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with Interfacial Energy and Entropy**

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# A PHASE-FIELD THEORY FOR SOLIDIFICATION BASED ON A GENERAL ANISOTROPIC SHARP-INTERFACE THEORY WITH INTERFACIAL ENERGY AND ENTROPY

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Using balance laws for microforce and energy in conjunction with constitutive equations consistent with the second law, we develop a general phase-field theory that allows for a constitutive dependence of the internal energy and entropy on the order-parameter gradient. A matched asymptotic analysis—appropriate to the limit of decreasing interface thickness—demonstrates the consonance of our theory with a general, thermodynamically consistent sharp-interface theory that accounts for anisotropic interfacial energy and entropy, interfacial tension and shear, and dissipative transition kinetics.

## 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

$$u = (\text{constant})K_{\delta} + (\text{constant})V_{\delta},$$

(latent heat) $V_{\delta}$  = jump in normal heat-flux across the interface, (1.1)

involve the total curvature<sup>1</sup>  $K_{\delta}$  and normal velocity  $V_{\delta}$  of the interface  $\delta$ , and consequently lead to problems of great difficulty. For that reason Langer [1],<sup>2</sup> 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  $\varphi$ , called the *phase field*;  $\varphi$  has nearly constant values in each bulk phase and, between phases, makes a smooth but rapid transition within a thin layer that represents the sharp interface<sup>3</sup> of the Stefan model.

<sup>1</sup>Twice the mean curvature, a measure of curvature that we use throughout the paper.

<sup>2</sup>Based on Model C of Halperin, Hohenberg, and Ma [2].

<sup>3</sup>An interface of zero thickness.

The phase-field model consists of a modified heat equation

$$cu' + \rho\varphi' = k\Delta u \quad (1.2)$$

supplemented by a Ginzburg-Landau equation

$$\bar{b}\varphi' = \bar{\psi}\Delta\varphi - \Psi'(\varphi) + \rho u, \quad (1.3)$$

where  $c$ ,  $k$ ,  $\bar{b}$ ,  $\bar{\psi}$ , and  $\rho$  are constants, with all but  $\rho$  strictly positive, and  $\Psi(\varphi)$  is a double-well potential whose wells "define" the phases. The Ginzburg-Landau equation (1.3) is obtained as the relaxation law  $\bar{b}\varphi' = -\delta\mathcal{F}/\delta\varphi$  for the "free-energy"

$$\mathcal{F}(u,\varphi) = \int_{\Omega} \left\{ \Psi(\varphi) + \frac{1}{2}\bar{\psi}|\nabla\varphi|^2 - \rho u\varphi \right\} dv \quad (\Omega = \text{underlying region of space}), \quad (1.4)$$

in which the gradient free-energy (density)  $\frac{1}{2}\bar{\psi}|\nabla\varphi|^2$  accounts for interfacial energy in the transition layer. (Here  $\delta\mathcal{F}/\delta\varphi$  is the variational derivative of  $\mathcal{F}$  with respect to  $\varphi$ .)

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 approaches the Stefan system based on (1.1) as the "interface thickness" tends to zero;<sup>4</sup> 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 physics. In fact, Penrose and Fife [18] and 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, and it is unclear from either of these derivations whether the Ginzburg-Landau equation should be viewed as a balance law, as a constitutive equation, or as a combination of the two.

Concurrently with [19], we developed, in [20], a framework for theories of phase-field type based on a perspective, common in continuum mechanics, in

<sup>4</sup>Earlier, Stoth [7,8] established convergence under radial symmetry for  $u = (\text{constant})K_g$ . Formal asymptotics for the general problem were given in [1,3-5], while [9-14] formally relate the phase-field equations to other equations of physical interest.

which balance laws are carefully distinguished from constitutive equations. What is new in [20] is the introduction of a balance law for microforces<sup>5</sup> (defined operationally as forces that expend power over changes in the order parameter); when supplemented by thermodynamically consistent constitutive equations, this force balance reduces to a Ginzburg-Landau equation. Here, in the spirit of [20], we develop and study a fairly general class of phase-field models. We were led to continue the program of [20] for two reasons:

(1) Although the models developed in [18] and [19] result in PDEs of seemingly suitable structure, the derivations fail to include the internal energy of the interfacial layer and fail to account for the working (i.e., power expenditure) associated with changes in the order parameter; for a thin interface this working is important as it represents surface-excess forces.

(2) While [20] provides a basic thermodynamic framework for phase-field theories, it lacks the constitutive specificity needed to capture the detailed physics of a *thin* interface.

The usual argument supporting the neglect of interfacial internal-energy in models of phase-field type seems based on the observation that  $(1.1)_2$ , which expresses balance of energy across the interface, neglects the internal energy of the interface. But  $(1.1)$  are the result of approximating general interface conditions that include both interfacial internal energy and interfacial entropy, and while the former is neglected in  $(1.1)_2$ , it is generally present in  $(1.1)_1$ , as the coefficient of  $K_g$  is typically proportional to the free energy at the transition temperature.<sup>6</sup> Further, the internal energy and entropy of the interface would generally seem of the same order, whereby a theory that retains the entropy of the interface but neglects its internal energy would appear unsound.

As in [20], we begin with balance of energy and growth of entropy in forms that allow for both power and heat flow induced by temporal and spatial variations in the order parameter  $\varphi$ , and we use this structure to establish thermodynamically admissible constitutive equations; in particular, we are led to relations in which the free energy  $\psi$  and entropy  $\eta$  depend not only on the temperature  $\theta$ , but also on  $\varphi$  and  $\nabla\varphi$ :<sup>7</sup>

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<sup>5</sup>We believe that kinematical variables introduced to model 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 we now prefer the term *microforces*.

<sup>6</sup>Cf., e.g., Mullins and Sekerka [21], Gurtin [22,23].

<sup>7</sup> $\partial_a F(\dots, a, b, \dots)$  denotes the partial derivative of  $F(\dots, a, b, \dots)$  with respect to  $a$ .

$$\psi = \hat{\psi}(\theta, \varphi, \nabla\varphi), \quad \eta = \hat{\eta}(\theta, \varphi, \nabla\varphi) = -\partial_\theta \hat{\psi}(\theta, \varphi, \nabla\varphi). \quad (1.5)$$

An essential ingredient of our theory is the exchange energy  $\Psi(\varphi)$ , which is the free energy  $\hat{\psi}(\theta_M, \varphi, 0)$  at the transition temperature  $\theta = \theta_M$  and  $\nabla\varphi = 0$ ; we assume that  $\Psi(\varphi)$  is a double-well potential whose minima are at  $\varphi = 0$  and  $\varphi = 1$  and satisfy  $\Psi(0) = \Psi(1)$ . Writing

$$\mathbf{m} = \nabla\varphi / |\nabla\varphi| \quad (1.6)$$

for the unit normal to level sets of  $\varphi$ , we express the free energy as a sum of  $\Psi(\varphi)$ , a bulk energy  $\hat{\psi}^{bu}(\theta, \varphi)$ , and a gradient energy  $\frac{1}{2} \bar{\psi}(\theta, \varphi, \mathbf{m}) |\nabla\varphi|^2$ ,

$$\hat{\psi}(\theta, \varphi, \nabla\varphi) = \Psi(\varphi) + \hat{\psi}^{bu}(\theta, \varphi) + \frac{1}{2} \bar{\psi}(\theta, \varphi, \mathbf{m}) |\nabla\varphi|^2, \quad (1.7)$$

a decomposition that uniquely defines the bulk energy and yields, for the entropy,

$$\hat{\eta}(\theta, \varphi, \nabla\varphi) = \hat{\eta}^{bu}(\theta, \varphi) + \frac{1}{2} \bar{\eta}(\theta, \varphi, \mathbf{m}) |\nabla\varphi|^2, \quad (1.8)$$

with  $\hat{\eta}^{bu} = -\partial_\theta \hat{\psi}^{bu}$  and  $\bar{\eta} = -\partial_\theta \bar{\psi}$ . We present strong arguments in support of a heat flux given constitutively as the sum of a standard flux down a temperature gradient plus a kinetic flux<sup>8</sup>

$$\mathbf{q}^{kin} = -\frac{1}{2} \theta \bar{\eta}(\theta, \varphi, \mathbf{m}) \varphi' \nabla\varphi. \quad (1.9)$$

Interestingly, in the relation for the entropy production the term involving  $\mathbf{q}^{kin}$  cancels with another term, rendering this kinetic flux *nondissipative*.

