Developments in phase-field modeling of thermoelastic and two-component materials

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Abstract

A discussion is given of recent advances in phase-field modeling of materials which change phase. On the one hand, general models incorporating elasticity properties of the material, nonconserved and conserved order parameters, and nonlocal effects are now available. On the other hand, gradient theories for binary alloys have been developed which reflect such effects as the dependence of capillarity on the concentration of impurities, solute trapping in its dependence on velocity of solidification fronts, and other nonequilibrium phenomena.

KEYWORDS: Solidification of alloys, phase field models, interfaces, nonlocal effects, solidus curves, solute trappings, partition coefficient, asymptotics.

Dedicated to John W. Cahn on the occasion of his 70th birthday.

1 Introduction

Phase field approaches to the modeling of complex interfacial phenomena in continuum mechanics have gained popularity in recent years (the literature is too large for us to attempt a survey or even an adequate list of references here). They are used not only as mathematical regularizations of sharp interface models, but also as attempts to extend the modeling process beyond the idealizations inherent in sharp-interface theories.

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These models postulate one or more order parameters as indicators of the state of the material, in addition to the usual ones such as temperature, elastic strain, etc. The order parameters vary continuously in the medium, including in the interfacial regions between phases, where analogous sharp interface theories would have them discontinuous.

In constructing appropriate evolution equations for such systems, one generally proceeds on the basis of concepts borrowed from classical equilibrium thermodynamics, but uses them in nonequilibrium situations. In this respect, they are offshoots of classical irreversible thermodynamics, and operate on the basis of analogy with simpler scenarios.

In this paper, we first (sec. 2) recount a phase-field framework based on [14] designed for materials whose states are described by order parameters, temperature, and elastic strain tensor. It allows for nonlocal interactions. Rather than viewed as a model for specific phenomena, it is rather to be considered a general approach which could be used in treating more specific problems. Among notable previous works using phase field models with elasticity effects, we mention those of Larché and Cahn ([26], for example).

Next, in sec. 3, we consider a much less general set of models for which there are two order parameters, namely a phase field (nonconserved) and a concentration field (conserved). These are models for the solidification/melting of a binary alloy. The order parameters, together with temperature, constitute the complete local description of the material. Our main object here is to investigate the properties of the concentration "jump" and surface tension at a solidification front, as they depend on the velocity and curvature of the front and the temperature. Our discussion begins by describing the results in [12] and [11].

In both cases, we follow an extension of the approach of classical irreversible thermodynamics. We begin by postulating the existence of a Helmholtz free energy function of the state of the system, with certain general properties. From this, we operate in analogy with more traditional thermodynamics to define internal energy and entropy functions. Balance equations for energy, entropy, and in one case momentum are then formulated, with the entropy source written in terms of fluxes and forces. Finally, an entropy principle of nonnegative local production of entropy is formulated, and expressions relating the fluxes to the forces postulated which guarantee the satisfaction of the entropy principle.

This provides equations for the time evolution of the state of the material. These are typically partial differential equations or integro-differential equations.

This procedure is similar (with differences) to many other phase field modeling approaches, such as those in the papers by Alt and Pawlow [2, 3, 4] and Umantsev [28]. Compare also Fried and Gurtin [20].

Phase interfaces are treated differently in phase field theories than they are in sharp interface ones. In sharp interface theories based on thermodynamic considerations (e.g. [21, 13, 23]), the material may consist of two, say, bulk phases with associated thermodynamic densities, separated by an interface with its own thermodynamic (surface) densities, such as surface tension and excess free energy. These concepts are only approximations to physical reality, but they conform to things which can often be measured experimentally with some accuracy. Phase field models, which are also only approximations to physical reality, have interfacial regions which are less precisely defined, and less precisely delineated from the bulk regions. Interfacial surface densities such as that of free energy are defined only to within $O(\epsilon^2)$ terms, where ϵ is a small parameter related to the thickness of the interface. But except for this type of impreciseness, correspondances can be set up between physically measurable interfacial properties, on the one hand, and the parameters of a phase field model, on the other.

The most important line of investigation in phase-field theories is to discover what they say about how traditional properties of the interface such as its surface tension, kinetic coefficient of undercooling, concentration jump, velocity, curvature and temperature, depend on each other. Once the parameters of the theory are understood in terms of traditional concepts in simple situations, the theory provides predictions about these dependences in more complex scenarios as well. Among other recent studies in this category, we merely mention the phase field model of hypercooled solidification of a pure substance in [7], certain nonequilibrium effects at the solidification/melting interface in [29, 10], and the phase field model of diffusion-induced motion of a grain boundary in [9].

In this paper, we look into this issue for materials with elasticity and (generally) nonlocal effects in sec. 2, and also for the solidification of alloys in sec. 3. In the latter, the effects of high front velocity and curvature on the concentration jump at the front are considered (separately). In this case, the parameters of the model are fixed in terms of surface tension and its dependence on concentration.

2 Thermoelastic materials with nonlocal effects

2.1 The framework

The material properties at each point in space-time $(\overline{x}, t) \in R^3 \times R$ are described in terms of temperature T, strain tensor ϵ_{ij}, and order parameters ϕ. This triple constitutes the state $A = (\epsilon_{ij}, T, \phi)$. We also wish to consider the effects that the entire functions $T(\overline{x})$, $\phi(\overline{x})$ (for fixed time) have on remote states, and our notation will reflect that. We think of the functions T and ϕ as belonging to certain Banach spaces Ω_T and Ω_ϕ.

We begin with a Helmholtz free energy density f, which is postulated to be a given function of position $\overline{x}$ as well as of the local value of ϵ_{ij} and the global functions T and ϕ. This is expressed by

$$f = \tilde{f}(\overline{x}, \epsilon_{ij}, [T], [\phi]), \tag{1}$$

a functional of T and ϕ.

