; t = \frac{X^2\hat{c}_{ap}}{\hat{K}}\bar{t}, \;\; e = L\bar{e}, \;\; f = L\bar{f}, \;\; T = \frac{L}{\hat{c}_{ap}}\bar{T}, \;\; M_2 = \hat{K}\bar{K}T^2. \quad (68)$$

Recall that we are assuming ϵ_F^2 to be a linear function of temperature. We write that relation as

$$\epsilon_F^2(T) = \epsilon_F^2(T_m)\left(1 + \tau(\bar{T} - \bar{T}_m)\right), \quad (69)$$

for some dimensionless parameter τ. It follows from (20) that

$$\epsilon_E = \beta\epsilon_F(T_m), \quad \beta^2 = 1 - \tau\bar{T}_m \tag{70}$$

(which restricts the size of τ), and from (8) that $\tau = \frac{L\epsilon_S^2}{\hat{c}_{ap}\epsilon_F^2(T_m)}$. This last relation implies $\tau \geq 0$, hence from (70), $\beta \leq 1$.

We now define a dimensionless small parameter ϵ by

$$\epsilon_F^2(T_m) = LX^2\epsilon^2, \quad \text{so that} \quad \epsilon_E = \sqrt{L}X\beta\epsilon. \tag{71}$$

Finally, our basic order parameter-kinetic coefficient γ is given by

$$\gamma = \frac{\hat{K}}{\epsilon^2 LM_1X^2\hat{c}_{ap}}, \tag{72}$$

which we take to be constant and $O(1)$, because in the well-studied case $\epsilon_E = 0, \ \ 0 < \epsilon_F \ll 1$, that is precisely the order of magnitude relation under which the Stefan problem with Gibbs-Thompson condition is approximated by the phase field equation (see for example [34, 35, 13]).

We rewrite (49) and (50) in terms of the dimensionless variables, but then drop the overbar from the notation for convenience. The resulting equations are

$$\gamma\epsilon^2\frac{\partial\Phi}{\partial t} = \epsilon^2(1+\tau(T-T_m))\nabla^2\Phi - \frac{\partial f}{\partial\Phi} - \alpha\beta^2\epsilon^2 T\nabla\Phi\cdot\nabla(1/T), \tag{73}$$

$$\frac{\partial e}{\partial t} = \nabla\cdot(K\nabla T) + \beta^2\epsilon^2\left(\frac{\partial\Phi}{\partial t}\nabla^2\Phi - \alpha\nabla\cdot\left(\nabla\Phi\frac{\partial\Phi}{\partial t}\right)\right). \tag{74}$$

We shall assume that K is constant to simplify the calculations, although their extension to the nonconstant case is straightforward.

We perform a layer analysis of (73) and (74) as in [34, 18], for example. The first step in this process is to identify the mobile interface $\Gamma(t)$ as the set where $\Phi(x,t) = 0$. We then write the evolution equations in terms of a local spatial coordinate system (r, s). Here $r(x,t)$ represents the signed distance from x to $\Gamma(t)$, with solid corresponding to $r > 0$, and s represents a generic point on Γ. Near Γ, this coordinate system is well defined; we may and shall take it to be orthogonal.

We transform (73), (74) to this system, writing only the terms which will contribute to the $O(1)$ and $O(\epsilon)$ terms in the inner equations to be detailed below. We obtain the following, where the symbol $v = -\frac{\partial r}{\partial t}$ is the normal velocity of the interface Γ, κ is the sum of the two principal curvatures of Γ, and the subscript "r" denotes differentiation with respect to r:

$$-\gamma\epsilon^2 v\Phi_r = \epsilon^2(1+\tau(T-T_m))(\Phi_{rr}+\kappa\Phi_r) - f_\Phi(\Phi,T) + \alpha T^{-1}\beta^2\epsilon^2\Phi_r T_r, \quad (75)$$

$$-ve_r = (KT_r)_r + \kappa KT_r - \beta^2\epsilon^2 v\left[(1-2\alpha)\Phi_r\Phi_{rr} + \kappa(1-\alpha)\Phi_r^2\right]. \quad (76)$$

Here and below, subscripts on functions denote partial derivatives.

