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GENERALIZED PHASE FIELD THEORIES

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Using balance laws for microforce and energy in conjunction with constitutive equations consistent with the second law, a general phase-field theory of solidification is developed in which gradients of the order parameter enter the constitutive equations for the internal energy and the entropy. The final results consist of anisotropic and isotropic phase-field equations at various levels of generality.

1. INTRODUCTION

Solidification is often described by a modified Stefan problem—for the deviation u of the temperature from its transition value—in which the free-boundary conditions

$$\begin{aligned} u &= (\text{constant})\bar{K} + (\text{constant})\bar{V}, \\ (\text{latent heat})\bar{V} &= \text{jump in normal heat-flux across the interface}, \end{aligned} \tag{1.1}$$

involve the mean curvature $\bar{K}$ and normal velocity $\bar{V}$ of the interface, and consequently lead to problems of great difficulty. For that reason Langer [1],[1] Fix [3], Collins and Levine [4], and Caginalp [5] introduce and study a model in which the phase of the material is characterized by an order parameter φ, called the *phase field;* φ has nearly constant values in each bulk phase and makes a smooth but rapid transition between phases within a thin transition layer that represents the sharp interface of the Stefan model.

The phase-field model consists of a modified heat equation

$$c\dot{u} + \rho\dot{\varphi} = k\Delta u \tag{1.2}$$

supplemented by a Ginzburg-Landau equation

$$\beta\dot{\varphi} = f\Delta\varphi - F'(\varphi) + \rho u, \tag{1.3}$$

where c, k, β, f, and ρ are constants, with all but ρ strictly positive, and $F(\varphi)$ is a

[1] Based in a Model C of Halperin, Hohenberg, and Ma [2].

double-well potential whose "wells" define the phases. The Ginzburg-Landau equation is based on the assumption that the variational derivative $\delta\Psi/\delta\varphi$ of the "free-energy functional"

$$\Psi(u,\varphi) = \int_{\Omega} \{F(\varphi) + \tfrac{1}{2}f|\nabla\varphi|^2 - \rho u\}\,dv \qquad (\Omega = \text{underlying region of space}) \qquad (1.4)$$

be consistent with the relaxation law: $\beta\varphi^{\cdot} = -\delta\Psi/\delta\varphi$.

There are now analytical and computational support for the use of phase-field models to regularize Stefan-type problems. Soner [6] proves that, modulo a suitable scaling, a slightly modified version of the phase-field equations approach the Stefan system based on (1.1) as the "interface thickness" tends to zero;[2] and computational studies of Caginalp and Socolovsky [15], Koboyashi [16], and Wheeler et al. [17], among others, demonstrate that phase-field models capture the qualitative features of solidification, including dendritic growth.

These studies present little information regarding the theoretical status of phase-field models within the framework of continuum thermodynamics. In fact, Penrose and Fife [18] and (later) Wang et al. [19], arguing that the derivations given in [1,3-5] are based on a free-energy functional and therefore applicable only under isothermal conditions, develop theories based on an entropy functional. The Ginzburg-Landau equation is derived variationally by Penrose and Fife as a relaxation law and by Wang et al. using a local formulation of the second law (the Clausius-Duhem inequality), and it is unclear from either of these derivations whether the Ginzburg-Landau equation should be viewed as a balance law, a constitutive equation, or a combination of the two. Concurrently with [19], Fried and Gurtin [20] develop a framework for theories of phase-field type based on arguments now common in continuum mechanics in which balance laws are carefully distinguished from constitutive equations. What is new in [20] is the introduction of a balance law for microforces[3] (defined operationally as forces that perform work over changes in the order parameter); this force balance leads to the Ginzburg-Landau equation.

Here, continuing in the spirit of [20], I develop a fairly general class of phase-

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[2] Earlier, Stoth [7,8] established convergence under radial symmetry for $u = (\text{constant})\,\bar{K}$. Formal asymptotic analyses for the general problem were given in [1,3-5]; see also [9-14] for formal results relating the phase-field equations to other problems of physical interest.

[3] Our belief is that kinematic variables introduced to model material microstructure require additional force and/or moment balances. Such microbalances can be motivated from statical considerations as Euler-Lagrange equations corresponding to independent variations of the microstructural kinetic-variables. In [20] we referred to such forces as *accretive;* but I now prefer the term *microforces.*

field models. What made me continue this program is the belief that, although the models developed in [18] and [19] are internally consistent and result in PDE's of the correct formal structure, the derivations seem flawed, as they neglect the internal energy of the interface (gradient energy).[4]

To explain my reasons for making this assertion consider the first two laws expressed schematically as

$$(d/dt)\{\mathcal{E}^{bulk} + \mathcal{E}^{xs}\} = \ldots\ldots\ldots, \qquad (d/dt)\{\mathcal{S}^{bulk} + \mathcal{S}^{xs}\} \geq \ldots\ldots\ldots \tag{1.5}$$

For a sharp interface $\mathcal{E}^{bulk}$ and $\mathcal{S}^{bulk}$ represent the internal energy and entropy in bulk, while $\mathcal{E}^{xs}$ and $\mathcal{S}^{xs}$ are the energy and entropy of the interface. For a generalized phase-field theory, the entropy per unit volume is given, constitutively, as a coarse-grain entropy $\eta^{cg}(u,\varphi)$ plus a gradient entropy $\eta^{gr}(u,\varphi,\nabla\varphi)$, and $\mathcal{S}^{bulk}$ is the integral of $\eta^{cg}(u,\varphi)$, while $\mathcal{S}^{xs}$ is the integral of $\eta^{gr}(u,\varphi,\nabla\varphi)$; similar interpretations apply to $\mathcal{E}^{bulk}$ and $\mathcal{E}^{xs}$. The usual argument supporting the neglect of interfacial energy seems based on the observation that $(1.1)_2$, which expresses balance of energy across the interface, neglects interfacial energy. But (1.1) are the result of approximating a set of general interface conditions that include both interfacial energy and entropy, and while interfacial energy is neglected in $(1.1)_2$, it is generally present in $(1.1)_1$, as τ typically represents the free energy at the transition temperature.[5]

Further, I would generally expect the internal energy and entropy of the interface to be roughly the same order (at least when the temperature is not too high), and similarly for the bulk energy and bulk entropy; and it would therefore seem unsound in a general theory to neglect interfacial energy in the energy balance $(1.5)_1$, but to retain interfacial entropy in the entropy inequality $(1.5)_2$. I believe that a more rational procedure[6] is to first derive general equations based on laws of the type (1.5), and then to apply whatever approximations one

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[4] After completing this study I saw notes of Wang, Sekerka, Wheeler, Murray, Coriell, Braun, and McFadden establishing an isotropic theory which includes gradient energy. These notes, which are based on [19], derive the PDE's (1.8).

[5] Cf., e.g., Mullins and Sekerka [21], Gurtin [22,23].

[6] An alternative procedure, developed in [23] and used by Fried and Gurtin [20], begins with an approximation of the general laws (1.6). The chief obstacle is that in (1.6) bulk terms dominate interfacial terms, so that neglecting lower-order terms results in the omission of interfacial effects. What is needed is an inequality with interfacial terms of the same order as bulk terms. The combination (internal energy) - (θ_0) (entropy) vanishes in bulk at the transition temperature θ_0. Thus if the entropy inequality is multiplied by θ_0 and subtracted from the energy equation, the resulting inequality has both bulk and interfacial terms small near θ_0. This inequality is then used (as an approximate second law) in conjunction with balance of energy assuming $\mathcal{E}^{xs}=0$.

wants to the resulting equations.