In analogy with classical thermodynamics, we construct an internal energy and entropy, each of them again with nonlocal dependences.

In traditional cases, they are related by

$$e = f + sT \quad \text{and} \quad s = -\frac{\partial f}{\partial T}. \tag{2}$$

However because of the possible nonlocal dependence of f on T, the right hand side of $(2)_2$ should be interpreted in a slightly different fashion. Namely, we propose that for each $\bar{x} \in R^3$, s (now called "pseudo-entropy") be an element of a dual space, namely Ω_T^*, the space of continuous linear functionals on Ω_T. The pairing in this setup is denoted by $\langle s, T \rangle$.

In place of the classical relation $(2)_1$, we now propose

$$e = f + \langle s, T \rangle. \tag{3}$$

As in traditional cases, e is also postulated to be given by a function of position $\overline{x}$, the local value of ϵ_{ij}, the local value of s and the global function ϕ; namely,

$$e(\overline{x}) = \tilde{e}(\overline{x}, \epsilon_{ij}, s(\overline{x}), [\phi]). \tag{4}$$

Note that local Helmhotz free energy density functions $f(\epsilon_{ij}, T, \phi)$ used in traditional theories are special cases of the general expression (1); one simply sets

$$\tilde{f}(\bar{x}, \epsilon_{ij}, [T], [\phi]) = \tilde{f}(\bar{x}, \epsilon_{ij}, \delta_{\bar{x}} T, \delta_{\bar{x}} \phi) = f(\epsilon_{ij}(\bar{x}), T(\bar{x}), \phi(\bar{x})),$$

where $\delta_{\overline{x}}$ is the evaluation functional at $\overline{x}$.

2.2 Balance equations and constitutive relations

The starting point for constructing model evolution equations is the postulated total energy density balance equation. The total energy of the solid is defined to be the sum of the solid's internal energy and kinetic energy. Assume that the work done on the system is performed by a contact force represented by $\sigma_{ij}n_j$, where σ_{ij} is the stress tensor and n_j is the j^{th} component of the outward unit normal vector on the contacting surface and the mass density ρ remains unchanged in changes of state. The total energy density balance equation is then taken to be

$$\dot{e} + \rho v_i \dot{v}_i = \dot{q} + \sigma_{ji,j} v_i + \sigma_{ji} v_{i,j} + \dot{p}, \tag{5}$$

where e, q, p and v are the internal energy density, the heat density, the phase potential energy density, and the particle velocity.

Requiring that (5) remain invariant under rigid motion of the solid, we obtain the equation of motion and symmetry of the stress tensor:

$$\sigma_{ij,j} - \rho \dot{v}_i = 0 \text{ and } \sigma_{ij} = \sigma_{ji}. \tag{6}$$

Therefore (5) is reduced to the internal energy balance equation

$$\dot{e} = \dot{q} + \sigma_{ij}\dot{\epsilon}_{ij} + \dot{p}. \tag{7}$$

We also assume that the total energy is conserved in the sense that

$$\dot{e} + \rho v_\alpha \dot{v}_\alpha = -\nabla \cdot \vec{J}_{tot}, \tag{8}$$

where $\vec{J}_{tot}$ is the total energy density flux. As a result, we arrive at

$$\dot{e} = -\nabla \cdot \vec{J}_e + \sigma_{ij}\dot{\epsilon}_{ij}, \tag{9}$$

where $\vec{J}_e = \vec{J}_{tot} + \sigma_{\cdot\alpha} v_\alpha$. Here $\vec{J}_e$ is considered to be the internal energy density flux, while $\sigma_{ij}\dot{\epsilon}_{ij}$ is the internal power supply.

Based on (4) and (7), we propose the generalized Gibbs relation,

$$\dot{e} = \langle \dot{s}, T \rangle + \sigma_{ij}\dot{\epsilon}_{ij} + \langle e_\phi, \dot{\phi} \rangle. \tag{10}$$

By (3) and (10), we derive

$$f_{\epsilon_{ij}} = \sigma_{ij}, \quad s = -f_T, \quad \text{and} \quad e_\phi = f_\phi, \tag{11}$$

the symbols f_T and f_ϕ denoting Frechet derivatives, which in this case will be functions from Ω_T and Ω_ϕ respectively into the real numbers.

2.3 Entropy principle, fluxes, and evolution laws

We shall assume that the elastic solid occupies the whole space R^3 with a uniform phase equilibrium state being attained at ∞, and consider only material dynamics with the property that all fluxes, spatial derivatives and time derivatives decay rapidly to zero in the far field. In addition, we assume that the phase is described by a non-conserved continuous phase field function ϕ, typically scalar-valued. Without loss of generality, we assume that $\phi(\overline{x}) \to 0$, as $|\overline{x}| \to \infty$. Namely, $\phi \in C_0(R^3)$, the space of continuous functions (possibly vector-valued) on R^3 vanishing at ∞.

By (7) and (10), we have $\dot{q} = \langle \dot{s}, T \rangle$. Let $\theta = \frac{1}{T}$. The function $\theta\langle \dot{s}, T\rangle$ is now chosen, in the non-local theory, as an extension of the time rate of entropy density in classical irreversible thermodynamics. In the classical case, one assumes that this time rate of change is, except for a redistribution function which integrates out to zero, nonnegative. We therefore propose a generalized entropy principle as follows.

Entropy Principle. The function $\theta\langle \dot{s}, T\rangle$ can be decomposed into the sum of two functions σ_s and h such that σ_s is a non-negative function and h is a redistribution function, i.e. $\sigma_s \geq 0$ and $\int_{R^3} h(\overline{x}) d\overline{x} = 0$.