The next step is to stretch the local coordinate r by defining $z = r/\epsilon$; the diffuse interface which is thin of thickness $O(\epsilon)$ in the original variables is now expanded to a size $O(1)$ in the stretched coordinate. We use the function notation

$$\Phi(r,s,t;\epsilon) = \phi(z,s,t;\epsilon), \quad T(r,s,t;\epsilon) = \theta(z,s,t;\epsilon)$$

to obtain from (75), (76)

$$(1+\tau(\theta-T_m))\phi_{zz} - f_\Phi(\phi,\theta) + (1+\tau(\theta-T_m))\epsilon\kappa\phi_z + \alpha\theta^{-1}\beta^2\phi_z\theta_z + \gamma\epsilon v\phi_z = 0, \quad (77)$$

$$K(\theta_{zz}+\epsilon\kappa\theta_z) + \epsilon ve_z - \beta^2\epsilon v(1-2\alpha)\phi_z\phi_{zz} = 0. \quad (78)$$

The inner asymptotic expansion comes about by replacing $\phi(z,s,t;\epsilon)$ in these two equations by $\phi^0(z,s,t) + \epsilon\phi^1(z,s,t) + ...$, and the same for θ. We then equate to zero all terms which are formally of order $O(1)$, and separately those of order $O(\epsilon)$.

The outer expansion, supposed valid away from the interface, is simpler: it comes from substituting such a power series expansion in ϵ for the functions Φ and T into (73) and (74) directly, and again collecting terms of equal orders. The terms of the inner and outer expansions must then be matched in a standard way [34, 18]. Thus

$$\theta^0_{(z=\infty)} = T^0_{(r=0+)}, \quad \theta^1_z|_{z=\infty} = T^0_r|_{r=0+}, \quad \text{etc.}$$

The results are as follows.

<u>$O(1)$ in (78)</u>

$$\theta^0_{zz} \equiv 0. \quad (79)$$

Since θ^0 must be bounded in order to effect matching, we get that θ^0 is independent of the coordinate z. Matching between θ^0 and T^0 then yields the conclusion that to lowest order, the outer temperature function T^0 is continuous across Γ.

$\underline{O(1) \text{ in } (77)}$

$$\left(1+\tau(\theta^0 - T_m)\right)\phi^0_{zz} - f_\Phi(\phi^0, \theta^0) = 0 \tag{80}$$

with matching conditions $\phi^0 = \pm 1$ at $z = \pm\infty$, since the solid domain is attained for positive z. Multiplying (80) by ϕ^0_z and integrating from $-\infty$ to ∞, we obtain $f(1, \theta^0) = f(-1, \theta^0)$. Hence by our assumptions on the double-well function f made in the introduction, we obtain that

$$\theta^0 = T_m \tag{81}$$

and

$$\phi^0(z) = \psi(z), \tag{82}$$

where $\psi(z)$ (suppressing its dependence on s and t) is the canonical interfacial profile corresponding to the bistable function $f_\Phi(\phi, T_m)$ of the variable ϕ. It satisfies

$$\psi'' - f_\Phi(\psi, T_m) = 0 \tag{83}$$

with boundary conditions and has the qualitative appearance of a constant times $\tanh z$.

$\underline{O(\epsilon) \text{ in } (78)}$

$$K\theta^1_{zz} + ve^0_z - \beta^2 v(1-2\alpha)\phi^0_z\phi^0_{zz} = 0, \tag{84}$$

where we have used the fact that θ^0 does not depend on z. Integrating, we get

$$K\theta^1_z + ve(\psi(z), T_m) - \frac{1}{2}\beta^2 v(1-2\alpha)(\psi'(z))^2 = \text{const.} \tag{85}$$

The last term on the left is a new effect, giving an $O(\epsilon)$ contribution to the temperature profile in the interface, depending on α, β, and v. It vanishes exponentially as $z \rightarrow \pm\infty$.

Differencing this equation at the values $z = \pm\infty$, we get

$$K\theta^1_z(\infty) - K\theta^1_z(-\infty) + v(e(1, T_m) - e(-1, T_m)) = 0. \tag{86}$$

Matching requires that the difference of the first two terms be set equal to $[K\partial_r T^0]_\Gamma$, i.e. the jump, as the interface is crossed, of the product of K

times the normal derivative of the lowest order outer temperature function T^0. Applying this same notation for jump discontinuity across the interface to the other terms in (86), we obtain

$$[K\partial_r T^0]_\Gamma = -v[e]_\Gamma, \tag{87}$$

which is the Stefan condition (note that the jump on the right of this equation is the latent heat at $T = T_m$).