Using this procedure I derive a hierarchy of phase-field equations at various levels of generality and approximation. For a material with constant specific heat c and constant conductivity tensor $\mathbf{K}$, with internal-energy ε and entropy η given by constitutive equations

$$\begin{aligned} &\varepsilon = c\theta + E(\varphi) + \tfrac{1}{2}e(\mathbf{m})|\nabla\varphi|^2, && \eta = c\ln\theta + S(\varphi) + \tfrac{1}{2}s(\mathbf{m})|\nabla\varphi|^2, \\ &\theta = \text{temperature}, && \mathbf{m} = \nabla\varphi/|\nabla\varphi|, \end{aligned} \tag{1.6}$$

and with $f(\theta,\mathbf{m}) := e(\mathbf{m}) - \theta s(\mathbf{m})$, the resulting PDE's are

$$\begin{aligned} &c\theta^{\cdot} + [E(\varphi)]^{\cdot} - \varphi^{\cdot}\operatorname{div}[e(\mathbf{m})\nabla\varphi] + \tfrac{1}{2}\ell^2[e(\mathbf{m})]^{\cdot} = \operatorname{div}\{\mathbf{K}\nabla\theta + \tfrac{1}{2}\ell\varphi^{\cdot}\partial_{\mathbf{m}}f(\theta,\mathbf{m})\}, \\ &\beta(\theta,\mathbf{m})\varphi^{\cdot} = \operatorname{div}[e(\mathbf{m})\nabla\varphi] - \theta\operatorname{div}[s(\mathbf{m})\nabla\varphi] + \tfrac{1}{2}\operatorname{div}[\ell\,\partial_{\mathbf{m}}f(\theta,\mathbf{m})] - E'(\varphi) + \theta S'(\varphi). \end{aligned} \tag{1.7}$$

For an isotropic material these PDE's have the simple form[7]

$$\begin{aligned} &c\theta^{\cdot} + [E(\varphi)]^{\cdot} - e\varphi^{\cdot}\Delta\varphi = k\Delta\theta, \\ &\beta(\theta)\varphi^{\cdot} = f(\theta)\Delta\varphi - E'(\varphi) + \theta S'(\varphi), \end{aligned} \tag{1.8}$$

and reduce to equations derived by Penrose and Fife [18] and Wang et. al. [19] if $e=0$, $s<0$, and $\beta(\theta) = \theta\beta_0$, and to equations given by Fried and Gurtin [20] if $s = 0$ and β = constant. Further, granted suitable approximations, (1.8) reduce to the original phase-field equations (1.2), (1.3) (cf. the discussion following (4.28)).

2. GENERAL THEORY[8]

a. Basic equations

The primitive quantities of the theory are the fields

ε	internal energy
θ	absolute temperature
η	entropy
$\mathbf{q}$	heat flux
φ	order parameter (scalar)
$\boldsymbol{\xi}$	microstress (vector)
π	internal microforce (scalar)

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[7] Cf. Footnote 4.

[8] This section is taken from [20], where arguments in support of (2.1) and (2.3) can be found.

defined for all time on the region of space Ω occupied by the material; the basic laws are *balance of energy*

$$\{\int_R \varepsilon\,dv\}^{\cdot} = -\int_{\partial R} \mathbf{q}\cdot\mathbf{n}\,da + \int_{\partial R} \varphi^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da, \tag{2.1}$$

growth of entropy

$$\{\int_R \eta\,dv\}^{\cdot} \geq -\int_{\partial R} (\mathbf{q}/\theta)\cdot\mathbf{n}\,da, \tag{2.2}$$

and a *microforce balance*

$$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{n}\,da + \int_R \pi\,dv = 0 \tag{2.3}$$

for each control volume R (subregion of Ω), where $\mathbf{n}$ is the outward unit normal to ∂R. These global laws have local forms

$$\begin{aligned} &\varepsilon^{\cdot} = -\operatorname{div}\mathbf{q} + \operatorname{div}(\varphi^{\cdot}\boldsymbol{\xi}), \\ &\eta^{\cdot} = -\operatorname{div}(\mathbf{q}/\theta) + \gamma, \qquad \gamma \geq 0, \\ &\operatorname{div}\boldsymbol{\xi} + \pi = 0, \end{aligned} \tag{2.4}$$

with γ the entropy production; together they yield the dissipation inequality

$$\psi^{\cdot} + \eta\theta^{\cdot} + \pi\varphi^{\cdot} - \boldsymbol{\xi}\cdot\nabla\varphi^{\cdot} + \theta^{-1}\mathbf{q}\cdot\nabla\theta = -\theta\gamma \leq 0, \tag{2.5}$$

with

$$\psi = \varepsilon - \theta\eta \tag{2.6}$$

the *free energy.*

An important feature of the thermodynamic structure is the existence of natural Lyapunov functionals: a direct consequence of (2.1), (2.2), and the second of (2.4) is that, granted $\varphi^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n} = 0$ on $\partial\Omega$,

$$\{\int_\Omega \varepsilon\,dv\}^{\cdot} = 0, \qquad \{\int_\Omega \eta\,dv\}^{\cdot} = \int_\Omega \gamma\,dv \geq 0 \qquad \text{if } \mathbf{q}\cdot\mathbf{n} = 0 \text{ on } \partial\Omega; \tag{2.7}$$

$$\{\int_{\Omega}(\varepsilon - \theta_0\eta)\,dv\}^{\cdot} = -\theta_0\int_{\Omega}\gamma\,dv \geq 0 \qquad \text{if } \theta = \theta_0 = \text{constant on } \partial\Omega. \tag{2.8}$$

b. Constitutive equations. Consequences of the dissipation inequality

I consider constitutive equations of the form

$$\begin{aligned} &\psi = \hat{\psi}(....), \qquad \eta = \hat{\eta}(....), \qquad \mathbf{q} = \hat{\mathbf{q}}(....),\\ &\boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(....), \qquad \pi = \hat{\pi}(....), \end{aligned} \tag{2.9}$$

with (....) shorthand for the list

$$(....) = (\theta,\nabla\theta,\varphi,\nabla\varphi,\varphi^{\cdot}). \tag{2.10}$$

A requirement of the theory is that the constitutive relations be compatible with the dissipation inequality (2.5). Writing

$$\mathbf{g} = \nabla\theta, \qquad r = \theta^{\cdot}, \qquad \mathbf{p} = \nabla\varphi, \qquad s = \varphi^{\cdot}, \tag{2.11}$$

it follows that, for any choice of the fields $\theta(\mathbf{x},t)$ and $\varphi(\mathbf{x},t)$,

$$\begin{aligned} &[\partial_{\varphi}\hat{\psi}(....) + \hat{\pi}(....)]s \;+\; [\partial_{\theta}\hat{\psi}(....) + \hat{\eta}(....)]r \;+\\ &[\partial_{\mathbf{p}}\hat{\psi}(....) - \hat{\boldsymbol{\xi}}(....)]\cdot\mathbf{p}^{\cdot} \;+\\ &[\partial_{\mathbf{g}}\hat{\psi}(....)]\cdot\mathbf{g}^{\cdot} \;+\; \partial_s\hat{\psi}(....)s^{\cdot} \;+\; \theta^{-1}\hat{\mathbf{q}}(....)\cdot\mathbf{g} = -\theta\gamma \leq 0. \end{aligned} \tag{2.12}$$

It is possible to find fields $\theta(\mathbf{x},t)$ and $\varphi(\mathbf{x},t)$ such that θ, $\mathbf{g}=\nabla\theta$, $\mathbf{g}^{\cdot}=\nabla\theta^{\cdot}$, $r=\theta^{\cdot}$, φ, $s=\varphi^{\cdot}$, $s^{\cdot}=\varphi^{\cdot\cdot}$, $\mathbf{p}=\nabla\varphi$, and $\mathbf{p}^{\cdot}=\nabla\varphi^{\cdot}$ have arbitrarily prescribed values at some chosen point and time. Since $(....) = (\theta,\mathbf{g},\varphi,\mathbf{p},s)$, the quantities r, $\mathbf{g}^{\cdot}$, $s^{\cdot}$, and $\mathbf{p}^{\cdot}$ appear linearly in (2.12); therefore $\partial_s\hat{\psi} = 0$, $\partial_{\mathbf{g}}\hat{\psi} = 0$, $\partial_{\theta}\hat{\psi} = \hat{\eta}$, and $\partial_{\mathbf{p}}\hat{\psi} = \hat{\boldsymbol{\xi}}$, for otherwise r, $\mathbf{g}^{\cdot}$, $s^{\cdot}$, and $\mathbf{p}^{\cdot}$ could be chosen to violate (2.12). The free energy, entropy, and microstress are thus independent of $\mathbf{g}$ and $\varphi^{\cdot}$ and related through

$$\begin{aligned} \hat{\eta}(\theta,\varphi,\nabla\varphi) &= -\partial_{\theta}\hat{\psi}(\theta,\varphi,\nabla\varphi),\\ \hat{\boldsymbol{\xi}}(\theta,\varphi,\nabla\varphi) &= \partial_{\mathbf{p}}\hat{\psi}(\theta,\varphi,\nabla\varphi), \end{aligned} \tag{2.13}$$