The part σ_s may be termed the entropy production, while h is called the entropy redistribution. [Note: a more general entropy principle can be formulated in which σ_s and h are replaced by measures [14]. We will not pursue that here.]

Let $|\alpha| = \alpha_1 + \alpha_2 + \alpha_3$, where $\alpha = (\alpha_1, \alpha_2, \alpha_3)$ is the multi-index of the partial differential operator D^α. Suppose that $\Omega_\phi = C_0^m(R^3) = \{\phi \in C_0(R^3) | D^\alpha \phi \in C_0(R^3),\ \forall\ |\alpha| \leq m\}$. $C_0^m(R^3)$ is a Banach space with the norm defined by $\|\phi\| = \sum_{|\alpha| \leq m} \|D^\alpha \phi\|_{sup}$.

Assume that the Helmholtz free energy density is given by

$$f(\overline{x}) = \tilde{f}(\overline{x}, \epsilon_{ij}, [T], [\phi]) = \overline{f}(\overline{x}, \epsilon_{ij}, [T], [D\phi]), \tag{12}$$

where the symbol $D\phi$ denotes the collection of all possible derivatives of ϕ of order $\leq m$. Let m^* be the number of them. The notation $\bar{f}(\cdots, [\overline{\psi}])$ will be used below, where $\overline{\psi} = (\psi_\alpha)$, $|\alpha| \leq m$, is an m^*-tuple of functions in $C_0(R^3)$. This function will be assumed F-differentiable on $R^3 \times R^{3\times 3} \times \Omega_T \times \left(C_0(R^3)\right)^{m^*}$.

By (12) and the chain rule, we have $\tilde{f}_\phi(\overline{x}, \epsilon_{ij}, [T], [\phi]) = \sum_{|\alpha| \leq m} \lambda_\alpha(\overline{x}) \circ D^\alpha$, where $\lambda(\overline{x}) = \lambda_\alpha(\overline{x}, \epsilon_{ij}, [T], [\phi]) = \overline{f}_{\psi_\alpha}(\overline{x}, \epsilon_{ij}, [T], [D\phi]) \in C_0^*(R^3)$, the continuous dual space of $C_0(R^3)$. Let $\overline{\lambda}_{\theta,\alpha} = \int_{R^3} \theta(\overline{y})\lambda_\alpha(\overline{y})d\overline{y} \in C_0^*(R^3)$. We restrict to the case that there exists a $\overline{\zeta}_{\theta,\alpha} \in L^1(R^3) \cap C_0^m(R^3)$ such that

$$\langle \overline{\lambda}_{\theta,\alpha}, \varphi \rangle = \int_{R^3} \overline{\zeta}_{\theta,\alpha}(\overline{y})\varphi(\overline{y})d\overline{y}, \ \forall \varphi \in C_0(R^3). \tag{13}$$

Since $\vec{J_e} \to 0$ and $D^\alpha \dot{\phi} \to 0$ rapidly as $|\overline{x}| \to 0$, by (9), (10), (13) and some manipulations, we have

$$\theta\langle \dot{s}, T\rangle = \sigma_s + h = \vec{J_e} \cdot \nabla\theta - \dot{\phi} \sum_{|\alpha| \leq m} (-1)^{|\alpha|} D^\alpha \overline{\zeta}_{\theta,\alpha} + h, \tag{14}$$

where h is a redistribution function. On the right side of (14) the fluxes and the thermodynamic forces are now identified as

flux: J_i	$\vec{J_e}$	$-\dot{\phi}$
force: X_i	$\nabla\theta$	$\sum_{\|\alpha\| \leq m} (-1)^{\|\alpha\|} D^\alpha \overline{\zeta}_{\theta,\alpha}$

. (15)

In accordance with practice in CIT and with the Curie principle, we propose linear phenomenological relations between the fluxes and forces, to ensure that $\sigma_s \geq 0$:

$$\vec{J_e} = -A\nabla T \quad \text{and} \quad \dot{\phi} = -c \sum_{|\alpha| \leq m} (-1)^{|\alpha|} D^\alpha \overline{\zeta}_{\theta,\alpha}, \tag{16}$$

where A is a non-negative definite matrix and $c \geq 0$. Here $(16)_2$ is the phase field evolution equation.

For example when $\bar{f}$ depends locally and quadratically on only the first order derivatives of ϕ, then the corresponding function $\overline{\zeta}_{\theta,\alpha}$ with $|\alpha| = 1$ is linear in those first order derivatives, and we obtain a 2nd order elliptic operator on ϕ on the right of $(16)_2$.

By (9), (10) $(11)_3$ and $(16)_1$, we obtain the the internal conduction equation,

$$\langle \dot{s}, T\rangle + \langle f_\phi, \dot{\phi}\rangle = \nabla \cdot (A\nabla T). \tag{17}$$

The system of basic equations governing the evolutions of state of the multiphase elastic solid consist of (17), $(16)_2$ and $(6)_1$. This system of basic equations is complemented by initial conditions and conditions in the far field.

Note that any choice of σ_s is potentially permissible as long as $\theta\langle \dot{s}, T\rangle = \sigma_s + h$, where h is a redistribution function.

When the elastic solid is quasi-static, the equation $(6)_1$ becomes $\sigma_{ij,j} = 0$. We assume the elastic solid is quasi-static in the rest of this section.

2.4 Interfaces for gradient theories with local dependence

A dimensionless local Helmholtz free energy density function is now postulated. The previous notation for dimensional variables is still used to denote the corresponding dimensionless variables. We take ϕ to be a non-conserved one-component order parameter whose range is in $[0,1]$.