We derive a hierarchy of phase-field equations at various levels of generality. For a material with  $\bar{\psi}$  and kinetic modulus  $\bar{\mathbf{b}}$  independent of  $\varphi$  and with conductivity tensor  $\mathbf{K}$  independent of  $\nabla\varphi$ , the resulting PDEs have the form

$$\begin{aligned} c(\theta, \varphi) \theta' + \theta \{ \partial_\varphi \hat{\eta}^{bu}(\theta, \varphi) \varphi' + \frac{1}{2} (|\nabla\varphi|^2 \bar{\eta}(\theta, \mathbf{m}))' - \frac{1}{2} \operatorname{div}(\bar{\eta}(\theta, \mathbf{m}) \varphi' \nabla\varphi) \} = \\ \operatorname{div}(\mathbf{K}(\theta, \varphi) \nabla\theta) + \bar{\mathbf{b}}(\theta, \mathbf{m}) (\varphi')^2, \\ \bar{\mathbf{b}}(\theta, \mathbf{m}) \varphi' = \operatorname{div}\{ \bar{\psi}(\theta, \mathbf{m}) \nabla\varphi + \frac{1}{2} |\nabla\varphi| \partial_{\mathbf{m}} \bar{\psi}(\theta, \mathbf{m}) \} + \\ - \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) - \Psi'(\varphi) + \frac{1}{2} \bar{\eta}(\theta, \mathbf{m}) \nabla\varphi \cdot \nabla\theta. \end{aligned} \quad (1.10)$$

<sup>8</sup>In a report of Gurtin [24] the kinetic heat-flux has the form  $\mathbf{q}^{kin} = -\theta \bar{\eta} \varphi' \nabla\varphi$  (\*) and hence differs from (1.9) by a factor of 2; we now believe that (\*) and hence the PDEs derived in [24] do not yield valid models for a thin interface.

with  $c(\theta, \varphi) = \theta \partial_\theta \hat{\eta}^{bu}(\theta, \varphi)$  the (bulk) specific heat. For an isotropic material these PDEs reduce to<sup>9</sup>

$$\begin{aligned} c(\theta, \varphi) \theta' + \theta \{ \partial_\varphi \hat{\eta}^{bu}(\theta, \varphi) \varphi' + \frac{1}{2} (|\nabla \varphi|^2 \bar{\eta}(\theta))' - \frac{1}{2} \operatorname{div}(\bar{\eta}(\theta) \varphi' \nabla \varphi) \} = \\ \operatorname{div}(k(\theta, \varphi) \nabla \theta) + \bar{B}(\theta) (\varphi')^2, \\ \bar{B}(\theta) \varphi' = \bar{\psi}(\theta) \Delta \varphi - \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) - \Psi'(\varphi) - \frac{1}{2} \bar{\eta}(\theta) \nabla \theta \cdot \nabla \varphi, \end{aligned} \quad (1.11)$$

with  $k(\theta, \varphi)$  the conductivity.

We present a formal matched-asymptotic analysis that compares the general (anisotropic) diffuse-interface theory developed here with the sharp-interface theory of Gurtin [22] (see also [23-26]), a theory that accounts for: (i) the energy and entropy of the interface; (ii) general surface-excess forces, including surface shear; and (iii) interface kinetics. Specifically, granted a simple scaling, with a (small) scale parameter  $\delta$ , in which the gradient free-energy and kinetic modulus are  $O(\delta)$ , the bulk free-energy and conductivity are  $O(1)$ , and the exchange energy is  $O(\delta^{-1})$ , we show that, formally, as  $\delta \rightarrow 0$ , the PDEs

(1.10) converge to the bulk PDEs and the interface conditions of [22].<sup>10</sup>

Further, because the forms of the basic laws upon which we base our theory are relatively new, we strengthen our results by showing that

*the global integral laws of our theory converge to those of [22].*

The theory developed here may be viewed as a regularization of the sharp-interface theory of [22]: given thermodynamically consistent constitutive functions (of arbitrary complexity) that characterize the interfacial and bulk behavior of a particular two-phase material with sharp interface, we show that one can always construct a corresponding regularizing diffuse-interface theory of the type developed here. The final section of the paper contains complete recipes for the construction of such a regularizing theory.

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<sup>9</sup>It seems important to leave  $\bar{\psi}(\theta)$  and  $\bar{\eta}(\theta)$  temperature dependent. If  $\bar{\psi}$  is constant, then  $\bar{\eta} = 0$ . More generally, if  $\bar{\eta}$  and its counterpart  $\bar{\epsilon}$  for the internal energy are constant, which may appear reasonable, then the equivalent sharp-interface free-energy  $\hat{f}(\theta)$  and entropy  $\hat{s}(\theta)$  have the (unexpected) forms:  $\hat{f}(\theta) = (\bar{\epsilon} - \theta \bar{\eta})^{\frac{1}{2}}$ ,  $\hat{s}(\theta) = -\frac{1}{2} \bar{\eta} (\bar{\epsilon} - \theta \bar{\eta})^{-\frac{1}{2}}$ .

<sup>10</sup>To our knowledge, all other theories of phase-field type have, as formal asymptotic limits, the sharp interface conditions of [22], but with terms missing or approximated. Of course, the missing terms may, under certain circumstances, be small and the approximations valid, but that should not preclude the search for a more inclusive theory.

## 2. GENERAL THEORY<sup>11</sup>

### 2.1. Basic equations

The primitive quantities of the theory are the fields

$\varepsilon$	internal energy
$\theta$	absolute temperature
$\eta$	entropy
$\mathbf{q}$	heat flux
$\varphi$	order parameter (scalar)
$\boldsymbol{\xi}$	microstress (vector)
$\pi$	internal microforce (scalar)

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

$$\left\{ \int_R \varepsilon \, dv \right\}' = - \int_{\partial R} \mathbf{q} \cdot \mathbf{n} \, da + \int_{\partial R} \varphi' \boldsymbol{\xi} \cdot \mathbf{n} \, da, \quad (2.1)$$

*growth of entropy*

$$\left\{ \int_R \eta \, dv \right\}' \geq - \int_{\partial R} (\mathbf{q}/\theta) \cdot \mathbf{n} \, da, \quad (2.2)$$

and a *microforce balance*

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

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

$$\begin{aligned} \varepsilon' &= -\operatorname{div} \mathbf{q} + \operatorname{div}(\varphi' \boldsymbol{\xi}), \\ \eta' &= -\operatorname{div}(\mathbf{q}/\theta) + \Gamma, \\ \operatorname{div} \boldsymbol{\xi} + \pi &= 0, \end{aligned} \quad (2.4)$$

with  $\Gamma \geq 0$  the entropy production; together they yield the dissipation inequality

$$\varphi' + \eta \theta' + \pi \varphi' - \boldsymbol{\xi} \cdot \nabla \varphi' + \theta^{-1} \mathbf{q} \cdot \nabla \theta = -\theta \Gamma \leq 0 \quad (2.5)$$

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<sup>11</sup>Sections 2.1-2.3 are taken from [20].