and the entropy production is given by

$$\theta^2\gamma = -\theta\pi^{\mathrm{dis}}(....)\varphi^{\cdot} - \hat{\mathbf{q}}(....)\cdot\nabla\theta \;\geq\; 0 \tag{2.14}$$

with

$$\pi^{\mathrm{dis}}(\ldots.) = \partial_{\varphi}\,\hat{\psi}(\theta,\varphi,\nabla\varphi) + \hat{\pi}(\ldots.) \qquad (2.15)$$

the dissipative part of the internal force. The general solution of (2.14) is

$$\begin{aligned} \hat{\mathbf{q}}(\ldots.) &= -\mathbf{a}(\ldots.)\varphi^{\cdot} - K(\ldots.)\nabla\theta, \\ \pi^{\mathrm{dis}}(\ldots.) &= -\beta(\ldots.)\varphi^{\cdot} - \mathbf{b}(\ldots.)\cdot\nabla\theta, \end{aligned} \qquad (2.16)$$

in which $\beta(\ldots.)$, a scalar kinetic modulus, $\mathbf{a}(\ldots.)$ and $\mathbf{b}(\ldots.)$, vector cross-coupling coefficients, and $K(\ldots.)$, the conductivity tensor, are consistent with

$$\theta\beta(\theta,\mathbf{g},\varphi,\mathbf{p},s)s^{2} + s\mathbf{g}\cdot[\theta\mathbf{b}(\theta,\mathbf{g},\varphi,\mathbf{p},s) + \mathbf{a}(\theta,\mathbf{g},\varphi,\mathbf{p},s)] + \mathbf{g}\cdot K(\theta,\mathbf{g},\varphi,\mathbf{p},s)\mathbf{g} \geq 0. \qquad (2.17)$$

The relations (2.7), $(2.13)_1$, and $(2.16)_2$ yield

$$\begin{aligned} \varepsilon &= \hat{\varepsilon}(\theta,\varphi,\nabla\varphi) = \hat{\psi}(\theta,\varphi,\nabla\varphi) - \theta\partial_{\theta}\hat{\psi}(\theta,\varphi,\nabla\varphi), \\ \pi &= -\partial_{\varphi}\hat{\psi}(\theta,\varphi,\nabla\varphi) - \beta(\ldots.)\varphi^{\cdot} - \mathbf{b}(\ldots.)\cdot\nabla\theta, \end{aligned} \qquad (2.18)$$

as well as a relation for the specific heat:

$$c(\theta,\varphi,\nabla\varphi) = \partial_{\theta}\,\hat{\varepsilon}(\theta,\varphi,\nabla\varphi) = -\,\theta\,\partial_{\theta\theta}\hat{\psi}(\theta,\varphi,\nabla\varphi). \qquad (2.19)$$

c. Generalized phase-field equations

The PDE's of the theory follow upon substituting the thermodynamically reduced constitutive relations for ε, $\mathbf{q}$, $\boldsymbol{\xi}$, and π into the local balances for energy and microforce. Writing

$$(\ldots.) = (\theta,\nabla\theta,\varphi,\nabla\varphi,\varphi^{\cdot}), \qquad (..) = (\theta,\varphi,\nabla\varphi), \qquad (2.20)$$

these PDE's become

$$\begin{aligned} c(..)\theta^{\cdot} + \partial_{\varphi}\,\hat{\varepsilon}(..)\varphi^{\cdot} + \partial_{\mathbf{p}}\,\hat{\varepsilon}(..)\cdot\nabla\varphi^{\cdot} &= \mathrm{div}\{K(\ldots.)\nabla\theta + [\mathbf{a}(\ldots.) + \partial_{\mathbf{p}}\hat{\psi}(..)]\varphi^{\cdot}\}, \\ \beta(\ldots.)\varphi^{\cdot} &= \mathrm{div}\{\partial_{\mathbf{p}}\hat{\psi}(..)\} - \partial_{\varphi}\hat{\psi}(..) - \mathbf{b}(\ldots.)\cdot\nabla\theta. \end{aligned} \qquad (2.21)$$

This is the most general system based on constitutive relations (2.9) that are consistent with the second law in the form of the dissipation inequality (2.5).

d. Decomposition of the heat flux and internal force

The constitutive equations (2.16) show $\nabla\theta$ and $\varphi^{\cdot}$ to be the fields that, in some sense, most influence $\hat{\mathbf{q}}$ and π^{dis}; in fact, for θ and φ close to constant values θ_0 and φ_0, so that $|\theta-\theta_0|$, $|\nabla\theta|$, $|\varphi-\varphi_0|$, $|\nabla\varphi|$, and $|\varphi^{\cdot}|$ are small, say $O(\delta)$,

$$\begin{aligned} \hat{\mathbf{q}}(\ldots.) &= -\mathbf{a}_0\varphi^{\cdot} - \mathbf{K}_0\nabla\theta + O(\delta^2), \\ \pi^{\mathrm{dis}}(\ldots.) &= -\beta_0\varphi^{\cdot} - \mathbf{b}_0\cdot\nabla\theta + O(\delta^2), \end{aligned} \tag{2.22}$$

with $\mathbf{a}_0$, $\mathbf{K}_0$, β_0, and $\mathbf{b}_0$ constant. An expansion of the form (2.22) holds also for $|\nabla\theta|$ and $|\varphi^{\cdot}|$ of $O(\delta)$, irrespective of $(\theta,\varphi,\nabla\varphi)$, but then the coefficients depend on $(\theta,\varphi,\nabla\varphi)$. Guided by this, I assume that

(A1) $\hat{\mathbf{q}}(\ldots.)$ and $\pi^{\mathrm{dis}}(\ldots.)$ are linear functions of $(\nabla\theta,\varphi^{\cdot})$:

$$\begin{aligned} \hat{\mathbf{q}}(\ldots.) &= -\mathbf{a}(\theta,\varphi,\nabla\varphi)\varphi^{\cdot} - \mathbf{K}(\theta,\varphi,\nabla\varphi)\nabla\theta, \\ \pi^{\mathrm{dis}}(\ldots.) &= -\beta(\theta,\varphi,\nabla\varphi)\varphi^{\cdot} - \mathbf{b}(\theta,\varphi,\nabla\varphi)\cdot\nabla\theta. \end{aligned} \tag{2.23}$$

Note that, by (2.17), the coefficient matrix

$$\begin{matrix} \mathbf{a}^{\mathsf{T}} & \mathbf{K} \\ \theta\beta & \theta\mathbf{b} \end{matrix}$$

is positive semi-definite.

The first of (2.23) yields the decomposition

$$\mathbf{q} = \mathbf{q}^{\mathrm{th}} + \mathbf{q}^{\mathrm{kin}}, \qquad \mathbf{q}^{\mathrm{th}} = -\mathbf{K}(\theta,\varphi,\nabla\varphi)\nabla\theta, \qquad \mathbf{q}^{\mathrm{kin}} = -\mathbf{a}(\theta,\varphi,\nabla\varphi)\varphi^{\cdot} \tag{2.24}$$

for $\mathbf{q}$ as the sum of a (classical) thermal flux $\mathbf{q}^{\mathrm{th}}$ down a temperature gradient plus a kinetic flux $\mathbf{q}^{\mathrm{kin}}$ induced by temporal variations in the order parameter. Similarly, π^{dis} may be decomposed

$$\pi^{\mathrm{dis}} = \pi^{\mathrm{th}} + \pi^{\mathrm{kin}}, \quad \pi^{\mathrm{th}} = -\mathbf{b}(\theta,\varphi,\nabla\varphi)\cdot\nabla\theta, \quad \pi^{\mathrm{kin}} = -\beta(\theta,\varphi,\nabla\varphi)\varphi^{\cdot}, \tag{2.25}$$

into thermal and kinetic parts π^{th} and π^{kin}.