We first assume that $(0_{ij}, 1, \phi_o)$ is the stress-free equilibrium state of the reference configuration of the solid, used in defining the strain tensor. We restrict ourselves to changes of state in which the temperature changes and deformations are small and slow, so that the linear theory of thermo-elasticity can be applied. Moreover, the elastic solid is assumed to be quasi-static homogeneous isotropic. The dimensionless Helmholtz free energy density is assumed to be of the form

$$f(\epsilon_{ij}, T, \phi) = f_0(T, \phi) + \frac{1}{2}\varepsilon^2|\nabla\phi|^2 + f_{el}(\epsilon_{ij}, T, \phi), \tag{18}$$

with $f_{el}(\epsilon_{ij}, T, \phi) = \varepsilon[\frac{1}{2}\lambda\epsilon_{\alpha\alpha}^2 + G\epsilon_{ij}\epsilon_{ij} - b_1(T-1)\epsilon_{\alpha\alpha} - b_2(\phi-\phi_o)\epsilon_{\alpha\alpha}]$, where the dilatation $\epsilon_{\alpha\alpha}$ is the trace of of ϵ_{ij}, ε is a small parameter, λ and G are Lamé constants, and b_1 and b_2 are two positive constants. All parameters are dimensionless. The bulk free energy density $f_0(T,\phi)$ is a quadratic function of T when ϕ is fixed, while it is a smooth double-well function of ϕ such that it is convex on $R \setminus (q_0, q_1)$ for some interval $(q_0, q_1) \subset (0,1)$, for every T fixed. For each given T, $f_0(T,\phi)$ has two minima at $\phi_\pm(T)$, and it has equal minima at $\phi_\pm(T)$ if and only if $T = \tau_c$. In addition, we assume $f_{0_T}(\tau_c, \phi_+(\tau_c)) - f_{0_T}(\tau_c, \phi_-(\tau_c)) > 0$ and $f_0(\tau_c, \phi)$ is symmetric about $\frac{1}{2}(\phi_-(\tau_c) + \phi_+(\tau_c))$.

Let

$$c_v(\phi) = -f_{0_{TT}}(T,\phi) \text{ and } q(\phi) = f_{0_T}(1,\phi) - f_0(1,\phi). \tag{19}$$

Then $c_v(\phi)$ represents the $O(1)$ specific heat of the solid at the phase ϕ and $-q(\phi)$ is the $O(1)$ internal energy density of the solid at $T=1$ and phase ϕ. By $(11)_1$, the stress tensor is given by

$$\sigma_{ij} = \varepsilon[\lambda\epsilon_{\alpha\alpha}\delta_{ij} + G\epsilon_{ij} - b_1(T-1)\delta_{ij} - b_1(\phi-\phi_o)\delta_{ij}]. \tag{20}$$

Using (20) and the basic equations in the previous subsection, also following the widely used simplification in thermo-elasticity that the internal energy conduction equation is linearized so that the coefficients of $\dot{T}$ and $\dot{\phi}$ in it are independent of T, we have

$$\begin{cases} c_v(\phi)\dot{T} - \nabla^2 T &= q'(\phi)\dot{\phi} - \varepsilon^2\nabla\phi\cdot\nabla\dot{\phi} - \varepsilon b_1\dot{\epsilon}_{\alpha\alpha} + \varepsilon b_2\epsilon_{\alpha\alpha}\dot{\phi} \\ \varepsilon^2\alpha\dot{\phi} &= -\theta f_{0_\phi}(T,\phi) + \varepsilon^2\nabla\cdot(\theta\nabla\phi) - \varepsilon b_2\theta\epsilon_{\alpha\alpha}, \end{cases} \tag{21}$$

where $\epsilon_{\alpha\alpha} = \frac{1}{\lambda+2G}[b_1(T-1)+b_2(\phi-\phi_o)]$ and α represents a dimensionless relaxation time. In view of the linearization of internal energy conduction, $l_0 = q(\phi_+(\tau_c)) - q(\phi_-(\tau_c))$ represents the $O(1)$ dimensionless latent heat density at $T = \tau_c$. Without loss of generality, we assume that $f_{0_T}(\tau_c, \phi_+(\tau_c)) - f_{0_T}(\tau_c, \phi_-(\tau_c)) = 1$ and $q(\phi_+(\tau_c)) = \frac{1}{2}l_0$.

We shall now summarize the implications of (21) regarding interface conditions of Gibbs-Thomson type. Define the phase interface by the level surface $\Sigma(t,\varepsilon) = \{\overline{x} : \phi(\overline{x},t,\varepsilon) = \hat{h}\}$, where $\hat{h} \in (q_0, q_1) \subset (0,1)$. Identify the "phase zero" region with $\{\overline{x} : \phi(\overline{x}) < q_0\}$ and "phase one" region with $\{\overline{x} : \phi(\overline{x}) > q_1\}$.

To pursue an asymptotic layer analysis, we assume that $T = T(\overline{x},t,\varepsilon) = T_0(\overline{x},t) + \varepsilon T_1(\overline{x},t) + O(\varepsilon^2)$, and $\phi = \phi(\overline{x},t,\varepsilon) = \phi_0(\overline{x},t) + \varepsilon\phi_1(\overline{x},t) + O(\varepsilon^2)$, when $\overline{x}$ is away from $\Sigma(t,\varepsilon)$. Near $\Sigma(t,\varepsilon)$, we define the local coordinates (s_1,s_2,r) by $\overline{x} = \overline{x}(s_1,s_2,r) = \mathbf{p}(s_1,s_2) + r\mathbf{n}(s_1,s_2)$, where $\mathbf{p}$ is a re-parameterization of the phase interface surface and $\mathbf{n}$ is the unit normal vector toward the phase one region. The stretched local coordinates are defined by (s_1,s_2,z), where $z = \frac{r}{\varepsilon}$. By solving inner basic equations with stretched local coordinates, we obtain the $O(1)$ inner temperature field $\tilde{T}(z,s_1,s_2) = \tau_c$ and the $O(1)$ inner phase field $\Phi(z,s_1,s_2) = \psi(z)$. Let $\hat{T}_{0_r}|_{\Sigma\pm}$ be the normal derivatives of T_0 on both sides of the phase interface. Let $\mathcal{A} = \int_R \psi_z^2(z')dz'$, $\gamma(z) = \int_0^z q(\psi(z'))dz' - \frac{1}{2}\int_0^z \psi_z^2(z')dz'$, $\kappa = -\int_R \gamma(z')\psi_z(z')z'dz' + \frac{1}{\tau_c}\mathcal{A}$, and $\Psi = \int_R f_{0_T}(\tau_c,\psi)\gamma\psi_z - \frac{1}{\tau_c}\int_R \gamma_z\psi_z^2 - \int_R \gamma\psi_{zz}\psi_z$. By the matching conditions of inner and outer temperature fields and phase fields, we have interface conditions $T_0|_\Sigma = \tau_c$, $\psi(\pm\infty) = \phi_\pm(\tau_c)$, and