in which

$$\psi = \varepsilon - \theta\eta \quad (2.6)$$

denotes 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  $\varphi^* \xi \cdot n = 0$  on  $\partial\Omega$ ,

$$\left\{ \int_{\Omega} \varepsilon dv \right\}' = 0, \quad \left\{ \int_{\Omega} \eta dv \right\}' = \int_{\Omega} \Gamma dv \geq 0 \quad \text{if } \mathbf{q} \cdot \mathbf{n} = 0 \text{ on } \partial\Omega; \quad (2.7)$$

$$\left\{ \int_{\Omega} (\varepsilon - \theta_0 \eta) dv \right\}' = -\theta_0 \int_{\Omega} \Gamma dv \leq 0 \quad \text{if } \theta = \theta_0 = \text{constant on } \partial\Omega. \quad (2.8)$$

## 2.2. Constitutive equations. Consequences of the dissipation inequality

We consider constitutive equations of the form<sup>12</sup>

$$\psi = \hat{\psi}(\dots), \quad \eta = \hat{\eta}(\dots), \quad \mathbf{q} = \hat{\mathbf{q}}(\dots), \quad \xi = \hat{\xi}(\dots), \quad \pi = \hat{\pi}(\dots), \quad (2.9)$$

with (...) shorthand for the list

$$(\dots) = (\theta, \nabla\theta, \varphi, \nabla\varphi, \varphi^*). \quad (2.10)$$

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

$$\mathbf{g} = \nabla\theta, \quad \mathbf{r} = \theta^*, \quad \mathbf{p} = \nabla\varphi, \quad \mathbf{s} = \varphi^*, \quad (2.11)$$

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

$$\begin{aligned} & \{ \partial_{\varphi} \hat{\psi}(\dots) + \hat{\pi}(\dots) \} s + \{ \partial_{\theta} \hat{\psi}(\dots) + \hat{\eta}(\dots) \} r + \{ \partial_{\mathbf{p}} \hat{\psi}(\dots) - \hat{\xi}(\dots) \} \cdot \mathbf{p} + \\ & \{ \partial_{\mathbf{g}} \hat{\psi}(\dots) \} \cdot \mathbf{g} + \partial_s \hat{\psi}(\dots) s + \theta^{-1} \hat{\mathbf{q}}(\dots) \cdot \mathbf{g} = -\theta \Gamma \leq 0. \end{aligned} \quad (2.12)$$

<sup>12</sup>We carefully distinguish between fields and their constitutive response functions; thus, e.g., the first of (2.9) signifies that the free-energy  $\psi(\mathbf{x},t)$  is given at each  $(\mathbf{x},t)$  through a constitutive relation of the form  $\psi(\mathbf{x},t) = \hat{\psi}(\theta(\mathbf{x},t), \nabla\theta(\mathbf{x},t), \varphi(\mathbf{x},t), \nabla\varphi(\mathbf{x},t), \varphi^*(\mathbf{x},t))$ , so that  $\hat{\psi}$  represents the constitutive response function for the free energy, while  $\psi = \psi(\mathbf{x},t)$  represents the actual free energy as a field over the body. We will consistently write  $\hat{\xi}$  for the constitutive function that delivers a field  $\xi$ . As is tacit from this discussion, we restrict attention to *homogeneous materials*.

It is possible to find fields  $\theta(\mathbf{x},t)$  and  $\varphi(\mathbf{x},t)$  such that  $\theta$ ,  $\mathbf{g}=\nabla\theta$ ,  $\mathbf{g}'=\nabla\theta'$ ,  $r=\theta'$ ,  $\varphi$ ,  $s=\varphi'$ ,  $s'=\varphi''$ ,  $\mathbf{p}=\nabla\varphi$ , and  $\mathbf{p}'=\nabla\varphi'$  have arbitrarily prescribed values at some chosen point and time. Since  $(\dots) = (\theta, \mathbf{g}, \varphi, \mathbf{p}, s)$ , the quantities  $r$ ,  $\mathbf{g}'$ ,  $s'$ , and  $\mathbf{p}'$  appear linearly in (2.12); therefore  $\partial_s \hat{\psi} = 0$ ,  $\partial_{\mathbf{g}} \hat{\psi} = 0$ ,  $\partial_{\theta} \hat{\psi} = -\hat{\eta}$ , and  $\partial_{\mathbf{p}} \hat{\psi} = \hat{\xi}$ , for otherwise  $r$ ,  $\mathbf{g}'$ ,  $s'$ , and  $\mathbf{p}'$  could be chosen to violate (2.12). The free energy, entropy, and microstress are thus independent of  $\mathbf{g}$  and  $\varphi'$  and related through

$$\hat{\eta}(\theta, \varphi, \nabla\varphi) = -\partial_{\theta} \hat{\psi}(\theta, \varphi, \nabla\varphi), \quad \hat{\xi}(\theta, \varphi, \nabla\varphi) = \partial_{\mathbf{p}} \hat{\psi}(\theta, \varphi, \nabla\varphi), \quad (2.13)$$

and the entropy production is given by

$$\theta^2 \Gamma = -\theta \Pi(\dots) \varphi' - \hat{\mathbf{q}}(\dots) \cdot \nabla\theta \geq 0 \quad (2.14)$$

with

$$\Pi(\dots) = \partial_{\varphi} \hat{\psi}(\theta, \varphi, \nabla\varphi) + \hat{\pi}(\dots). \quad (2.15)$$

The general solution of (2.14) is

$$\begin{aligned} \hat{\mathbf{q}}(\dots) &= -\mathbf{d}(\dots) \varphi' - \mathbf{K}(\dots) \nabla\theta, \\ \Pi(\dots) &= -\bar{\mathbf{b}}(\dots) \varphi' - \mathbf{a}(\dots) \cdot \nabla\theta, \end{aligned} \quad (2.16)$$

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

$$\theta \bar{\mathbf{b}}(\theta, \mathbf{g}, \varphi, \mathbf{p}, s) s^2 + \mathbf{sg} \cdot \{ \theta \mathbf{a}(\theta, \mathbf{g}, \varphi, \mathbf{p}, s) + \mathbf{d}(\theta, \mathbf{g}, \varphi, \mathbf{p}, s) \} + \mathbf{g} \cdot \mathbf{K}(\theta, \mathbf{g}, \varphi, \mathbf{p}, s) \mathbf{g} \geq 0. \quad (2.17)$$

The relations (2.7), (2.13)<sub>1</sub>, and (2.16)<sub>2</sub> yield

$$\begin{aligned} \varepsilon &= \hat{\varepsilon}(\theta, \varphi, \nabla\varphi) = \hat{\psi}(\theta, \varphi, \nabla\varphi) - \theta \partial_{\theta} \hat{\psi}(\theta, \varphi, \nabla\varphi), \\ \pi &= -\partial_{\varphi} \hat{\psi}(\theta, \varphi, \nabla\varphi) - \bar{\mathbf{b}}(\dots) \varphi' - \mathbf{a}(\dots) \cdot \nabla\theta, \end{aligned} \quad (2.18)$$

as well as the identity

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

Further, because of (2.14), the entropy balance (2.4)<sub>2</sub> implies that

$$\theta \eta' = -\operatorname{div} \mathbf{q} - \Pi(\cdot) \varphi', \quad (2.20)$$

which, granted the constitutive equations (2.13) and (2.16), is equivalent to the energy balance (2.4)<sub>1</sub>.