Finally, (2.23) leads to the following relation for the entropy production (2.14):

$$\theta^2\gamma = \theta\beta(\theta,\varphi,\nabla\varphi)(\dot{\varphi})^2 + \dot{\varphi}[\theta\mathbf{b}(\theta,\varphi,\nabla\varphi)\cdot\nabla\theta + \mathbf{a}(\theta,\varphi,\nabla\varphi)]\cdot\nabla\theta + \nabla\theta\cdot\mathbf{K}(\theta,\varphi,\nabla\varphi)\nabla\theta \ \geq\ 0. \qquad (2.26)$$

3. COMPARISON WITH THE SHARP-INTERFACE THEORY. CONSTITUTIVE RELATION FOR THE KINETIC HEAT-FLUX

In the theory developed here the phase interface is *diffuse,* with no sharp distinction between phases; in a sense each value of the order parameter represents a particular phase of the material. For that reason sets $\mathcal{S}(t)$ of the form $\{\varphi(\mathbf{x},t)=\text{constant}\}$ play an important role, as they represent sets of uniform phase. I will refer to such sets as *uniformity surfaces*. Phase transitions are also described by theories in which the regions occupied by the individual phases are separated by a phase interface of zero thickness. Such interfaces are *sharp.*

In applications of the diffuse-interface theory the interface is often thin: solutions are close to particular order-parameter values φ_1 and φ_2 in regions Ω_1 and Ω_2, with the "interface" separating Ω_1 and Ω_2 resembling a "thin surface"; the interface is then a collection of closely-packed uniformity surfaces.

Based on these observations, I now use the sharp-interface theory to motivate additional constitutive assumptions that hopefully render the sharp and diffuse theories asymptotic in the limit of small diffuse-interface thickness. The essential idea in comparing these theories is a *correspondence between uniformity surfaces of the diffuse theory and the interface of the sharp theory.*

a. Basic laws for a sharp interface

For comparison purposes I now write the first two laws[9] for a sharp interface evolving with (scalar) normal velocity $\bar{V}$. Let R be an arbitrary control volume, let $\mathcal{G} = \mathcal{G}(t)$ denote the portion of the interface in R, let $\bar{\boldsymbol{\nu}}$, a vector field tangent to the interface, denote the outward unit normal to the boundary curve $\partial\mathcal{G}$, and let $\bar{V}_{\partial\mathcal{G}}$ denote the (scalar) normal velocity of this boundary curve in the direction $\bar{\boldsymbol{\nu}}$. Then balance of energy and growth of entropy for R have the form

$$\begin{aligned}
&\Big\{\int_R \varepsilon^b dv + \int_{\mathcal{G}} \varepsilon^{xs} da\Big\}^{\cdot} = -\int_{\partial R} \mathbf{q}^b\cdot\mathbf{n}\,da + \int_{\partial\mathcal{G}} Q\bar{V}_{\partial\mathcal{G}}\, ds + \int_{\partial\mathcal{G}} (\sigma\bar{V}_{\partial\mathcal{G}} + \bar{V}\bar{\mathbf{c}}\cdot\bar{\boldsymbol{\nu}})\, ds,\\
&\Big\{\int_R \eta^b dv + \int_{\mathcal{G}} \eta^{xs} da\Big\}^{\cdot} \geq -\int_{\partial R} (\mathbf{q}^b/\theta)\cdot\mathbf{n}\,da + \int_{\partial\mathcal{G}} (Q/\theta)\bar{V}_{\partial\mathcal{G}}\, ds,
\end{aligned} \qquad (3.1)$$

with θ the temperature; ε^b, η^b, and $\mathbf{q}^b$ the bulk energy, entropy, and heat flux;

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[9] As developed in [22,23,25].

ε^{xs} and η^{xs} the energy and entropy of the interface; σ the surface tension; $\bar{\mathbf{c}}$, a vector field tangent to the interface, the surface shear; and Q an apparent heat flow induced the motion of the interface.

Let

$$\psi^{xs} = \varepsilon^{xs} - \theta\eta^{xs} \tag{3.2}$$

denote the surface free energy. Then[10] $\sigma = \psi^{xs}$ and $Q = \theta\eta^{xs}$, so that

$$\int_{\partial\mathcal{Q}} \varepsilon^{xs}\bar{V}_{\partial\mathcal{Q}}\,ds = \int_{\partial\mathcal{Q}} Q\bar{V}_{\partial\mathcal{Q}}\,ds + \int_{\partial\mathcal{Q}} \sigma\bar{V}_{\partial\mathcal{Q}}\,ds, \qquad \int_{\partial\mathcal{Q}} \eta^{xs}\bar{V}_{\partial\mathcal{Q}}\,ds = \int_{\partial\mathcal{Q}} (Q/\theta)\bar{V}_{\partial\mathcal{Q}}\,ds, \tag{3.3}$$

a result that allows (3.1) to be written in a form

$$\begin{aligned} \Big\{\int_R \varepsilon^b dv + \int_{\mathcal{Q}} \varepsilon^{xs} da\Big\}^{\cdot} &= -\int_{\partial R} \mathbf{q}^b\cdot\mathbf{n}\,da + \int_{\partial\mathcal{Q}} \varepsilon^{xs}\bar{V}_{\partial\mathcal{Q}}\,ds + \int_{\partial\mathcal{Q}} \bar{V}\bar{\mathbf{c}}\cdot\boldsymbol{\nu}\,ds, \\ \Big\{\int_R \eta^b dv + \int_{\mathcal{Q}} \eta^{xs} da\Big\}^{\cdot} &\geq -\int_{\partial R} (\mathbf{q}^b/\theta)\cdot\mathbf{n}\,da + \int_{\partial\mathcal{Q}} \eta^{xs}\bar{V}_{\partial\mathcal{Q}}\,ds, \end{aligned} \tag{3.4}$$

in which $\varepsilon^{xs}\bar{V}_{\partial\mathcal{Q}}$ and $\eta^{xs}\bar{V}_{\partial\mathcal{Q}}$ represent fluxes of internal energy and entropy into R across $\partial\mathcal{Q}$.

b. Comparison of the sharp and diffuse theories

Bearing in mind (2.24), a comparison of the basic laws (3.1) of the sharp-interface theory with (2.1) and (2.2) of the diffuse theory seems to indicate the associations[11]

sharp interface		**order-parameter theory**		
$\int_{\partial\mathcal{Q}} (\sigma\bar{V}_{\partial\mathcal{Q}} + \bar{V}\bar{\mathbf{c}}\cdot\bar{\boldsymbol{\nu}})\,ds$		$\int_{\partial R} \varphi^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da$		(3.5)
$\int_{\partial R} \mathbf{q}^b\cdot\mathbf{n}\,da$	$\int_{\partial\mathcal{Q}} Q\bar{V}_{\partial\mathcal{Q}}\,ds$	$\int_{\partial R} \mathbf{q}^{th}\cdot\mathbf{n}\,da$	$-\int_{\partial R} \mathbf{q}^{kin}\cdot\mathbf{n}\,da$	(3.6)

To further relate the sharp and diffuse theories it is convenient to write the basic laws with respect to uniformity surfaces $\mathcal{S}(t) = \{\varphi(\mathbf{x},t) = \text{constant}\}$. To ensure that such surfaces are well defined, I restrict attention to situations with

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[10] These identities are consequences of the requirement that the interface be invariant under reparametrization [25].

[11] It would be interesting to show that, granted suitable scalings, these associations, (3.12), and (3.13) are formal asymptotic approximations (cf. [26]).

$$\ell = |\nabla\varphi| \neq 0; \tag{3.7}$$

then

$$\mathbf{m} = \nabla\varphi/\ell, \qquad V = -\varphi^{\cdot}/\ell \tag{3.8}$$

represent, at each $(\mathbf{x},t)$, a unit normal field and corresponding normal velocity for the uniformity surface through $\mathbf{x}$ at time t.

Let R be a control volume such that, at each t, ∂R is tangent to uniformity surfaces at most on a set of zero surface-measure. Choose $\mathbf{x} \in \partial R$ and t, let $\mathcal{S}(t)$ denote the uniformity surface through $\mathbf{x}$, let $\mathcal{Q}(t)$ denote the portion of $\mathcal{S}(t)$ in R, and let $\boldsymbol{\nu}(\mathbf{x},t)$, a vector in the tangent space to $\mathcal{S}(t)$ at $\mathbf{x}$, denote the outward unit normal to the boundary curve $\partial\mathcal{Q}(t)$. Then the vectors $\mathbf{m}$, $\mathbf{n}$, and $\boldsymbol{\nu}$ are coplanar, and the (intrinsic) velocity of the curve $\partial\mathcal{Q}(t)$ has two components: $V\mathbf{m}$, which is normal to $\mathcal{S}$, and $V_{\partial\mathcal{Q}}\boldsymbol{\nu}$, which is tangent to $\mathcal{S}(t)$, but normal to $\partial\mathcal{Q}$. Let α denote the angle between $\mathbf{m}$ and $\mathbf{n}$ and assume that $\alpha \neq 0, \pi$. Then

$$\mathbf{n} = (\cos\alpha)\mathbf{m} + (\sin\alpha)\boldsymbol{\nu}, \qquad \cos\alpha = \mathbf{m}\cdot\mathbf{n}, \qquad V_{\partial\mathcal{Q}} = -V\cot\alpha. \tag{3.9}$$

It is convenient to introduce the measure

$$dA = \ell\sin\alpha\, da \tag{3.10}$$

on R. The measure $\sin\alpha\, da$ is the area on ∂R projected onto the plane perpendicular to $\boldsymbol{\nu}$; roughly speaking, the multiplier $\ell = |\nabla\varphi|$ allows dA to be written as the product of a measure $d\varphi$ and an arc-length measure on the boundary curves $\partial\mathcal{Q}$.