$$\begin{aligned} & T_1|_{\Sigma\pm} - \kappa\hat{T}_{0_r}|_{\Sigma\pm} + 2H_0\mathcal{A} - R_{el} \\ = & \quad -v_0\left[-\int_0^{\pm\infty}(q(\psi) \mp \frac{1}{2}l_0)dz \mp \frac{1}{4}\mathcal{A} + \alpha\tau_c\mathcal{A} + \Psi + \frac{1}{2}\kappa l_0\right], \end{aligned} \tag{22}$$

where

$$R_{el} = \frac{b_1 b_2}{\lambda+2G}(\tau_c - 1)[\phi_0]_\Sigma + \frac{b_2^2}{\lambda+2G}\left(\frac{[\phi_0]_\Sigma^2}{2} - \int_R \tilde{\phi}_o\psi_z\right). \tag{23}$$

Here $\tilde{\phi}_o$ is the reference phase parameter in the stretched local coordinates near the phase interface.

Eq. (22) is the Gibbs Thomson relation that characterizes the mechanics of the phase interface. This relation connects the phase front normal velocity v_0 to the temperature on both sides of the phase interface, the mean curvature H_0 of the phase interface surface, the relaxation time α, the latent heat density l_0, the phase interface surface tension represented by $\mathcal{A}$, and an elastic effect represented by R_{el} (all, except for the temperature, to lowest order). The typical kinetic under-cooling (super-heating) condition is recovered when the temperature is constant in a neighborhood of a flat phase interface and the elastic effect is ignored.

2.5 Interfaces with nonlocal dependence

As a non-local analogue to the local Helmholtz free energy density function in (18), the term $\frac{1}{2}\varepsilon|\nabla\phi|^2$ is replaced by

$$\int_{R^3} J_\varepsilon(\overline{x}-\overline{y}, T(\overline{x}), T(\overline{y}))(\phi(\overline{y})-\phi(\overline{x}))^2 d\overline{y},$$

where $J_\varepsilon(\overline{x}, \tau_1, \tau_2) = \frac{1}{\varepsilon^3} J(\frac{\overline{x}}{\varepsilon}, \tau_1, \tau_2)$, and the influence function J is smooth. Moreover, J is even in $\overline{x}$ and quadratic in τ_1 and τ_2 with certain decay properties as $|\bar{x}| \to \infty$. Besides nonlocality, this replacement allows a great deal of anisotropy through the function J.

Basic equations can be formulated as was done previously. To develop the asymptotics, we use a coordinate system tied to the interface and write $k(\overline{\sigma}, \overline{\tau}) = k(\sigma_1, \sigma_2, \sigma_3, \tau_1, \tau_2) = J(\sigma_1 \mathbf{p}_{s_1} + \sigma_2 \mathbf{p}_{s_2} + \sigma_3 \mathbf{n}, \tau_1, \tau_2)$, where $\mathbf{p}_{s_i} = \frac{\partial}{\partial s_i}\mathbf{p}$ for $i = 1, 2$. In addition, we assume $\phi_\pm(\tau_c) = 1, 0$, $\int_{R^3} k(\overline{\sigma}, \overline{\tau_c}) d\overline{\sigma} = 1$, and $f_{0_{\phi\phi}}(\tau_c, \phi) < 2$, for all $\phi \in R$.

By an asymptotic layer analysis, the inner basic equations in stretched local coordinates are solvable under the assumed conditions. We obtain, as $O(1)$ inner temperature field, $\tilde{T}(s_1, s_2, z) = \tau_c$ and as $O(1)$ inner phase field, $\Phi(s_1, s_2, z) = \psi^*(z)$. By matching conditions, we obtain $T_0|_\Sigma = \tau_c$ and $\psi^*(\pm\infty) = 1, 0$.

Finally, a Gibbs-Thomson relation analogous to (22) is obtained. It takes the form

$$\begin{aligned} & T_1|_{\Sigma\pm} - \kappa^* \hat{T}_{0_r}|_{\Sigma\pm} - \int_R \omega \psi_z^* - R_{el} \\ = \; & -v_0 \left[\int_0^{\pm\infty} \xi g(\xi) d\xi + \alpha \tau_c \mathcal{A}^* + \Psi^* + \kappa^* \int_0^{\pm\infty} g(z) dz \right], \qquad (24) \end{aligned}$$

where $\mathcal{A}^* = \int_R \psi_z^{*^2}$, the symbols such as κ^*, Ψ^* and g are given by complicated expressions involving k, ψ^*, f_0, q (and some of their derivatives), and R_{el} is given by (23).

The curvature effect in this case is embodied in the term $\int \omega \psi_z^*$; here the function $\omega(z)$ is expressed by a sum of integrals involving the first and second fundamental forms of the interfacial surface, and their derivatives along that surface. The effect of curvature is more complicated than one is accustomed to expect from the usual Gibbs-Thomson relation. Part of the reason is that we have not assumed isotropy of the influence function J.