### 2.3. Generalized phase-field equations

The PDEs of the theory, which follow upon substituting the thermodynamically reduced constitutive relations for  $\varepsilon$ ,  $\mathbf{q}$ ,  $\xi$ , and  $\pi$  into the local balances for energy and microforce, are

$$\begin{aligned} \partial_\theta \hat{\varepsilon}(\theta, \varphi, \nabla \varphi) \theta' + \partial_\varphi \hat{\varepsilon}(\theta, \varphi, \nabla \varphi) \varphi' + \partial_p \hat{\varepsilon}(\theta, \varphi, \nabla \varphi) \cdot \nabla \varphi' = \\ \operatorname{div} \{ \mathbf{K}(\cdot) \nabla \theta + [\mathbf{d}(\cdot) + \partial_p \hat{\psi}(\theta, \varphi, \nabla \varphi)] \varphi' \}, \quad (2.21) \\ \bar{\mathbf{b}}(\cdot) \varphi' = \operatorname{div} \{ \partial_p \hat{\psi}(\theta, \varphi, \nabla \varphi) \} - \partial_\varphi \hat{\psi}(\theta, \varphi, \nabla \varphi) - \mathbf{a}(\cdot) \cdot \nabla \theta. \end{aligned}$$

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). An equation equivalent to (2.21)<sub>1</sub>—and one we will generally use—is the following consequence of (2.20) and the constitutive equations:

$$\begin{aligned} \theta \partial_\theta \hat{\eta}(\cdot) \theta' + \theta \partial_\varphi \hat{\eta}(\cdot) \varphi' + \theta \partial_p \hat{\eta}(\cdot) \cdot \nabla \varphi' = \\ \operatorname{div} \{ \mathbf{K}(\cdot) \nabla \theta + \mathbf{d}(\cdot) \varphi' \} + \bar{\mathbf{b}}(\cdot) (\varphi')^2 + \varphi' \mathbf{a}(\cdot) \cdot \nabla \theta. \quad (2.22) \end{aligned}$$

### 2.4. Decomposition of the heat flux and internal force

The constitutive equations (2.16) show  $\nabla \theta$  and  $\varphi'$  to be the fields that, in some sense, most influence  $\hat{\mathbf{q}}$  and  $\Pi$ ; in fact, for  $\theta$  and  $\varphi$  close to constant values  $\theta_0$  and  $\varphi_0$ , so that  $|\theta - \theta_0|$ ,  $|\nabla \theta|$ ,  $|\varphi - \varphi_0|$ ,  $|\nabla \varphi|$ , and  $|\varphi'|$  are small, say  $O(H)$ ,

$$\begin{aligned} \hat{\mathbf{q}}(\cdot) &= -\mathbf{d}_0 \varphi' - \mathbf{K}_0 \nabla \theta + O(H^2), \\ \Pi(\cdot) &= -\bar{\mathbf{b}}_0 \varphi' - \mathbf{a}_0 \cdot \nabla \theta + O(H^2), \end{aligned} \quad (2.23)$$

with  $\mathbf{d}_0$ ,  $\mathbf{K}_0$ ,  $\bar{\mathbf{b}}_0$ , and  $\mathbf{a}_0$  constant. An expansion of the form (2.23) holds also for  $|\nabla \theta|$  and  $|\varphi'|$  of  $O(H)$ , irrespective of  $(\theta, \varphi, \nabla \varphi)$ , but then the coefficients depend on  $(\theta, \varphi, \nabla \varphi)$ . Guided by this, we assume that

(A1)  $\hat{\mathbf{q}}(\cdot)$  and  $\Pi(\cdot)$  are linear functions of  $(\nabla \theta, \varphi')$ :<sup>13</sup>

<sup>13</sup>Fried and Stiehl [27] relax this assumption, allowing more general dependence of  $\hat{\mathbf{q}}$  and  $\Pi$  on  $(\nabla \theta, \varphi')$  and, consequently, for both interfacial conductivity and nonlinear

$$\begin{aligned}\hat{q}(\dots) &= -d(\theta, \varphi, \nabla\varphi)\varphi' - K(\theta, \varphi, \nabla\varphi)\nabla\theta, \\ \Pi(\dots) &= -\bar{b}(\theta, \varphi, \nabla\varphi)\varphi' - a(\theta, \varphi, \nabla\varphi)\cdot\nabla\theta.\end{aligned}\tag{2.24}$$

Consequences of (2.24) are the relation

$$\theta^2\Gamma = \theta\bar{b}(\theta, \varphi, \nabla\varphi)(\varphi')^2 + \varphi'\nabla\theta\cdot\{\theta a(\theta, \varphi, \nabla\varphi) + d(\theta, \varphi, \nabla\varphi)\} + \nabla\theta\cdot K(\theta, \varphi, \nabla\varphi)\nabla\theta \geq 0\tag{2.25}$$

for the entropy production (2.14), the decomposition

$$\mathbf{q} = \mathbf{q}^{\text{th}} + \mathbf{q}^{\text{kin}}, \quad \mathbf{q}^{\text{th}} = -K(\theta, \varphi, \nabla\varphi)\nabla\theta, \quad \mathbf{q}^{\text{kin}} = -d(\theta, \varphi, \nabla\varphi)\varphi'\tag{2.26}$$

of  $\mathbf{q}$  into a thermal flux  $\mathbf{q}^{\text{th}}$  down a temperature gradient and a *kinetic flux*  $\mathbf{q}^{\text{kin}}$  induced by temporal variations in the order parameter, and the decomposition

$$\Pi = \pi^{\text{th}} + \pi^{\text{kin}}, \quad \pi^{\text{th}} = -a(\theta, \varphi, \nabla\varphi)\cdot\nabla\theta, \quad \pi^{\text{kin}} = -\bar{b}(\theta, \varphi, \nabla\varphi)\varphi',\tag{2.27}$$

of  $\Pi$  into thermal and kinetic parts  $\pi^{\text{th}}$  and  $\pi^{\text{kin}}$ .

## 2.5. Configurational fields. Basic laws for evolving control volumes

Configurational fields represent power and heat associated with the addition and removal of material, and are therefore central to the study of phase interfaces. Following Gurtin [25], we consider a configurational stress tensor  $\mathbf{C}$  and a scalar configurational heating  $Q$ , which we describe using *control volumes*  $R(t)$  that evolve with time: if  $\mathbf{v}(\mathbf{x}, t)$  is a velocity field for  $\partial R(t)$ , constructed using a time-dependent parametrization for  $\partial R(t)$ , and if  $\mathcal{V} = \mathbf{v}\cdot\mathbf{n}$  is the corresponding normal velocity, then

$$\int_{\partial R} \mathbf{C}\mathbf{n}\cdot\mathbf{v}da, \quad \int_{\partial R} Q\mathcal{V}da, \quad \int_{\partial R} (Q/\theta)\mathcal{V}da\tag{2.28}$$

represent power expended on  $R$  and flows of heat and entropy into  $R$  associated with the motion of  $\partial R$ . Using these fields we write balance of energy and growth of entropy—for an arbitrary evolving control volume  $R=R(t)$ —in the form

$$\left\{ \int_R \varepsilon dv \right\}' = - \int_{\partial R} \mathbf{q} \cdot \mathbf{n} da + \int_{\partial R} Q \mathcal{V} da + \mathcal{W}(R), \quad (2.29)$$

$$\left\{ \int_R \eta dv \right\}' \geq - \int_{\partial R} (\mathbf{q}/\theta) \cdot \mathbf{n} da + \int_{\partial R} (Q/\theta) \mathcal{V} da, \quad (2.30)$$

where

$$\mathcal{W}(R) = \int_{\partial R} \varphi^\square \boldsymbol{\xi} \cdot \mathbf{n} da + \int_{\partial R} \mathbf{C} \mathbf{n} \cdot \mathbf{v} da \quad (2.31)$$

is the working with

$$\varphi^\square = \dot{\varphi} + \nabla \varphi \cdot \mathbf{v} \quad (2.32)$$

the rate of change of  $\varphi$  following the evolution of  $\partial R$  as described by  $\mathbf{v}$ .