I now make the following geometric correspondences between the sharp and diffuse theories:

sharp interface	**order-parameter theory**
interface	uniformity surface
$\bar{V}$, $\bar{\boldsymbol{\nu}}$, $\bar{V}_{\partial\mathcal{Q}}$	V, $\boldsymbol{\nu}$, $V_{\partial\mathcal{Q}}$

Using (3.8)-(3.10), the working can be written in the form

$$\int_{\partial R} \varphi^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\, da = \int_{\partial R} (\boldsymbol{\xi}\cdot\mathbf{m}V_{\partial\mathcal{Q}} - \boldsymbol{\xi}\cdot\boldsymbol{\nu}V)\, dA. \tag{3.11}$$

Comparing (3.11) with the last integral in $(3.1)_1$, which represents the working for the sharp-interface theory, and using the identity $\sigma = \psi^{xs}$, it seems reasonable to make the associations

sharp interface	**order-parameter theory**	
$\int_{\partial\mathcal{G}} \bar{V}\bar{\mathbf{c}}\cdot\bar{\boldsymbol{\nu}}\, ds$	$\int_{\partial R} V\boldsymbol{\xi}\cdot\boldsymbol{\nu}\, da$	(3.12)
$\int_{\partial\mathcal{G}} \psi^{xs}\bar{V}_{\partial\mathcal{G}}\, ds$	$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{m}V_{\partial\mathcal{G}}\, da$	(3.13)

Guided by (3.6) and (3.12), I now presume that that the first two laws (2.1) and (2.2) can be written in a form that more closely resembles (3.4); namely,[12]

$$\begin{aligned} \Big\{\int_R \varepsilon\, dv\Big\}^{\boldsymbol{\cdot}} &= -\int_{\partial R}\mathbf{q}^{th}\cdot\mathbf{n}\, da - \int_{\partial R}\boldsymbol{\varepsilon}^{flx}\cdot\mathbf{n}\, da - \int_{\partial R} V\boldsymbol{\xi}\cdot\boldsymbol{\nu}\, dAa, \\ \Big\{\int_R \eta\, dv\Big\}^{\boldsymbol{\cdot}} &\geq -\int_{\partial R}(\mathbf{q}^{th}/\theta)\cdot\mathbf{n}\, da - \int_{\partial R}\boldsymbol{\eta}^{flx}\cdot\mathbf{n}\, da, \end{aligned} \tag{3.14}$$

in which there are an energy flux $\boldsymbol{\varepsilon}^{flx}$ and an entropy flux $\boldsymbol{\eta}^{flx}$, given by constitutive equations

$$\boldsymbol{\varepsilon}^{flx} = \hat{\boldsymbol{\varepsilon}}^{flx}(\ldots.), \qquad \boldsymbol{\eta}^{flx} = \hat{\boldsymbol{\eta}}^{flx}(\ldots.), \qquad (\ldots.) = (\theta, \nabla\theta, \varphi, \nabla\varphi, \varphi^{\boldsymbol{\cdot}}) \tag{3.15}$$

consistent with standard thermodynamics. Precisely, defining the free-energy flux

$$\boldsymbol{\psi}^{flx} = \hat{\boldsymbol{\psi}}^{flx}(\ldots.) = \hat{\boldsymbol{\varepsilon}}^{flx}(\ldots.) - \theta\hat{\boldsymbol{\eta}}^{flx}(\ldots.), \tag{3.16}$$

I assume that:

(A2) There are vector fields $\boldsymbol{\varepsilon}^{flx}$ and $\boldsymbol{\eta}^{flx}$, defined by constitutive equations (3.15), such that the basic laws (2.1) and (2.2) can be rewritten as (3.14), and such that $\hat{\boldsymbol{\psi}}^{flx}(\ldots.)$ generates $\hat{\boldsymbol{\eta}}^{flx}(\ldots.)$ through the thermodynamic relation:

$$\hat{\boldsymbol{\eta}}^{flx}(\ldots.) = -\partial_\theta\, \hat{\boldsymbol{\psi}}^{flx}(\ldots.), \tag{3.17}$$

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[12] Within a mechanical theory a free-energy flux of this form was introduced in [27] (Remark 4). Wang et al [19] introduce an entropy flux of this type, but their gradient energy is isotropic, so they do not need the working term $V\boldsymbol{\xi}\cdot\boldsymbol{\nu}$.

In (3.11) $\boldsymbol{\xi}\cdot\mathbf{m}$ acts as a surface tension within uniformity surfaces that works against the tangential velocity of $\mathcal{G}(t)$ and hence works to increase the area of $\mathcal{G}(t)$; thus and by (3.13), it seems reasonable to expect that

$$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{m} V_{\partial\mathcal{G}} dA = -\int_{\partial R} \psi^{flx}\cdot\mathbf{n}\, da. \tag{3.18}$$

On the other hand, $\hat{\boldsymbol{\xi}}(..)=\partial_{\mathbf{p}}\hat{\psi}(..)$, $(..)=(\theta,\varphi,\nabla\varphi)$; thus (3.11) yields

$$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{m} V_{\partial\mathcal{G}} dA = \int_{\partial R} \varphi^{\cdot}[\mathbf{m}\cdot\partial_{\mathbf{p}}\hat{\psi}(..)]\mathbf{m}\cdot\mathbf{n}\, da. \tag{3.19}$$

Based on (3.18) and (3.19), I assume that:

(A3) The free-energy flux is given by

$$\hat{\psi}^{flx}(\theta,\varphi,\nabla\varphi,\varphi^{\cdot}) = -\varphi^{\cdot}[\mathbf{m}\cdot\partial_{\mathbf{p}}\hat{\psi}(\theta,\varphi,\nabla\varphi)]\mathbf{m}. \tag{3.20}$$

Then by (2.6), $(2.13)_1$, (3.16), and (3.17),

$$\begin{aligned} \hat{\eta}^{flx}(\theta,\varphi,\nabla\varphi,\varphi^{\cdot}) &= -\varphi^{\cdot}[\mathbf{m}\cdot\partial_{\mathbf{p}}\hat{\eta}(\theta,\varphi,\nabla\varphi)]\mathbf{m}, \\ \hat{\varepsilon}^{flx}(\theta,\varphi,\nabla\varphi,\varphi^{\cdot}) &= -\varphi^{\cdot}[\mathbf{m}\cdot\partial_{\mathbf{p}}\hat{\varepsilon}(\theta,\varphi,\nabla\varphi)]\mathbf{m}. \end{aligned} \tag{3.21}$$

b. Constitutive relation for the kinetic heat-flux

In view of (3.18) and the the required equivalency of (2.1) and (2.2) with (3.14),

$$-\int_{\partial R} \varepsilon^{flx}\cdot\mathbf{n}\, da = -\int_{\partial R} \mathbf{q}^{kin}\cdot\mathbf{n}\, da - \int_{\partial R} \psi^{flx}\cdot\mathbf{n}\, da, \quad -\int_{\partial R} \eta^{flx}\cdot\mathbf{n}\, da = -\int_{\partial R} (\mathbf{q}^{kin}/\theta)\cdot\mathbf{n}\, da, \tag{3.22}$$

while (3.16) and $(3.22)_1$ imply that

$$-\int_{\partial R} \theta\eta^{flx}\cdot\mathbf{n}\, da = -\int_{\partial R} \mathbf{q}^{kin}\cdot\mathbf{n}\, da. \tag{3.23}$$

The identities $(3.22)_2$ and (3.23), when localized, yield the conclusion $(\theta\eta^{flx} - \mathbf{q}^{kin})\cdot\nabla\theta = 0$. By (2.24) and $(3.21)_1$, the constitutive relations for η^{flx} and $\mathbf{q}^{kin}$ do not contain $\nabla\theta$ as an independent constitutive variable. Thus $\mathbf{q}^{kin} = \theta\eta^{flx}$, which represents a counterpart of the identity $Q = \theta\eta^{xs}$ in the sharp-interface theory. Thus, appealing again to $(3.21)_1$, *the kinetic heat-flux is related to the entropy through the explicit relation*

$$\mathbf{q}^{\mathrm{kin}} = -\mathbf{a}(\theta,\varphi,\nabla\varphi)\varphi^{\cdot}, \qquad \mathbf{a}(\theta,\varphi,\nabla\varphi) = \theta[\mathbf{m}\cdot\partial_{\mathbf{p}}\hat{\eta}(\theta,\varphi,\nabla\varphi)]\mathbf{m}, \tag{3.24}$$

which is the main result of this section.