Lowest order outer problem

In the outer regions, we may set $\Phi^0 = \pm 1$, since these constants are exact solutions representing liquid and solid, respectively, and the terms in ϵ^2 in (74) vanish. Hence the outer solution $T^0(x,t)$ satisfies

$$\frac{\partial}{\partial t} e(\pm 1, T^0) = \nabla \cdot K \nabla T^0, \quad x \notin \Gamma(t), \tag{88}$$

$$T^0 = T_m, \quad x \in \Gamma(t),$$

$$[KT_r^0] = -v[e]_\Gamma, \quad x \in \Gamma(t).$$

This is the classical Stefan problem, when supplied with boundary and initial conditions.

$O(\epsilon)$ in (77)

$$\phi_{zz}^1 - f_{\Phi\Phi}(\psi, T_m)\phi^1 - (f_{\Phi T}(\psi, T_m) - \tau\phi_{zz}^0)\theta^1 + (\kappa + \gamma v)\psi'(z) + \frac{\alpha}{T_m}\beta^2\psi'(z)\theta_z^1 = 0. \tag{89}$$

To evaluate the last term, we go to (85), wherein we know the constant to be $K\partial_r T_{\Gamma\pm}^0 + ve(\pm 1, T_m)$, where the subscript $\Gamma\pm$ means the limit as Γ is approached from the solid side (+) or the liquid side (-). The value of this expression is independent of the choice of sign. We obtain, in the case that K is constant,

$$\theta_z^1 = (T_r^0)_{\Gamma\pm} - \frac{v}{K}[e(\psi(z), T_m) - e(\pm 1, T_m)] + \frac{\beta^2 v(1 - 2\alpha)}{2K}(\psi'(z))^2. \tag{90}$$

Integrating (90), we may express $\theta^1(z)$ in the form

$$\theta^1(z) = \theta^1(0) + \tilde{\theta}^1(z), \tag{91}$$

where $\tilde{\theta}^1(z)$ is known, with $\tilde{\theta}^1(0) = 0$. It grows linearly as $z \to \pm\infty$. But $\theta^1(0)$ is not known as yet. Substituting into (89), we find

$$\phi^1_{zz} - f_{\Phi\Phi}(\psi, T_m)\phi^1 + \left(\kappa + \gamma v + \frac{\alpha}{T_m}\beta^2 T^0_r|_{\Gamma\pm}\right)\psi'(z) -$$

$$-(f_{\Phi T}(\psi, T_m) - \tau\psi''(z))\left(\theta^1(0) + T^0_r|_{\Gamma\pm} z\right) + vF_\pm(\alpha, \beta^2, \psi(z), \psi'(z), \psi''(z)) = 0, \tag{92}$$

the functions $F_\pm$ being known (see appendix).

Multiply (92) by $\psi'(z)$ and integrate from $-\infty$ to ∞. It turns out that the terms in ϕ^1 vanish, and we may solve for $\theta^1(0)$ in the form

$$\theta^1(0) = A(\kappa + \gamma v) + B\left(T^0_r\right)_{\Gamma\pm} + vG_\pm(\alpha, \beta), \tag{93}$$

for coefficients to be given as follows.

$$A = T_m \int_{-1}^{1} \sqrt{2f(\phi)}\,d\phi, \tag{94}$$

where we use the notation $f(\phi) = f(\phi, T_m)$. Similar usages appear below for the functions $e(\phi)$ and $h(\phi)$. We define

$$e^\pm(\phi) = e(\phi, T_m) - e(\pm 1, T_m) \quad \text{and} \quad h(\phi) = f(\phi) - \frac{1}{\tau} f_T(\phi, T_m).$$