To ensure that the energy balance (2.29) be independent of the choice of parametrization used in the construction of the velocity field  $\mathbf{v}$ , we require that (2.29) hold for all parameterizations, an assumption equivalent to the requirement that the *working* (2.31) be invariant under changes in parameterization, and hence, by (3.5), that

$$\int_{\partial R} \mathbf{v} \cdot \{ \mathbf{C} + (\nabla \varphi \otimes \boldsymbol{\xi}) \} \mathbf{n} da \quad (2.33)$$

be invariant under such changes. Changes in parameterization affect the tangential component of  $\mathbf{v}$ , but leave the normal component unaltered. In fact, invariance of (2.33) is equivalent to the requirement that  $\mathbf{t} \cdot [ \mathbf{C} + (\nabla \varphi \otimes \boldsymbol{\xi}) ] \mathbf{n} = 0$  on  $\partial R$  for all tangential vector fields  $\mathbf{t}$  on  $\partial R$ ; thus, since  $R$  is arbitrary,  $[ \mathbf{C} + (\nabla \varphi \otimes \boldsymbol{\xi}) ] \mathbf{n}$  must be parallel to  $\mathbf{n}$  for all  $\mathbf{n}$ , and there is a scalar field  $\Phi$  such that

$$\mathbf{C} + \nabla \varphi \otimes \boldsymbol{\xi} = \Phi \mathbf{1}. \quad (2.34)$$

Thus

$$\mathcal{W}(R) = \int_{\partial R} \dot{\varphi} \boldsymbol{\xi} \cdot \mathbf{n} da + \int_{\partial R} \Phi \mathcal{V} da, \quad (2.35)$$

and (2.29), (2.30), the identity

$$\left\{ \int_R f dv \right\}' = \int_R \dot{f} dv + \int_{\partial R} f \mathcal{V} da \quad (2.36)$$

with  $f=\varepsilon$  and  $f=\eta$ , and the fact that  $\mathcal{V}$  can be chosen arbitrarily yield  $\varepsilon = Q + \bar{\Phi}$  and  $\eta = Q/\theta$ . The configurational fields  $\mathbf{C}$  and  $Q$  therefore have the specific forms:<sup>14</sup>

$$\mathbf{C} = \psi \mathbf{1} - \nabla \varphi \otimes \xi, \quad Q = \theta \eta, \quad (2.37)$$

relations that are independent of particular constitutive assumptions.

The microforce balance (2.4)<sub>3</sub> and the reduced constitutive relations (2.13) and (2.18) then yield the configurational force balance

$$\operatorname{div} \mathbf{C} + \mathbf{f} = \mathbf{0}, \quad (2.38)$$

where

$$\mathbf{f} = \{ \bar{b}(\dots) \varphi' + \mathbf{a}(\dots) \cdot \nabla \theta \} \nabla \varphi + \eta \nabla \theta \quad (2.39)$$

represents internal configurational forces. Conversely, granted (2.13) and (2.18), (2.38) implies the microforce balance (2.4)<sub>3</sub>.

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<sup>14</sup>This argument is analogous to that leading to (3.21) and (6.6) of [25].

### 3. UNIFORMITY SURFACES

#### 3.1. Definition. Basic identities for normal velocity and curvature

In the theory developed here the phase interface is *diffuse*, with no sharp distinction between phases; loosely speaking, each value of the order parameter represents a particular phase of the material. For that reason the level sets

$$\mathcal{S}(t) = \{x : \varphi(x,t) = \text{constant}\} \quad (3.1)$$

play an important role; we will refer to the sets  $\mathcal{S}(t)$  as *uniformity surfaces*. In applications of the diffuse-interface theory the interface is often a thin surface-like region consisting of closely-packed uniformity surfaces.

To ensure that uniformity surfaces are well-defined, we require that

$$\ell = |\nabla\varphi| \neq 0. \quad (3.2)$$

Then

$$\mathbf{m} = \nabla\varphi/\ell, \quad V = -\varphi'/\ell \quad (3.3)$$

represent, at each  $(x,t)$ , a unit normal field and corresponding normal velocity for the uniformity surface through  $x$  at time  $t$ ; the tensor field

$$P = 1 - \mathbf{m} \otimes \mathbf{m} \quad (3.4)$$

projects vector fields onto their components tangent to uniformity surfaces;

$$L = -(\nabla\mathbf{m})P, \quad K = \text{tr}L = -\text{div}\mathbf{m} \quad (3.5)$$

are the *curvature tensor* and *total curvature* (twice the mean curvature) of uniformity surfaces; and, for  $\Phi$  a scalar field and  $\mathbf{v}$  a vector field,

$$\Phi^\circ = \Phi' + \nabla\Phi \cdot (\nabla\mathbf{m}), \quad \mathbf{v}^\circ = \mathbf{v}' + (\nabla\mathbf{v})(\nabla\mathbf{m}) \quad (3.6)$$

represent time derivatives following the normal trajectories of uniformity surfaces. Consequences of these definitions are the identities

$$\nabla\ell = (\nabla\nabla\varphi)\mathbf{m}, \quad \ell' = \mathbf{m} \cdot \nabla\varphi', \quad \ell\nabla\mathbf{m} = P\nabla\nabla\varphi, \quad \ell\mathbf{m}' = P\nabla\varphi', \quad (3.7)$$

and, hence, the relations

$$\begin{aligned} L &= -\ell^{-1}P(\nabla\nabla\varphi)P, & K &= -\ell^{-1}(\Delta\varphi - \mathbf{m}\cdot(\nabla\nabla\varphi)\mathbf{m}), \\ m^\circ &= -P\nabla V, & \ell^\circ &= -\ell\mathbf{m}\cdot\nabla V. \end{aligned} \quad (3.8)$$

### 3.2. The zero-flux condition

Consider an evolving control volume  $R$  and, as before, let  $\mathbf{n}$  and  $\mathcal{V}$  denote the outward unit normal and corresponding normal velocity of  $\partial R$ . Assume that  $\partial R$  intersects the uniformity surfaces tangentially at most on a set of zero surface-measure. Let  $\mathcal{S}(t)$  be a uniformity surface that intersects  $\partial R(t)$  transversely along a smooth closed curve  $\mathcal{U}(t)$ . Let

$$\boldsymbol{\nu} = (1 - (\mathbf{n}\cdot\mathbf{m})^2)^{-\frac{1}{2}}P\mathbf{n}; \quad (3.9)$$

then  $\boldsymbol{\nu}(\mathbf{x},t)$  is tangent to  $\mathcal{S}(t)$  at  $\mathbf{x}\in\mathcal{U}(t)$  and represents the unit normal to  $\mathcal{U}(t)$  directed outward from  $R(t)$ . Since  $\mathbf{m}$ ,  $\mathbf{n}$ , and  $\boldsymbol{\nu}$  are coplanar, the (intrinsic) velocity  $\mathbf{u}$  of  $\mathcal{U}$  has two components:  $V\mathbf{m}$ , which is normal to  $\mathcal{S}$ , and  $U\boldsymbol{\nu}$ , which is normal to  $\mathcal{U}$ , but tangent to  $\mathcal{S}$ :

$$\mathbf{u} = V\mathbf{m} + U\boldsymbol{\nu}. \quad (3.10)$$

$U$ , the scalar normal velocity of  $\mathcal{U}$ , represents a flux of uniformity-surface area across  $\partial R$ ; that is, the rate at which uniformity-surface area enters or leaves  $R$  through  $\partial R$  as  $\mathcal{S}$  and  $R$  evolve. By considering all uniformity surfaces that cross  $\partial R$  transversally, the flux  $U$  may be defined almost everywhere on  $\partial R$ .