3 Binary alloys

During the process of solidification of an alloy, it is important to be able to predict the composition of the material on the solid and liquid sides of the phase interface. Generally they differ from one another, and depend on the temperature, velocity, and curvature of the interface.

Well documented equilibrium phase diagrams for a great number of alloys provide this information when the rate of solidification, hence the velocity of the solidification front, is small enough.

At higher velocities, the picture is not so well known. As the velocity increases, the jump in concentration decreases; this is the solute trapping effect. The concentration may even be subject to an oscillatory instability. There are various nonequilibrium theories which address the question of how the compositional change at the phase interface depends on velocity, as well as temperature. Notable among them are the classical theories of Baker and Cahn [6] and of Aziz and coworkers (see for example [5]), the Cahn-Hilliard-type theory of Langer and Sekerka [25], and the more recent phase field theories of Ahmad, Wheeler, Boettinger, and McFadden [30, 31, 1] and the authors [12]. See [8] for a phase field model without trapping. Conti [16, 17] has made numerical studies of trapping based on phase field models.

Oscillatory phenomena were studied in the context of sharp interface models such as that of Aziz in [19, 27, 24, 22], and numerically in a phase-field context in [18].

A more complete review of solute trapping can be found in [1].

When it comes to modeling alloy solidification with phase and concentration fields, a crucial issue arises concerning the relative magnitudes of the gradients of the two fields within the solidification front; or equivalently the relative thickness of the concentration jump interface, as compared with that of the solid-liquid phase interface. In most of the existing theories, either it is assumed implicitly that the two interfaces coincide, or the question does not arise. In [25] a model was built consisting of a concentration field alone; the phase of the material was thought of as being tied to the concentration field, with intermediate states existing between solid and liquid. In [31], concentration and phase fields were postulated, and the Helmholtz free energy contained gradients of both fields. The ratio of the coefficients of such gradient terms effectively determine the ratio of the two interface thicknesses, except that the concentration interface is always at least as thick as the phase interface. In [12], this model was generalized in several ways and extensive asymptotic approximations constructed. In this latter paper, the question of relative size of the two interfaces was left open, and asymptotic analyses performed under several different assumptions, including the case when they are the same size.

In [1] a two-field phase field model was constructed and studied with no gradient terms for the concentration, thus effectively assuming that the two interfaces coincide. Such a model was analyzed numerically in [17]. Good agreement was found between this model and the Aziz continuous growth model [5] in some cases, in the sense that when parameters in the two models are correlated in a certain way, they both predict almost the same relation between the partition coefficient and the front velocity.

The issue of the relative interface thicknesses is difficult to resolve experimentally. Moreover, molecular dynamical simulations such as those in [32] have generally not been directed to this question. They can best be performed in regimes where little light is shed on the question. It has been difficult to simulate conditions under which the maximal deviation of the concentration in the liquid from that in the solid does not occur at the edge of the phase interface [15]. For these reasons, we have left this issue open in [12], allowing a range of possible relative thicknesses.

In this section, we describe the phase-field model used in [12], as well as its implications on how the velocity and curvature of the solidification front affects the concentrations at the solid and liquid sides of the front. The model, a generalization of the one in [31], involves two small phase-field-type interaction parameters ϵ and δ. The first has physical relevance regarding the magnitude of the surface tension of the front, and the second is strongly related to the question of how the surface tension depends on concentration.

3.1 Basic formulation and evolution equations

The material in question is now a binary alloy describable, at each point, by the values of the temperature T, the mole fraction c of solute in the alloy, and a continuous scalar phase order parameter ϕ, representing liquid and solid at the two extremes $\phi = -1$ and $\phi = 1$. We neglect volume changes in the solidification process and consider the molar volume of both components of the alloy to be equal to some average value.

As in sec. 2.1, we begin with an assumed Helmholtz free energy density. This time it is of the form

$$f'(\phi, c, T, \nabla\phi, \nabla c) = f(\phi, c, T) + \bar{\epsilon}^2|\nabla\phi|^2 + \bar{\delta}^2|\nabla c|^2. \tag{25}$$

Here the only type of nonlocality we have is in the gradients of ϕ and c. Gradient terms are well known to be associated with the surface free energy of interfaces.

The bulk part f of f' is merely required to satisfy the general conditions that it be convex as a function of c and that its second derivative with respect to T be negative (positive heat capacity). However, it will be convenient to use a prototypical form for an ideal solution:

$$f(\phi, c, T) = (1-c)f_A(\phi, T) + cf_B(\phi, T) + \frac{RT}{v_m}[(1-c)\ln(1-c) + c\ln c]. \tag{26}$$

Clearly f_A and f_B are the free energies of the two pure materials, represented by $c = 0$ and $c = 1$, respectively. Here R is the gas constant and v_m is the molar volume.

We now define the entropy $s' = -\left(\frac{\partial f'}{\partial T}\right)_{\phi,c}$ and the internal energy $e' = f' + Ts'$. Both of these latter quantities will in general involve gradient terms similar to those in (25).

The equations of evolution of our system follow from (i) the energy and entropy balance equations, (ii) linear relations between the thermodynamic forces and fluxes, and (iii) the requirement that the local entropy production be nonnegative. This is in accord with the procedure of classical irreversible thermodynamics.