Now

$$B = \alpha\beta^2 \int_{-1}^{1} \sqrt{2f(\phi)}\,d\phi - \tau T_m \int_{-1}^{1} \frac{h(\phi)}{\sqrt{2f(\phi)}}\,d\phi, \tag{95}$$

$$G_\pm = \frac{1}{K}[G^\pm_0 + G_1\beta^2(1-2\alpha) + G^\pm_2\alpha\beta^2 + G_3\beta^4\alpha(1-2\alpha)], \tag{96}$$

$$G^\pm_0 = \tau T_m \int_{-1}^{1} \frac{e^\pm(\phi)h(\phi)}{\sqrt{2f(\phi)}}\,d\phi,$$

$$G_1 = -\frac{1}{2}\tau T_m \int_{-1}^{1} \sqrt{2f(\phi)}\,h(\phi)\,d\phi,$$

$$G^\pm_2 = -\int_{-1}^{1} e^\pm(\phi)\sqrt{2f(\phi)}\,d\phi,$$

and

$$G_3 = \frac{1}{2}\int_{-1}^{1} (2f(\phi))^{3/2}\,d\phi.$$

The expression (93) is independent of choice of sign. The details of this calculation are given in the appendix.

The last terms in (93) are terms not normally present in the Gibbs-Thompson relation, which takes the form (since $\theta^1(0) = T^1(0)$)

$$T_\Gamma = T_m + \epsilon A(\kappa + \gamma v) + \epsilon \left(B \left(T_r^0 \right)_{\Gamma\pm} + vG_\pm(\alpha, \beta) \right) + O(\epsilon^2). \qquad (97)$$

The coefficients A, B and $G_\pm$ in (97) depend only on the properties of the function f (which governs ψ by (83) and e by (12)) and the parameters T_m, α and β (recall τ is related to β by (70)). The parameters α and β figure only in the two nonequilibrium effects (the coefficients B and $G_\pm$); the capillarity undercooling remains unchanged when α and β are varied.

The coefficient ϵA of κ in (97) is our nondimensional Gibbs-Thompson coefficient. In dimensional terms, that part of (97) becomes (using the symbols $\hat{T}$ and $\hat{\kappa}$ to denote dimensional temperature and curvature)

$$\hat{T}_\Gamma - \hat{T}_m = \frac{\epsilon AL}{\hat{c}_{ap}} \hat{\kappa} + ...,$$

which must be compared with the Gibbs-Thompson expression

$$\hat{T}_\Gamma - \hat{T}_m = \frac{\sigma \hat{T}_m}{L} \hat{\kappa} + ...,$$

where σ is the surface energy density. We therefore identify $\epsilon A = \frac{\sigma \hat{T}_m \hat{c}_{ap}}{XL^2}$, which is a dimensionless surface tension (see a similar calculation in [18]).

The term with coefficient B in (97) represents the non-equilibrium influence that the temperature gradient, i.e. heat flux, through the interface has on the temperature T_Γ there. Notice that it does not vanish when $\beta = 0$. A similar term was found in [18].

The terms in (97) in which v is multiplied by $\epsilon A\gamma$ and $\epsilon G_\pm(\alpha, \beta)$ are kinetic undercooling terms. The first one, with γ, is related directly to the postulated kinetic coefficient M_1 in (49) by means of (72). The other term depends in a complicated fashion on f, α, β, T_m and K; notice that it also does not vanish when $\beta = 0$ (see [18]). It gives an extension of the usual kinetic undercooling coefficient.

The various parameters would ideally be determined by experiments. Let us suppose that the surface tension σ, hence ϵA, is known, and that the variation of the surface tension with temperature can be measured and determines τ, hence β (69), (70). Then further experiments on the undercooling and on the temperature gradient effects may serve to tell us the coefficients $\epsilon(A\gamma + G_{\pm})$ and ϵB, and this information may be used in finding the two remaining parameters α and γ.

The asymptotic analysis performed above up to the first order in ϵ involves (in dimensional terms) the values of ϵ_F^2 and its derivative with respect to temperature, namely ϵ_S^2, or equivalently ϵ_E^2, all evaluated at $T = T_m$. This corresponds to the expansion of a rather general temperature dependent ϵ_F^2 near $T = T_m$ up to the first order in $T - T_m$. One might consider the higher order terms as well. However, it can be shown by following the above calculations that these terms do not affect the $O(\epsilon)$ asymptotics of the more general field equations incorporating temperature dependent parameters ϵ_F, ϵ_E, and ϵ_S. This justifies our assumption (following (14)) that ϵ_E and ϵ_S are constants and hence that ϵ_F^2 depends linearly on T, the three being subject to (8).