Since each of the curves  $\mathcal{U}$  evolves on the surface  $\partial R$ ,  $\mathbf{u}$  is a velocity field for  $\partial R$ ; consequently,

$$\mathcal{V} = \mathbf{n}\cdot\mathbf{u} = V\mathbf{n}\cdot\mathbf{m} + U\mathbf{n}\cdot\boldsymbol{\nu}. \quad (3.11)$$

Note that for  $R$  stationary, if the uniformity surfaces meet  $\partial R$  orthogonally, then  $U = 0$ . More generally, an *evolving control volume*  $R$  satisfies the *zero-flux condition* if  $U=0$  almost everywhere on  $\partial R$ , or equivalently, by (3.10) and (3.11), if

$$\mathcal{V} = V\mathbf{n}\cdot\mathbf{m}. \quad (3.12)$$

Finally, for  $R$  stationary we have the equivalent identities

$$U\mathbf{n}\cdot\boldsymbol{\nu} = -V\mathbf{n}\cdot\mathbf{m}, \quad U = -(1 - (\mathbf{n}\cdot\mathbf{m})^2)^{-\frac{1}{2}}(\mathbf{n}\cdot\mathbf{m})V. \quad (3.13)$$

#### 4. CONSTITUTIVE RELATIONS FOR A THIN INTERFACE. EXCHANGE ENERGY. BULK AND EXCESS QUANTITIES. KINETIC HEAT-FLUX

We now introduce assumptions that make precise our physical prejudices concerning the behavior of bulk phases separated by a *thin* interfacial layer. These assumptions yield a natural decomposition of each thermodynamic field into a field associated with the bulk material and one associated with the interfacial layer. A basic premise of our theory is that, with a simple exception,

*constitutive dependences on  $\varphi$  (as opposed to  $\nabla\varphi$ ) reflect the structure of the bulk phases rather than that of the interfacial layer;* (4.1)

the exception being the exchange energy  $\Psi(\varphi)$  (the coarse-grain free-energy at the transition temperature), which is a double-well potential that promotes the separation into bulk phases and represents an important contribution to both the free energy and the internal energy of the interfacial layer.

##### 4.1. Exchange energy. Bulk and excess constitutive relations

By a *double-well potential* we mean a smooth function  $\Theta(\varphi)$  on  $\mathbb{R}$  with the following properties:  $\Theta(\varphi)$  is strictly convex on disjoint intervals  $(-\infty, \rho_1)$  and  $(\rho_2, \infty)$  with a minimum in  $(-\infty, \rho_1)$  and a minimum in  $(\rho_2, \infty)$ ;  $\Theta(\varphi)$  is strictly concave on the *spinodal* interval  $(\rho_1, \rho_2)$ .

To model the individual phases we assume that:

- (A2) (i) the coarse-grain free energy  $\hat{\psi}(\theta, \varphi, 0)$ , as a function of  $\varphi$  at fixed  $\theta$ , is a double-well potential whose minima, at  $\varphi_\alpha(\theta) < \varphi_\beta(\theta)$ , say, define the phases;
- (ii) there is a *transition temperature*  $\theta_M$  such that  $\varphi_\alpha(\theta)$  is the unique global minimum of  $\hat{\psi}(\theta, \varphi, 0)$  for  $\theta < \theta_M$ , while  $\varphi_\beta(\theta)$  is the unique global minimum of  $\hat{\psi}(\theta, \varphi, 0)$  for  $\theta > \theta_M$ ;<sup>15</sup>
- (iii)  $\hat{\psi}(\theta, \varphi, 0)$  is strictly concave in  $\theta$  for all  $\varphi$ .

The free energy

$$\Psi(\varphi) = \hat{\psi}(\theta_M, \varphi, 0) \tag{4.2}$$

is then a double-well potential whose (two) minimum values coincide. We refer to  $\Psi$  as the *exchange energy* and assume, without loss in generality, that

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<sup>15</sup>For solidification  $\alpha$  would then be the solid phase,  $\beta$  the liquid phase.

$$\begin{aligned} \varphi_\alpha(\theta_M) &= 0, & \varphi_\beta(\theta_M) &= 1, \\ \Psi(\varphi) > 0, \quad \varphi &= 0,1; & \Psi(0) = \Psi(1) &= 0. \end{aligned} \quad (4.3)$$

Roughly speaking, the order-parameter values  $\varphi \approx 0$  and  $\varphi \approx 1$  characterize the bulk material of phase  $\alpha$  and phase  $\beta$ , respectively, while  $0 < \varphi < 1$  defines the interfacial layer, a thin layer within which  $\nabla\varphi$  and  $\varphi'$  are large.

The gradient energy  $\hat{\psi}(\theta, \varphi, \nabla\varphi) - \hat{\psi}(\theta, \varphi, 0)$  plays an important role within the interfacial layer. Phase-field theories are generally based on gradient energies that are independent of  $\varphi$  (cf. (4.1)) and quadratic in  $\nabla\varphi$ . Here, to model diverse types of anisotropy, we consider the dependence on  $\nabla\varphi = |\nabla\varphi| \mathbf{m}$  in terms of dependences on  $|\nabla\varphi|$  and  $\mathbf{m}$ , with gradient energy quadratic in  $|\nabla\varphi|$ , but an arbitrary function of  $\mathbf{m}$ ; precisely, we assume that:

(A3) the gradient energy  $\hat{\psi}(\theta, \varphi, \nabla\varphi) - \hat{\psi}(\theta, \varphi, 0)$  is independent of  $\varphi$  and homogeneous<sup>16</sup> of degree two in  $\nabla\varphi$ :

$$\hat{\psi}(\theta, \varphi, \nabla\varphi) = \hat{\psi}(\theta, \varphi, 0) + \frac{1}{2} \bar{\psi}(\theta, \mathbf{m}) |\nabla\varphi|^2 \quad (4.4)$$

(the factor of  $\frac{1}{2}$  being for convenience).

Since  $\Psi(0) = \Psi(1) = 0$ , the exchange energy does not sensibly contribute to the bulk energy, but it does contribute to the energy of the layer. For that reason, we introduce the decomposition

$$\begin{aligned} \hat{\psi}(\theta, \varphi, \nabla\varphi) &= \hat{\psi}(\theta, \varphi, 0) - \Psi(\varphi) &+& \Psi(\varphi) + \frac{1}{2} \bar{\psi}(\theta, \mathbf{m}) |\nabla\varphi|^2, \\ \text{free energy} & \quad \text{bulk free-energy} && \text{excess free-energy} \\ & && \text{of the interfacial layer} \end{aligned} \quad (4.5)$$

which will be basic to all of what follows; as we shall see, in the limit of vanishingly small interfacial thickness the *bulk free-energy*

$$\psi^{bu} = \hat{\psi}^{bu}(\theta, \varphi) = \hat{\psi}(\theta, \varphi, 0) - \Psi(\varphi) = \hat{\psi}(\theta, \varphi, 0) - \hat{\psi}(\theta_M, \varphi, 0) \quad (4.6)$$

at  $\varphi=0$  and  $\varphi=1$ , respectively, corresponds to the free energy of the bulk material of phase  $\alpha$  and phase  $\beta$ , while the *excess free-energy*

$$\psi^{xs} = \hat{\psi}^{xs}(\theta, \varphi, \nabla\varphi) = \Psi(\varphi) + \frac{1}{2} \bar{\psi}(\theta, \mathbf{m}) |\nabla\varphi|^2 \quad (4.7)$$

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<sup>16</sup> $\bar{\psi}(\mathbf{z})$  is homogeneous of degree  $p$  if, given any scalar  $\lambda$ ,  $\bar{\psi}(\lambda\mathbf{z}) = \lambda^p \bar{\psi}(\mathbf{z})$  for all  $\mathbf{z}$ .

integrated over the layer corresponds to the free energy of the interface.