We make some simplifications, such as neglecting the gradient terms in the internal energy and the cross effects in the transport matrix. We nondimensionalize using typical values of latent heat, heat capacity, and thermal diffusivity to obtain dimensionless partial differential equations of the form

$$\alpha\epsilon\rho\phi_t = \epsilon^2\nabla^2\phi - F(\phi, c, \vartheta), \quad \rho e_t = \nabla^2\vartheta, \quad \frac{1}{\mathcal{L}}c_t = \nabla D\nabla(g - \delta^2\nabla^2 c). \tag{27}$$

Here F and g are dimensionless versions of $\frac{1}{T}\frac{\partial f}{\partial\phi}$ and $\frac{1}{T}\frac{\partial f}{\partial c}$ respectively, e and ϑ are dimensionless internal energy and temperature, ϵ^2 and δ^2 are dimensionless versions of $\frac{\bar{\epsilon}^2}{T}$ and of $\frac{\bar{\delta}^2}{T}$, and ρ is a dimensionless characteristic velocity, which governs the time scale. Also $\mathcal{L}$ is the Lewis number (the ratio of mass to thermal diffusivity in the liquid) and D is a mass diffusivity, a function of ϕ and c which varies greatly in order of magnitude from liquid ($\phi = -1$) to solid ($\phi = 1$). Let $\lambda \gg 1$ be the ratio D_{liq}/D_{sol}, assumed to be constant. The parameter α appearing on the left of $(27)_1$ is a dimensionless combination proportional to μ^{-1}, where μ is a kinetic undercooling material constant, namely the proportionality constant in the expression

$$V = \mu(T_m - T)$$

relating the velocity V of a planar solidification front for the pure material "A" to the deviation of its temperature from the melting temperature T_m.

We have thus identified all the parameters in (27) except ϵ and δ with traditional material constants. In the next section, we do the same with these remaining ones.

3.2 Layers and interfaces; significance of ϵ and δ

We are interested in solutions of these equations (27) which depict solid and liquid regions with interfaces between them. Near the interfaces, there will in general be an abrupt change in c as well as ϕ. Our method is to use standard layer perturbation techniques to develop inner and outer approximations based in part on parameters ϵ and δ, both of which we assume to be small.

As was brought out above, concepts traditionally associated with physical properties of interfaces can be naturally associated also with the parameters in (27).

In this vein, there is a basic question as to the physical meaning which should be assigned to the parameters $\bar{\epsilon}$, $\bar{\delta}$, hence to ϵ, δ. In phase field models of a pure material, the gradient term appearing second on the right of (25) is well known to be associated with surface tension and capillarity effects. In fact, a standard layer analysis, based on the smallness of ϵ, applied to a hypothetical dimensionless Helmhotz free energy function $f(\phi, T) + \epsilon^2|\nabla\phi|^2$, with f a double well function of ϕ, leads to the following expression for the excess surface free energy associated with the interface:

$$\sigma_0 = \epsilon \int_{-\infty}^{\infty} \Phi_z^2(z) dz,$$

where $z = r/\epsilon$ is a coordinate representing scaled signed distance from the interface ($r =$ signed distance). Here $\Phi(z)$ is the dominant part (lowest order approximation to) the phase field ϕ, when expressed in terms of the scaled coordinates. This dominant part turns out to be independent of position on the interface and of time; thus σ_0 as given above can indeed be thought of as a material constant. Typically, Φ is like an arctan function of z.

In the present case, when interfacial free energy terms come from the gradient of c as well, as in (25), the corresponding expression for the excess free energy will be

$$\sigma = \epsilon \int_{-\infty}^{\infty} \left[\Phi_z^2(z) + \frac{\delta^2}{\epsilon^2} C_z^2(z) \right] dz, \tag{28}$$

where C is concentration c, written in terms of the scaled inner coordinates.

Approximate expressions for Φ and C can be obtained from (27) by singular perturbation methods. The problem really has four independent small parameters: ϵ, δ, $\mathcal{L}$, $\frac{1}{\lambda}$, plus a parameter ρ which can be of any order of magnitude. The approximate expression for $\Phi(z)$ is, under reasonable assumptions, independent of the parameters, but the one for C is quite parameter-dependent.

In [12], the authors made an extensive lowest-order asymptotic analysis of the interfacial structure for various ratios $r' = \frac{\delta}{\epsilon}$, including the limiting case $r' = 0$. In one general parameter regime with $r' \gg 1$, the function ϕ at the interface varies on the scale of ϵ, whereas the change in c occurs on the scale of δ [31]. In this case, an expression of the following type is found for the surface tension:

$$\sigma = S(\vartheta, \epsilon, \delta), \tag{29}$$

where ϑ is the temperature at the solidification front. If we assume that the concentration c is small, then its value at the front is bracketed by the solidus and liquidus concentrations, which are both given approximately by linear functions of ϑ. Thus we may invert these linear functions to obtain, *in order of magnitude*, c as a function of ϑ. Putting them into (29), we obtain, again in order of magnitude, the dependence of σ on c and δ. In short, the dependence of σ on c itself depends on δ, and we can characterize δ as regulating or measuring how much the surface tension varies as a function of c.

This variation is a physical phenomenon giving some meaning to the parameter δ. The specific expression comes out to be

$$\sigma \approx \sigma_A S_1(c) + \delta \cdot S_2(c), \tag{30}$$

where σ_A is the surface tension of the pure material with $c = 0$. If we know this value and also know what σ is at another value, say $c = 0.1$, then this gives us an order-of-magnitude estimate for the parameter δ, which will of course depend on the alloy. Using Ni-Cu data, one may estimate that δ/ϵ is large in that case.

Thus we may associate ϵ with the surface tension of the pure material "A", and δ with a measure of how strongly it varies with c.

3.3 Curvature effects on the concentration jump

Since phase-field models provide interfaces whose properties may be derived by asymptotic analysis, they provide a source of models in situations where the correct physical laws may not be entirely evident. One such law is the manner in which the solidus and liquidus curves, giving the temperature as a function of concentration on the two sides of the solidification front, are affected by the speed and curvature of the front. We call these effects the kinetic phase diagram, which is what materials scientists would like to have. Typically the planar case diagrams are derived on the basis of the sharp interface models of Aziz, but the curvature corrections are added in the form of a Gibbs-Thomson effect without an underlying theory.