Note that $\mathbf{q}^{\mathrm{kin}}(\mathbf{x},t)$ on ∂R vanishes when $\mathbf{n}(\mathbf{x},t)$ is perpendicular to $\mathbf{m}(\mathbf{x},t)$; in this case $\partial\mathcal{Q}(t)$—the portion in R of the uniformity surface through $\mathbf{x}$—does not locally add area at $\mathbf{x}$, so there is no apparent heat flow induced by the addition of area (and hence entropy).

4. THEORY FOR A GRADIENT ENERGY THAT IS HOMOGENEOUS OF DEGREE 2

a. Further simplification of the constitutive equations

I now decompose the constitutive functions for the free energy into a coarse-grain energy $\psi^{cg}(\theta,\varphi)$ and a gradient energy $\psi^{gr}(\theta,\varphi,\nabla\varphi)$:

$$\begin{aligned} \hat{\psi}(\theta,\varphi,\nabla\varphi) &= \psi^{cg}(\theta,\varphi) + \psi^{gr}(\theta,\varphi,\nabla\varphi), \\ \psi^{cg}(\theta,\varphi) &= \hat{\psi}(\theta,\varphi,0), \\ \psi^{gr}(\theta,\varphi,\nabla\varphi) &= \hat{\psi}(\theta,\varphi,\nabla\varphi) - \hat{\psi}(\theta,\varphi,0), \end{aligned} \tag{4.1}$$

and similarly for the internal energy and entropy. Then

$$\begin{aligned} \psi^{cg} &= \varepsilon^{cg} - \theta\eta^{cg}, \qquad & \psi^{gr} &= \varepsilon^{gr} - \theta\eta^{gr}, \\ \eta^{cg} &= -\partial_{\theta}\psi^{cg}, \qquad & \eta^{gr} &= -\partial_{\theta}\psi^{gr}. \end{aligned} \tag{4.2}$$

Phase-field theories are generally based on free-energies that are quadratic in $\nabla\varphi$. Here, to model diverse types of anisotropy, I consider the dependence on $\nabla\varphi = |\nabla\varphi|\mathbf{m}$ in terms of dependences on $|\nabla\varphi|$ and $\mathbf{m}$, with $\psi^{gr}(\theta,\varphi,\nabla\varphi)$ quadratic in $|\nabla\varphi|$, but an arbitrary function of $\mathbf{m}$; precisely, I assume that:

(A4) $\psi^{gr}(\theta,\varphi,\nabla\varphi)$ is homogeneous[13] of degree two in $\nabla\varphi$.

Consequences of (A4), (3.24), (4.1), and (4.2) are that

$$\begin{aligned} &\eta^{gr}(\theta,\varphi,\nabla\varphi) \text{ is homogeneous of degree two in } \nabla\varphi, \\ &\mathbf{a}(\theta,\varphi,\nabla\varphi) \quad \text{is homogeneous of degree one in } \nabla\varphi. \end{aligned} \tag{4.3}$$

The next two hypotheses concern the moduli that govern the production of

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[13] $\Phi(\mathbf{z})$ is homogeneous of degree p if, given any $\lambda > 0$, $\Phi(\lambda\mathbf{z}) = \lambda^{p}\Phi(\mathbf{z})$ for all $\mathbf{z}$.

entropy. Phase-field theories generally have K independent of $\nabla\varphi$, and β dependent on $\nabla\varphi$ at most through **m**. Here I assume that

(A5) $\beta(\theta,\varphi,\nabla\varphi)$ and $K(\theta,\varphi,\nabla\varphi)$ are homogeneous of degree zero in $\nabla\varphi$.

I have little intuition concerning the modulus $\mathbf{b}(\theta,\varphi,\nabla\varphi)$ and therefore assume only that

(A6) $\mathbf{b}(\theta,\varphi,\nabla\varphi)$ is a homogeneous function of $\nabla\varphi$.

By (A5), (A6), and (4.3), the entropy-production inequality (2.26) may be written in the form

$$\theta\beta(\theta,\varphi,\mathbf{m})(\varphi^{\cdot})^2 + \varphi^{\cdot}[|\nabla\varphi|^k\theta\mathbf{b}(\theta,\varphi,\mathbf{m}) + |\nabla\varphi|\mathbf{a}(\theta,\varphi,\mathbf{m})]\cdot\nabla\theta + \nabla\theta\cdot\mathbf{K}(\theta,\varphi,\mathbf{m})\nabla\theta \geq 0, \tag{4.4}$$

with k the degree of homogeniety of **b**. This inequality must hold for all θ, $\nabla\theta$, φ, $\nabla\varphi$, and $\varphi^{\cdot}$. Therefore $|\nabla\varphi|^k\theta\mathbf{b}(\theta,\varphi,\mathbf{m})+|\nabla\varphi|\mathbf{a}(\theta,\varphi,\mathbf{m}) = 0$ for $|\nabla\varphi|$ sufficiently large, for otherwise $\varphi^{\cdot}\nabla\theta$ of appropriate direction would violate (4.4). Thus $k=1$ and

$$\mathbf{a}(\theta,\varphi,\nabla\varphi) = -\theta\mathbf{b}(\theta,\varphi,\nabla\varphi), \tag{4.5}$$

so that, by (2.25) and (3.24),

$$\pi^{th} = -\mathbf{b}(\theta,\varphi,\nabla\varphi)\cdot\nabla\theta, \qquad \mathbf{b}(\theta,\varphi,\nabla\varphi) = -[\mathbf{m}\cdot\partial_{\mathbf{p}}\eta^{gr}(\theta,\varphi,\nabla\varphi)]\mathbf{m}, \tag{4.6}$$

and both the kinetic heat-flux $\mathbf{q}^{kin}$ and the thermal internal-force π^{th} are related to the gradient entropy. Further, and what is surprising, *$\mathbf{q}^{kin}$ and π^{th} do not contribute to the production of entropy:*

$$\theta^2\gamma = \theta\beta(\theta,\varphi,\mathbf{m})(\varphi^{\cdot})^2 + \nabla\theta\cdot\mathbf{K}(\theta,\varphi,\mathbf{m})\nabla\theta \geq 0. \tag{4.7}$$

b. Phase-field equations

Substituting the expressions in (3.24) and (4.6) for **a** and **b** into (2.21) and using the notation

$$(..) = (\theta,\varphi,\nabla\varphi) \tag{4.8}$$

results in the PDE's

$$\begin{aligned} c(..)\theta^{\cdot} + \partial_{\varphi}\hat{\varepsilon}(..)\varphi^{\cdot} + \partial_{\mathbf{p}}\varepsilon^{gr}(..)\cdot\nabla\varphi^{\cdot} &= \\ \operatorname{div}\{K(..)\nabla\theta + [\partial_{\mathbf{p}}\psi^{gr}(..) &+ \theta(\mathbf{m}\cdot\partial_{\mathbf{p}}\eta^{gr}(..))\mathbf{m}]\varphi^{\cdot}\}, \\ \beta(..)\varphi^{\cdot} = \operatorname{div}\{\partial_{\mathbf{p}}\psi^{gr}(..)\} - \partial_{\varphi}\hat{\psi}(..) &+ \mathbf{m}\cdot\partial_{\mathbf{p}}\eta^{gr}(..)\mathbf{m}\cdot\nabla\theta. \end{aligned} \tag{4.9}$$

In view of (A4), the gradient free-energy ψ^{gr} may be written in the form

$$\psi^{gr}(\theta,\varphi,\nabla\varphi) = \tfrac{1}{2}\ell^2 f(\theta,\varphi,\mathbf{m}) \tag{4.10}$$