Bearing in mind (2.6) and (2.13)<sub>1</sub>, we define bulk and excess values for the entropy and internal energy through the thermodynamic relations

$$\begin{aligned}
 \eta^{bu} &= \hat{\eta}^{bu}(\theta, \varphi) = -\partial_{\theta} \hat{\psi}^{bu}(\theta, \varphi), \\
 \eta^{xs} &= \hat{\eta}^{xs}(\theta, \nabla\varphi) = -\partial_{\theta} \hat{\psi}^{xs}(\theta, \varphi, \nabla\varphi), \\
 \epsilon^{bu} &= \hat{\epsilon}^{bu}(\theta, \varphi) = \hat{\psi}^{bu}(\theta, \varphi) + \theta \hat{\eta}^{bu}(\theta, \varphi), \\
 \epsilon^{xs} &= \hat{\epsilon}^{xs}(\theta, \varphi, \nabla\varphi) = \hat{\psi}^{xs}(\theta, \varphi, \nabla\varphi) + \theta \hat{\eta}^{xs}(\theta, \varphi, \nabla\varphi).
 \end{aligned} \tag{4.8}$$

Then for  $\rho$  equal to  $\psi$ ,  $\epsilon$ , or  $\eta$ ,

$$\rho = \hat{\rho}(\theta, \varphi, \nabla\varphi) = \hat{\rho}^{bu}(\theta, \varphi) + \hat{\rho}^{xs}(\theta, \varphi, \nabla\varphi); \tag{4.9}$$

in addition,

$$\begin{aligned}
 \eta^{bu} &= \hat{\eta}(\theta, \varphi, 0), \\
 \epsilon^{bu} &= \hat{\epsilon}(\theta, \varphi, 0) - \Psi(\varphi), \\
 \eta^{xs} &= \frac{1}{2} \bar{\eta}(\theta, \mathbf{m}) |\nabla\varphi|^2, & \bar{\eta} &= -\partial_{\theta} \bar{\Psi}, \\
 \epsilon^{xs} &= \Psi(\varphi) + \frac{1}{2} \bar{\epsilon}(\theta, \mathbf{m}) |\nabla\varphi|^2, & \bar{\epsilon} &= \bar{\Psi} + \theta \bar{\eta}, \\
 \xi &= \partial_{\mathbf{p}} \hat{\psi}^{xs}(\theta, \varphi, \mathbf{p}) = \bar{\Psi}(\theta, \mathbf{m}) \nabla\varphi + \frac{1}{2} |\nabla\varphi| \partial_{\mathbf{m}} \bar{\Psi}(\theta, \mathbf{m}),
 \end{aligned} \tag{4.10}$$

#### 4.2. Constitutive equations for $\mathbf{q}^{kin}$ and $\pi^{th}$

We begin by rewriting the entropy inequality (2.30) for an evolving control volume  $R(t)$  in the form

$$\left\{ \int_R (\eta^{bu} + \eta^{xs}) dv \right\}' \geq \int_{\partial R} \{ (\eta^{bu} + \eta^{xs}) \mathcal{V} - \theta^{-1} (\mathbf{q}^{th} + \mathbf{q}^{kin}) \cdot \mathbf{n} \} da, \tag{4.11}$$

where we have used the relation  $Q = \theta \eta$ . If (4.11) is appropriate to the physics of a thin interfacial layer, then for  $R$  consistent with the zero-flux condition we would not expect the terms relevant to the layer to give rise to flows of entropy across  $\partial R$ . We therefore assume that:

(A4) for each evolving control volume consistent with the zero-flux condition  
 $U = 0,$

$$\int_{\partial R} (\theta^{-1} \mathbf{q}^{\text{kin}} \cdot \mathbf{n} - \eta^{xs} \mathcal{V}) da = 0. \quad (4.12)$$

By (2.26) and (3.12), the integrand in (4.12) has the form  $\varphi^* \mathbf{j} \cdot \mathbf{n}$ , where

$$\mathbf{j} = \mathbf{j}(\theta, \varphi, \nabla \varphi) = \theta^{-1} \mathbf{d}(\theta, \varphi, \nabla \varphi) - \hat{\eta}^{xs}(\theta, \nabla \varphi) \nabla \varphi / \ell^2, \quad \ell = |\nabla \varphi|. \quad (4.13)$$

Thus, applying the divergence theorem and using the fact that  $R$  is arbitrary,

$$\varphi^* \text{div} \mathbf{j} + \mathbf{j} \cdot \nabla \varphi^* = 0. \quad (4.14)$$

Since  $\varphi^*$  and  $\nabla \varphi^*$  appear linearly in (4.14), this equality can hold for all fields  $\theta(\mathbf{x}, t)$  and  $\varphi(\mathbf{x}, t)$  only if  $\mathbf{j} = 0$ . Thus

$$\mathbf{d}(\theta, \nabla \varphi) = \theta \hat{\eta}^{xs}(\theta, \nabla \varphi) \nabla \varphi / \ell^2 = \frac{1}{2} \theta \bar{\eta}(\theta, m) \nabla \varphi \quad (4.15)$$

and the kinetic heat flux is related to the gradient entropy through the relation

$$\mathbf{q}^{\text{kin}} = \theta \hat{\eta}^{xs}(\theta, \nabla \varphi) \nabla m = -\frac{1}{2} \theta \bar{\eta}(\theta, m) \varphi^* \nabla \varphi. \quad (4.16)$$

This, a main result of the section, should be viewed as a constitutive relation defining a specific class of phase-field theories.

The next hypothesis concerns the moduli that govern the production of entropy (2.25). We do not allow for heat flow driven by temperature gradients within the interface, and therefore drop the dependence of  $K$  on  $\nabla \varphi$ . Further, we allow the dependence of  $\bar{b}$  on  $\nabla \varphi$  to at most reflect anisotropy. Bearing this and (4.1) in mind, and since we have little intuition concerning  $\mathbf{a}$ , we assume that

- (A5) the kinetic modulus  $\bar{b}(\theta, \varphi, \nabla \varphi)$  is independent of  $\varphi$  and homogeneous of degree zero in  $\nabla \varphi$ ; the conductivity  $K(\theta, \varphi, \nabla \varphi)$  is independent of  $\nabla \varphi$ ;  $\mathbf{a}(\theta, \varphi, \nabla \varphi)$  is a homogeneous function (of some degree  $k \geq 0$ ) in  $\nabla \varphi$ .

By (A5) and (4.15), the entropy-production inequality (2.25) has the form

$$\theta \bar{b}(\theta, m) (\varphi^*)^2 + \varphi^* \nabla \theta \cdot \{ |\nabla \varphi|^k \theta \mathbf{a}(\theta, \varphi, m) + |\nabla \varphi| \mathbf{d}(\theta, \varphi, m) \} + \nabla \theta \cdot K(\theta, \varphi) \nabla \theta \geq 0, \quad (4.17)$$

and must hold for all values of  $\theta$ ,  $\nabla \theta$ ,  $\varphi$ ,  $\nabla \varphi$ , and  $\varphi^*$ . Therefore  $|\nabla \varphi|^k \theta \mathbf{a}(\theta, \varphi, m) + |\nabla \varphi| \mathbf{d}(\theta, \varphi, m) = 0$  for  $|\nabla \varphi|$  sufficiently large, for otherwise  $\varphi^* \nabla \theta$  of appropriate direction would violate (4.17). Thus  $k=1$  and

$$d(\theta, \nabla\varphi) = -\theta \mathbf{a}(\theta, \varphi, \nabla\varphi), \quad (4.18)$$

so that, by (2.27) and (4.15),

$$\pi^{\text{th}} = -\mathbf{a}(\theta, \nabla\varphi) \cdot \nabla\theta, \quad \mathbf{a}(\theta, \nabla\varphi) = -\frac{1}{2} \bar{\eta}(\theta, m) \nabla\varphi; \quad (4.19)$$

therefore both the kinetic heat flux  $\mathbf{q}^{\text{kin}}$  and the thermal internal force  $\pi^{\text{th}}$  are related to the gradient entropy. Further, and what is surprising,  $\mathbf{q}^{\text{kin}}$  and  $\pi^{\text{th}}$  contribute neither to the production of entropy nor to the normal component of the internal configurational force:

$$\begin{aligned} \theta^2 \Gamma &= \nabla\theta \cdot \mathbf{K}(\theta, \varphi) \nabla\theta + \theta \bar{b}(\theta, m) (\varphi')^2 \geq 0, \\ \mathbf{f} \cdot \mathbf{m} &= \hat{\eta}^{\text{bu}}(\theta, \varphi) \mathbf{m} \cdot \nabla\theta + \ell \bar{b}(\theta, m) \varphi'. \end{aligned} \quad (4.20)$$