6 Concluding remarks

Phase-field models are widely used in computational modeling of phase transitions. Indeed, they are usually more amenable to computations than are free boundary formulations. A second purpose which they have served is to provide competing theories of interfacial dynamics within those contexts where hard and fast physical theories are lacking. Examples are rapid solidification [32, 33, 36] and chemically induced grain boundary motion [37]. In this same vein, one of the goals of the present paper was to use phase-field formulations to cast light on, among other things, the kinetic terms in the Gibbs-Thompson relation during solidification or melting. They are closely connected with the basic physics of the surface tension.

Although they can arise in statistical mechanics, phase-field models are basically phenomenological theories. As pointed out in [13], one difficulty with phase field models of nonisothermal processes lies in their derivation. Following Wang at al. [24], we believe that such models should satisfy two basic requirements: (i) thermodynamic consistency, and (ii) the functions and parameters involved should agree asymptotically with empirical data. With this perspective, the derivation of the field equations from the second law of thermodynamics is a major issue of physics. It was addressed in the first part of our paper within the framework of Extended Irreversible Thermodynamics. The second part of the paper was concerned with the associated sharp interface models for the case of a pure substance. Those models involve effects which might enable one to assign specific values to the parameters of the theory from empirical data.

Let us summarize the relationship between the present paper and its predecessors and clarify the significance of the new terms in the field equations.

The thermodynamically consistent models for nonisothermal solidification proposed in the past, such as [13, 18, 24, 32, 33, 34], typically incorporate gradient terms in the entropy and free energy densities. Some of the more recent models introduce, as do we, gradient terms also in the internal energy [25, 26]. The coefficient ϵ_F^2 of the gradient term in the free energy is associated with the dimensionless surface tension at the coexistence temperature. The decomposition of ϵ_F^2 into terms involving ϵ_E and ϵ_S according to (8) and (20) corresponds to a splitting of the surface tension into an energetic and entropic part. Moreover, the latter is directly related to the temperature dependence of the surface tension.

Such a splitting of the surface tension has been an important ingredient in many past theoretical approaches within equilibrium statistical mechanics—static models, Monte-Carlo simulations, density functional theories; these results were reviewed by Boettinger and Perepezko [22], Spaepen [19], and others. Although there is no definitive answer as to the correct splitting, these concepts have physical significance with regard to the structural features of the interface.

We have shown that the specification of the entropy and energy fluxes adopted in its predecessors [25, 26] within the framework of EIT is not unique. Still in that frame, we exhibited a one-parameter family of models which are consistent with the requirement of positive local entropy production. This new degree of freedom, embodied in a parameter we call α, is not present in models formulated in the past, which would correspond to $\alpha = 0$. Taking α different from zero modifies not only the heat diffusion equation but also the phase-field equation via gradient terms in the internal energy. This is an important difference between the present theory and its predecessors.

The next issue addressed in the paper is whether all the parameters entering the field equations can be assigned certain values from empirical data. For this purpose we developed, using layer asymptotics, the corresponding free boundary problem up to first order in the small parameter which measures the width of the diffuse interface and the dimensionless surface tension. This free boundary problem yields, to first order, three undercooling effects.

The first one is the standard Gibbs-Thompson capillarity effect, not affected by our corrections at this order. (Certainly corrections will occur at higher orders.) The next first order effect is the kinetic undercooling. The latter is indeed affected by the parameter α and by the gradient terms in the internal energy. The third undercooling correction is a nonequilibrium effect induced by the heat flux through the interface. It is a qualitatively new effect pointed out in [18] (where the gradient terms in the free energy were neglected). We show that this third effect also depends on the parameter α and on the gradient contribution to the internal energy. To the best of our knowledge this effect has not been measured yet and perhaps could be. Notice that even if this effect is extremely small this does not imply that either α or the coefficient of the gradient terms in the internal energy vanish.

We have suggested that measuring the above first order undercooling effects as well as the temperature dependence of the surface tension in the vicinity of the coexistence temperature would suffice to fix the parameters of the model up to the choice of the homogeneous part of the free energy. The latter has not been specified in our work for the sake of generality, but that part of the problem has been already discussed in the past, e.g. in the papers mentioned above. Thus, performing a set of measurements as indicated, one could determine the parameters of the model and check whether α equal to zero, adopted in the past, is a suitable choice.