(the $\frac{1}{2}$ being for convenience), so that

$$\begin{aligned} &\varepsilon^{gr}(\theta,\varphi,\nabla\varphi) = \tfrac{1}{2}\ell^2 e(\theta,\varphi,\mathbf{m}), &&\eta^{gr}(\theta,\varphi,\nabla\varphi) = \tfrac{1}{2}\ell^2 s(\theta,\varphi,\mathbf{m}), \\ &f(\theta,\varphi,\mathbf{m}) = e(\theta,\varphi,\mathbf{m}) - \theta s(\theta,\varphi,\mathbf{m}), &&s(\theta,\varphi,\mathbf{m}) = -\partial_{\theta} f(\theta,\varphi,\mathbf{m}), \\ &c(\theta,\varphi,\nabla\varphi) = \partial_{\theta}\varepsilon^{cg}(\theta,\varphi) + \tfrac{1}{2}\ell^2\partial_{\theta} e(\theta,\varphi,\mathbf{m}), \end{aligned} \tag{4.11}$$

and, by (3.24) and (4.6),

$$\begin{aligned} &\mathbf{q}^{kin} = -\mathbf{a}(\theta,\varphi,\nabla\varphi)\varphi^{\cdot}, &&\mathbf{a}(\theta,\varphi,\nabla\varphi) = \theta s(\theta,\varphi,\mathbf{m})\nabla\varphi, \\ &\pi^{th} = -\mathbf{b}(\theta,\varphi,\nabla\varphi)\cdot\nabla\theta, &&\mathbf{b}(\theta,\varphi,\nabla\varphi) = -s(\theta,\varphi,\mathbf{m})\nabla\varphi. \end{aligned} \tag{4.12}$$

Further,

$$\boldsymbol{\xi} = \partial_{\mathbf{p}}\psi^{gr}(\theta,\varphi,\nabla\varphi) = f(\theta,\varphi,\mathbf{m})\nabla\varphi + \mathbf{c}(\theta,\varphi,\mathbf{m}), \tag{4.13}$$

with

$$\mathbf{c}(\theta,\varphi,\mathbf{m}) = \tfrac{1}{2}\ell\,\partial_{\mathbf{m}} f(\theta,\varphi,\mathbf{m}) \tag{4.14}$$

orthogonal to $\mathbf{m}$. In (3.11), $\boldsymbol{\xi}\cdot\boldsymbol{\nu} = \mathbf{c}\cdot\boldsymbol{\nu}$ works against the normal velocity V; hence $\mathbf{c}(\theta,\varphi,\mathbf{m})$ represents microshearing stresses within uniformity surfaces (cf. (3.12)).

Let

$$(..) = (\theta,\varphi,\nabla\varphi), \qquad (*) = (\theta,\varphi,\mathbf{m}). \tag{4.15}$$

By (4.14) and its counterpart for ε^{gr},

$$\begin{aligned} &\partial_{\mathbf{p}}\varepsilon^{gr}(..)\cdot\nabla\varphi^{\cdot} = e(*)\nabla\varphi\cdot\nabla\varphi^{\cdot} + \tfrac{1}{2}\ell^2\partial_{\mathbf{m}} e(*)\cdot\mathbf{m}^{\cdot}, \\ &\operatorname{div}[\varphi^{\cdot} e(*)\nabla\varphi] = e(*)\nabla\varphi\cdot\nabla\varphi^{\cdot} + \varphi^{\cdot}\operatorname{div}[e(*)\nabla\varphi], \\ &\partial_{\mathbf{p}}\psi^{gr}(..) + \theta s(*)\nabla\varphi = e(*)\nabla\varphi + \mathbf{c}(*); \end{aligned} \tag{4.16}$$

hence, appealing to the analog of (4.13) for η^{gr}, (4.9) may also be written as

$$\begin{aligned} c(..)\theta^{\cdot} + \partial_{\varphi}\hat{\varepsilon}(..)\varphi^{\cdot} - \varphi^{\cdot}\mathrm{div}[e(*)\nabla\varphi] + \tfrac{1}{2}\ell^2\partial_{\mathbf{m}}e(*)\cdot\mathbf{m}^{\cdot} &= \\ \mathrm{div}\{\mathbf{K}(*)\nabla\theta + \varphi^{\cdot}\mathbf{c}(*)\}, & \qquad (4.17) \\ \beta(*)\varphi^{\cdot} = \mathrm{div}[e(*)\nabla\varphi] - \theta\,\mathrm{div}[s(*)\nabla\varphi] + \mathrm{div}\mathbf{c}(*) - \partial_{\varphi}\hat{\psi}(..). & \end{aligned}$$

If $(4.17)_2$ is multiplied by $\varphi^{\cdot}$ and then subtracted from $(4.17)_1$, using (2.6) and (4.14), the result is an alternative form for $(4.17)_1$ (in which, roughly speaking, entropy rather than energy is balanced):

$$\begin{aligned} c(..)\theta^{\cdot} + \theta\partial_{\varphi}\hat{\eta}(..)\varphi^{\cdot} - \theta\varphi^{\cdot}\mathrm{div}[s(*)\nabla\varphi] + \tfrac{1}{2}\theta\ell^2\partial_{\mathbf{m}}s(*)\cdot\mathbf{m}^{\cdot} &= \\ \mathrm{div}\{\mathbf{K}(*)\nabla\theta\} + \beta(*)(\varphi^{\cdot})^2. & \qquad (4.18) \end{aligned}$$

The general equations derived above are complicated. The next section develops two simpler theories: one anisotropic with specific heat and conductivity constant; the other isotropic with specific heat and conductivity allowed to depend on the order parameter.

5. SIMPLIFIED THEORIES

a. Anisotropic theory with constant specific heat and conductivity

If the specific heat c is constant, then, by (2.13), (2.19), (4.1), and (4.2),

$$\begin{aligned} \varepsilon^{cg}(\theta,\varphi) &= c\theta + E(\varphi), \\ \eta^{cg}(\theta,\varphi) &= c\ln\theta + S(\varphi), \qquad (5.1) \\ \psi^{cg}(\theta,\varphi) &= c(\theta - \theta\ln\theta) + E(\varphi) - \theta S(\varphi), \end{aligned}$$

while ε^{gr} and η^{gr} are independent of θ. If, in addition, ψ^{gr} and (hence) ε^{gr} and η^{gr} are independent of φ, then

$$\psi^{gr}(\theta,\nabla\varphi) = \varepsilon^{gr}(\nabla\varphi) - \theta\eta^{gr}(\nabla\varphi). \qquad (5.2)$$

Assuming that (5.1) and (5.2) hold, and that the conductivity tensor **K** is constant and the kinetic modulus β depends only on **m**, the PDE's (4.9) become

$$\begin{aligned} &c\theta^{\cdot} + [E(\varphi) + \varepsilon^{gr}(\nabla\varphi)]^{\cdot} = \operatorname{div}\{\mathbf{K}\nabla\theta + [\partial_{\mathbf{p}}\psi^{gr}(\theta,\nabla\varphi) + \theta(\mathbf{m}\cdot\partial_{\mathbf{p}}\eta^{gr}(\nabla\varphi))\mathbf{m}]\,\varphi^{\cdot}\}, \\ &\beta(\mathbf{m})\varphi^{\cdot} = \operatorname{div}\{\partial_{\mathbf{p}}\psi^{gr}(\theta,\nabla\varphi)\} - E'(\varphi) + \theta S'(\varphi) + \mathbf{m}\cdot\partial_{\mathbf{p}}\eta^{gr}(\nabla\varphi)\mathbf{m}\cdot\nabla\theta. \end{aligned} \tag{5.3}$$