When the front is planar and stationary, equilibrium theory provides the concentrations $c_\ell(\vartheta)$ and $c_s(\vartheta)$ by the common-tangent construction:

$$f_\ell(c_\ell, \vartheta) - f_s(c_s, \vartheta) = Q(c_\ell - c_s), \quad Q = \frac{\partial f_\ell}{\partial c}|_{c=c_\ell} = \frac{\partial f_s}{\partial c}|_{c=c_s}. \tag{31}$$

If f_ℓ and f_c are given strictly convex functions of c for each ϑ, these equations give unique values of $c_\ell(\vartheta)$ and $c_s(\vartheta)$, hence of the partition coefficient

$$k(\vartheta) = \frac{c_s(\vartheta)}{c_\ell(\vartheta)}. \tag{32}$$

This law (31) is also a conclusion of phase-field theory, again via asymptotic analysis, when we identify $f_\ell(c, \vartheta) = f(-1, c, \vartheta)$, $f_s(c, \vartheta) = f(1, c, \vartheta)$. Corrections due to curvature are readily derived the same way, and the result is

$$f_\ell(c_\ell, \vartheta) - f_s(c_s, \vartheta) = Q(c_\ell - c_s) - \kappa\sigma, \quad Q = \frac{\partial f_\ell}{\partial c}|_{c=c_\ell} = \frac{\partial f_s}{\partial c}|_{c=c_s}, \tag{33}$$

where κ is the sum of principal curvatures of the interface, and σ is its surface tension. This provides a curvature correction to the common tangent construction in (31).

3.4 Velocity effects on the concentration jump

The concentration jump at a solidification front decreases as the velocity of the front increases. This trapping effect is inherent in phase field models. Although it occurs at all values of the ratio $r' = \frac{\delta}{\epsilon}$ considered so far ([31, 12, 1], the last paper concentrating on the case $r' = 0$), the law by which the jump depends on speed is very much affected by the magnitude of r'. Here we give some results in the case $r' \gg 1$.

In order to isolate the kinetic from other effects in our consideration, we treat planar interfaces with known velocity V. We suppose that the melting temperature T_{mA} of the pure substance "A" is greater than that for "B", so that the partition coefficient $k < 1$ (this is the case referred to by the relevant literature in our references). We define an important characteristic velocity

$$V_1 = \frac{c_0(1-c_0)D_{cs}}{X\delta}, \tag{34}$$

where c_0 is the concentration at the phase interface, X is a characteristic macrolength, and D_{cs} is the mass diffusivity of the solid. In terms of the coefficient D appearing in (27), this constant would be given by the relations $D(c) = D_{cs}c(1-c)$ in the solid alloy, and $D(c) = \lambda D_{cs}c(1-c)$ in the liquid.

Recall that $\lambda \gg 1$, and consider now the range of velocities

$$V_1 \ll V \ll \lambda V_1. \tag{35}$$

This is the range in which we most clearly see the dependence of the (kinetic) liquidus and solidus curves on the velocity.

In this range, the concentration profile in the interfacial region can be found by asymptotic analysis of $(27)_3$ on the basis of the smallness of δ and of V_1/V. It is found that c varies spatially on the scale of δ on the liquid side of the interface, and on a smaller scale of $(V_1/V)^{1/3}$ on the solid side. Moreover by matching this profile with an asymptotic analysis of the thinner phase interface (with width $O(\epsilon)$), we can determine the approximate values of c on both sides of the concentration interface. Their difference, i.e. the concentration jump, and the partition coefficient k, are given by

$$\Delta c = O(V_1/V)^{1/3}; \quad k = 1 - O(V_1/V)^{1/3}. \tag{36}$$

Other cases which can be readily analyzed are these:

When $V \ll V_1$, then (approximately) the concentration is given by its equilibrium values (common tangent construction) on the two sides of the concentration interface.

When $V \gg V_2$, then to a good approximation, there is no jump in the concentration at the interface.

In terms of the solute trapping effect, we can say that these last two cases represent no trapping and complete trapping respectively, whereas the intermediate case yields partial trapping, and in particular (36) gives the extent of it as a function of the velocity V.

The same methods can be used [12] under many other assumptions about the ratio r', even when $r' = \delta = 0$ [1].

It is relevant to ask how these kinetic effects alter the common tangent construction (31). It is replaced by more general response functions that define the kinetic phase diagram in terms of the driving force for solute redistribution and the driving force for solidification. Both of them follow by integrating the governing field equations. Explicit forms of these response functions are given in [1] (for $\delta = 0$) and in [11] for $\epsilon \ll \delta$.

4 Discussion

In nonequilibrium studies of materials which change phase, there are areas which lack hard and fast theoretical and experimental underpinning. In some cases, phase-field concepts provide possible frameworks for building models to aid in our understanding of these phenomena. They in fact may suggest topics for experimental investigation. These modeling efforts proceed, as in many natural scientific disciplines, on the basis of analogy with concepts and principles in fields where they are more firmly grounded.

In this paper we have illustrated this modeling process by reviewing its application to materials which change phase in the presence of effects due to thermoelasticity, nonlocal influences, thermal gradients, and changing composition of an alloy.

The ultimate goal is to develop some understanding of the basic physical processes involved. As in all modeling efforts, comparisons between the predictions and hypotheses of different models are of the utmost importance. In this respect we have focussed on implications of phase-field models on conditions at interfaces, thus enabling some comparison with sharp interface models.

In the case of highly nonequilibrium alloy solidification, models abound but more experimental studies are needed to cast light on their validity.

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