Measuring the temperature dependence of the surface tension is indeed a very difficult task. Typically, it is recovered by fitting homogeneous nucleation data. (Such data, obtained by Turnbull for mercury, was recently reconsidered by Spaepen [19].) In principle, such information could be obtained and used to fix the splitting.

So in principle, the parameters in the phase field equations having to do with the gradient contributions are meaningful physically and could be fixed using either existing theories of the structure of the equilibrium interface, or eventually from empirical data.

Appendix

Here we give the details of the derivation of (93). Integrating (90), we obtain (91) with

$$\tilde{\theta}^1(z) = \left(T_r^0\right)_{\Gamma\pm} z - \frac{v}{K}\int_0^z [e(\psi(z),T_m) - e(\pm 1, T_m)]dz + \frac{\beta^2 v(1-2\alpha)}{2K}\int_0^z (\psi')^2 dz'.$$

From this, the function $F_\pm$ in (92) is seen to be

$$F_\pm(\alpha,\beta^2,z) = \frac{1}{K}\left(f_{\Phi T}(\psi(z),T_m) - \tau\psi''(z)\right)\int_0^z [e(\psi(z),T_m) - e(\pm 1,T_m)]dz'$$

$$-\frac{\beta^2(1-2\alpha)}{2K}\int_0^z (\psi')^2\left(f_{\Phi T}(\psi(z'),T_m) - \tau\psi''(z')\right)dz' -$$

$$-\frac{\alpha}{KT_m}\beta^2\psi'(z)[e(\psi,T_m) - e(\pm 1,T_m)] + \frac{\beta^2(1-2\alpha)}{2K}\frac{\alpha\beta^2}{T_m}(\psi'(z))^3.$$

Let the operator $\mathcal{L}$ be defined by $\mathcal{L}\phi = \phi_{zz} - f_{\Phi\Phi}(\psi(z),T_m)\phi$. Then by differentiating (83) with respect to z, we see that $\mathcal{L}\psi' = 0$. When we multiply (92) by ψ' and integrate, the terms in ϕ^1 disappear because $\int_{-\infty}^{\infty}\psi'(z)\mathcal{L}\phi^1(z)dz = \int_{-\infty}^{\infty}\phi^1(z)\mathcal{L}\psi'(z)dz = 0$.

The coefficient of $\theta^1(0)$ takes the form

$$-\int_{-\infty}^{\infty} f_{\Phi T}(\psi(z),T_m)\psi'(z)dz = -\int_{-1}^{1} f_{\Phi T}(\psi,T_m)d\psi =$$

$$= -\frac{d}{dT}\left[f(1,T) - f(-1,T)\right]_{(T=T_m)} = -\frac{1}{T_m};$$

this last is the dimensionless version of (13).

In view of these facts and the above expression for F, we obtain an expression like (93) directly, but with expressions for the coefficients which are different from those given. For example, $A = T_m\int_{-\infty}^{\infty}(\psi'(z))^2dz$. But this reduces to the expression given in (94); in fact it follows from (83) that

$$(\psi'(z))^2 = 2f(\psi(z),T_m),$$

so that $dz = \frac{d\psi(z)}{\sqrt{2f(\psi(z)}}$.

To derive the coefficients G_i as given we change the variable of integration from z to $\phi = \psi(z)$ and integrate by parts. We give the details only for $G_0^\pm$. The above expression for $F_\pm$ yields the following for $KG_\pm$ when $\alpha = \beta = 0$:

$$KG_\pm = G_0^\pm = \int_{-\infty}^{\infty}\int_0^z e^\pm(\psi(\bar{z}))d\bar{z}h'(\psi(z))\psi'(z)dz$$

$$= \int_{-\infty}^{\infty}\int_0^z e^\pm(\psi(\bar{z}))d\bar{z}\frac{d}{dz}h(\psi(z))dz$$

$$= -\int_{-\infty}^{\infty} e^\pm(\psi(z))h(\psi(z))dz$$

$$= -\int_{-1}^{1} \frac{e^{\pm}(\phi)h(\phi)}{\sqrt{2f(\phi)}} d\phi.$$

The others are derived in the same way.

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