Further, since (5.2) has the alternative form

$$f(\theta,\mathbf{m}) = e(\mathbf{m}) - \theta s(\mathbf{m}), \tag{5.4}$$

(4.17) reduces to

$$\begin{aligned} &c\theta^{\cdot} + [E(\varphi)]^{\cdot} - \varphi^{\cdot}\operatorname{div}[e(\mathbf{m})\nabla\varphi] + \tfrac{1}{2}\ell^2[e(\mathbf{m})]^{\cdot} = \operatorname{div}\{\mathbf{K}\nabla\theta + \tfrac{1}{2}\ell\varphi^{\cdot}\,\partial_{\mathbf{m}}f(\theta,\mathbf{m})\}, \\ &\beta(\mathbf{m})\varphi^{\cdot} = \operatorname{div}[e(\mathbf{m})\nabla\varphi] - \theta\operatorname{div}[s(\mathbf{m})\nabla\varphi] + \tfrac{1}{2}\operatorname{div}[\ell\,\partial_{\mathbf{m}}f(\theta,\mathbf{m})] - E'(\varphi) + \theta S'(\varphi). \end{aligned} \tag{5.5}$$

while (4.18) becomes

$$c\theta^{\cdot} + \theta[S(\varphi)]^{\cdot} - \theta\varphi^{\cdot}\operatorname{div}[s(\mathbf{m})\nabla\varphi] + \tfrac{1}{2}\theta\ell^2[s(\mathbf{m})]^{\cdot} = \operatorname{div}\{\mathbf{K}\nabla\theta\} + \beta(\mathbf{m})(\varphi^{\cdot})^2. \tag{5.6}$$

b. Isotropic theory

Returning to the general theory of Section 4b, if the material is isotropic,

$$\begin{aligned} &\mathbf{K}(*) = k(\theta,\varphi)\mathbf{1}, \qquad \beta(*) = \beta(\theta,\varphi), \qquad e(*) = e(\theta,\varphi), \\ &s(*) = s(\theta,\varphi), \qquad f(*) = f(\theta,\varphi), \qquad \mathbf{c}(*) = 0, \end{aligned} \tag{5.7}$$

and if $\beta(\theta)$, $e(\theta)$, and $s(\theta)$ are independent of the order parameter, then, since

$$\operatorname{div}[e(\theta)\nabla\varphi] - \theta\operatorname{div}[s(\theta)\nabla\varphi] = f(\theta)\Delta\varphi \tag{5.8}$$

(cf. (4.11)), (4.17) reduce to

$$\begin{aligned} &c(\theta,\varphi,\nabla\varphi)\theta^{\cdot} + \partial_{\varphi}\varepsilon^{cg}(\theta,\varphi)\varphi^{\cdot} - \varphi^{\cdot}\operatorname{div}[e(\theta)\nabla\varphi] = \operatorname{div}[k(\theta,\varphi)\nabla\theta], \\ &\beta(\theta)\varphi^{\cdot} = f(\theta)\Delta\varphi - \partial_{\varphi}\psi^{cg}(\theta,\varphi), \end{aligned} \tag{5.9}$$

while (4.18) becomes

$$c(\theta,\varphi,\nabla\varphi)\theta^{\cdot} + \theta\partial_{\varphi}\eta^{cg}(\theta,\varphi)\varphi^{\cdot} - \theta\varphi^{\cdot}\operatorname{div}[s(\theta)\nabla\varphi] = \operatorname{div}[k(\theta,\varphi)\nabla\theta] + \beta(\theta)(\varphi^{\cdot})^2. \tag{5.10}$$

The PDE's (5.9), although restricted to isotropic materials, are quite general. Note that, by the last of (4.11), the specific heat $c(\theta,\varphi,\nabla\varphi)$ is the sum of a coarse-grain specific-heat $\partial_\theta \varepsilon^{cg}(\theta,\varphi)$ and a gradient specific-heat $\frac{1}{2}\ell^2 \partial_\theta e(\theta,\mathbf{m})$.

A standard assumption is that the specific heat $c(\varphi)$ depends only on the order parameter. Granted this, (2.13), (2.19), (4.1), and (4.2) yield

$$\begin{aligned}
\varepsilon^{cg}(\theta,\varphi) &= c(\varphi)\theta + E(\varphi),\\
\eta^{cg}(\theta,\varphi) &= c(\varphi)\ln\theta + S(\varphi),\\
\psi^{cg}(\theta,\varphi) &= c(\varphi)\theta(1-\ln\theta) + E(\varphi) - \theta S(\varphi),\\
f(\theta) &= e - \theta s, \qquad e,\ s = \text{constant},
\end{aligned} \tag{5.11}$$

and (5.9) become

$$\begin{aligned}
c(\varphi)\dot{\theta} + \theta[c(\varphi)]^{\cdot} + [E(\varphi)]^{\cdot} - e\dot{\varphi}\Delta\varphi &= \operatorname{div}[k(\theta,\varphi)\nabla\theta],\\
\beta(\theta)\dot{\varphi} &= f(\theta)\Delta\varphi + c'(\varphi)(\theta\ln\theta - \theta) - E'(\varphi) + \theta S'(\varphi),
\end{aligned} \tag{5.12}$$

with $(5.12)_1$ equivalent to (cf. (5.10))

$$c(\varphi)\dot{\theta} + \theta\ln\theta[c(\varphi)]^{\cdot} + \theta[S(\varphi)]^{\cdot} - \theta s\dot{\varphi}\Delta\varphi = \operatorname{div}[k(\theta,\varphi)\nabla\theta] + \beta(\theta)(\dot{\varphi})^2. \tag{5.13}$$

Finally, for c and k constant,

$$\begin{aligned}
c\dot{\theta} + [E(\varphi)]^{\cdot} - e\dot{\varphi}\Delta\varphi &= k\Delta\theta,\\
\beta(\theta)\dot{\varphi} &= f(\theta)\Delta\varphi - E'(\varphi) + \theta S'(\varphi),
\end{aligned} \qquad (5.14)^{14}$$

with $(5.14)_1$ equivalent to

$$c\dot{\theta} + \theta[S(\varphi)]^{\cdot} - \theta s\dot{\varphi}\Delta\varphi = k\Delta\theta + \beta(\theta)(\dot{\varphi})^2. \tag{5.15}$$

Generally, $\psi^{cg}(\theta,\varphi)$, as a function of φ, is a double-well potential in which each well has a strict minimum and for which one well furnishes a global minimum for $\theta<\theta_0$ and the other for $\theta>\theta_0$, with θ_0 the transition temperature. Granted this I may, without loss in generality, assume that the minima at $\theta=\theta_0$ occur at $\varphi=0$ and $\varphi=1$. Then $\psi^{cg}(\theta_0,0)=\psi^{cg}(\theta_0,1)$ and, granted the assumptions leading to (5.14),

$$E(1) - E(0) = \theta_0(S(1) - S(0)). \tag{5.16}$$

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[14] After completing this workl saw notes notes of Wang, Sekerka, Wheeler, Murray, Coriell, Braun, and McFadden in which these equations are derived.

Consider $(5.14)_2$ and (5.15) with the terms involving $\varphi^{\cdot}\nabla\varphi$ and $(\varphi^{\cdot})^2$ neglected, with $\beta(\theta)$, $f(\theta)$, and $\theta[S(\varphi)]^{\cdot}$ approximated by $\beta(\theta_0)$, $f(\theta_0)$, and $\theta_0[S(\varphi)]^{\cdot}$, and with

$$E(\varphi)-\theta_0 S(\varphi) = \tfrac{1}{2}\lambda[\varphi(1-\varphi)]^2 =: \theta_0 F(\varphi), \qquad S(\varphi) = \rho\varphi, \qquad (\lambda,\rho>0). \tag{5.17}$$

Define $u=(\theta-\theta_0)/\theta_0$, $\bar{\beta}=\beta(\theta_0)/\theta_0$, and $\bar{f}=f(\theta_0)/\theta_0$. Then, dropping the overbars, the resulting PDE's are the original phase-field equations (1.2) and (1.3). Here there seems to be an ambiguity, since the equivalent approximations in $(5.14)_1$ yield (1.2) with $\rho\varphi^{\cdot}$ $(=[S(\varphi)]^{\cdot})$ replaced by $[E(\varphi)]^{\cdot}/\theta_0$; because of (5.16), for a sufficiently thin interface this difference should have negligible effect.

If gradient energy is neglected, if $s<0$, and if $\beta(\theta)=\theta\beta_0$, then (5.14) reduce to

$$c\theta^{\cdot} + [E(\varphi)]^{\cdot} = k\Delta\theta, \qquad \beta_0\varphi^{\cdot} = |s|\Delta\varphi - \theta^{-1}E'(\varphi) + S'(\varphi), \tag{5.18}$$

which are the equations derived by Penrose and Fife [18] (eqs. (6.1), (6.2)) and Wang et. al. [19] (eqts. (32), (33)). On the other hand, neglecting, instead, gradient entropy, and assuming that β is constant, leads to

$$c\theta^{\cdot} + \theta[S(\varphi)]^{\cdot} = k\Delta\theta + \beta(\theta)(\varphi^{\cdot})^2., \qquad \beta\varphi^{\cdot} = e\Delta\varphi - E'(\varphi) + \theta S'(\varphi), \tag{5.19}$$

which is given by Fried and Gurtin [20].

Finally, for a discussion of specific models the reader is referred to references [15-20].

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