#### 4.3. Normal configurational force balance

We define the excess configurational stress through

$$\mathbf{C}^{\text{xs}} = \psi^{\text{xs}} \mathbf{1} - \nabla\varphi \otimes \xi. \quad (4.21)$$

Then (4.9) and the last of (4.10) yield the important relation

$$\mathbf{C}^{\text{xs}} = \psi^{\text{xs}} \mathbf{P} + \mathbf{m} \otimes \boldsymbol{\tau} + \mathbf{J} \mathbf{m} \otimes \mathbf{m}, \quad (4.22)$$

where

$$\begin{aligned} \boldsymbol{\tau} &= \mathbf{P}(\mathbf{C}^{\text{xs}})^{\text{T}} \mathbf{m} = -\ell \mathbf{P} \xi = -\frac{1}{2} \ell^2 \partial_{\mathbf{m}} \bar{\psi}(\theta, m), \\ \mathbf{J} &= \bar{\Psi}(\varphi) - \frac{1}{2} \ell^2 \bar{\psi}(\theta, m). \end{aligned} \quad (4.23)$$

Since  $\mathbf{P}$  is the projection onto uniformity surfaces, while  $\boldsymbol{\tau}$  is tangent to such surfaces, for a thin layer  $\mathcal{L}$  bounded by uniformity surfaces,  $\psi^{\text{xs}} \mathbf{P}$  represents surface tension within  $\mathcal{L}$ , while  $\mathbf{m} \otimes \boldsymbol{\tau}$  represents shearing stresses within  $\mathcal{L}$  in the direction  $\mathbf{m}$ .

Mimicking (2.38), we define  $\mathbf{f}^{\text{xs}}$  through the balance

$$\text{div} \mathbf{C}^{\text{xs}} + \mathbf{f}^{\text{xs}} = \mathbf{0}. \quad (4.24)$$

By (4.9),  $\mathbf{C}^{\text{xs}} = \mathbf{C} - \psi^{\text{bu}} \mathbf{1}$ ; thus

$$f^{xs} = f + \nabla\psi^{bu}, \quad (4.25)$$

and (4.25), (4.20)<sub>2</sub>, and the relation  $\hat{\eta}^{bu}(\theta, \varphi) = -\partial_\theta \hat{\psi}^{bu}(\theta, \varphi)$  imply that

$$f^{xs} \cdot m = m \cdot \{ \nabla\psi^{bu} + \eta^{bu} \nabla\theta \} - \ell^2 \bar{b} V, \quad (4.26)$$

where  $\bar{b} = \bar{b}(\theta, m)$ . Next, since  $m \cdot \text{div} P = -\text{div} m = K$ ,

$$m \cdot \text{div} C^{xs} = \psi^{xs} K + \text{div} \tau + \text{div} (Jm), \quad (4.27)$$

and the last two equations combine with (4.24) to give the normal configurational force balance

$$m \cdot \{ \nabla\psi^{bu} + \eta^{bu} \nabla\theta \} + \psi^{xs} K + \text{div} \tau + \text{div} (Jm) = \ell^2 \bar{b} V, \quad (4.28)$$

an equation that will be crucial to our discussion of the asymptotics of a thin interfacial layer. (The term  $m \cdot \{ \nabla\psi^{bu} + \eta^{bu} \nabla\theta \}$  can also be written as  $\ell \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi)$ .)

#### 4.4. Specific heat. Latent heat. Examples of coarse-grain free-energies

The specific heat,  $c(\theta, \varphi)$ , and the latent heat (of fusion),  $\lambda$ , are defined by

$$c(\theta, \varphi) = \partial_\theta \hat{\varepsilon}^{bu}(\theta, \varphi), \quad \lambda = \hat{\varepsilon}^{bu}(\theta_M, 1) - \hat{\varepsilon}^{bu}(\theta_M, 0). \quad (4.29)$$

By (4.8) and the relation  $\hat{\psi}^{bu}(\theta_M, 0) = \hat{\psi}^{bu}(\theta_M, 1)$ ,

$$\begin{aligned} c(\theta, \varphi) &= \theta \partial_\theta \hat{\eta}^{bu}(\theta, \varphi) = -\theta \partial_\theta \partial_\theta \hat{\psi}^{bu}(\theta, \varphi), \\ \lambda &= \theta_M \{ \hat{\eta}^{bu}(\theta_M, 1) - \hat{\eta}^{bu}(\theta_M, 0) \} = \theta_M \{ \partial_\theta \hat{\psi}^{bu}(\theta_M, 0) - \partial_\theta \hat{\psi}^{bu}(\theta_M, 1) \}; \end{aligned} \quad (4.30)$$

therefore, in view of (A2),

$$c(\theta, \varphi) > 0, \quad \lambda > 0. \quad (4.31)$$

If the specific heat is constant, then the coarse-grain free-energy necessarily has the form

$$\begin{aligned}\hat{\Psi}(\theta, \varphi, 0) &= \Psi(\varphi) + cA(\theta) - z(\varphi)(\theta - \theta_M)\lambda/\theta_M, \\ A(\theta) &= \theta - \theta_M - \theta \ln(\theta/\theta_M),\end{aligned}\tag{4.32}$$

with

$$z(0) = 0, \quad z(1) = 1.\tag{4.33}$$

The following particular forms have been proposed for  $\Psi(\varphi)$  and  $z(\varphi)$ :

$$\Psi(\varphi) = \frac{1}{2}\nu\varphi^2(1-\varphi)^2, \quad z(\varphi) = \varphi^2(3-2\varphi),\tag{4.34}$$

with  $\nu > 0$  constant.<sup>17</sup> A problem with this choice of  $z(\varphi)$  is that, since  $z(-\infty) = -\infty$ , at sufficiently high temperatures the global minimum of  $\hat{\Psi}(\theta, \varphi, 0)$ , as a function of  $\varphi$ , shifts from  $\varphi=1$  to a value  $\varphi < 0$ , yielding a spurious change in "most stable phase" from liquid to solid. For  $\lambda/\nu$  sufficiently large an analogous problem arises at low temperatures. This difficulty can be overcome by constraining<sup>18</sup>  $\varphi$  to the interval  $[0,1]$  or by assuming that

$$z(\varphi) = 0 \text{ for } \varphi \leq 0, \quad z(\varphi) = 1 \text{ for } \varphi \geq 1.\tag{4.35}$$

(The discontinuities in  $z''(\varphi)$  at  $\varphi=0$  and  $\varphi=1$  do not lead to discontinuous coefficients in the resulting phase-field equations.)

A more general form of free energy is obtained by assuming that the bulk free-energy is a convex combination:

$$\hat{\Psi}^{bu}(\theta, \varphi) = (1-z(\varphi))\tilde{\Psi}^\alpha(\theta) + z(\varphi)\tilde{\Psi}^\beta(\theta)\tag{4.36}$$

of bulk free-energies  $\tilde{\Psi}^\alpha(\theta)$  and  $\tilde{\Psi}^\beta(\theta)$  for phases  $\alpha$  and  $\beta$ , where  $z(\varphi)$  is consistent with (4.33) and (4.35). Then, since  $\hat{\Psi}(\theta_M, \varphi, 0) = 0$  at  $\varphi=0$  and  $\varphi=1$ , if we assume, without loss in generality, that  $\hat{\eta}(\theta_M, 0, 0) = 0$ , then (4.36) must necessarily have the form

$$\hat{\Psi}^{bu}(\theta, \varphi) = (1-z(\varphi))F^\alpha(\theta) + z(\varphi)F^\beta(\theta) - z(\varphi)(\theta - \theta_M)\lambda/\theta_M,\tag{4.37}$$

where  $F^\alpha(\theta)$  and  $F^\beta(\theta)$  are concave functions with

<sup>17</sup>The exchange energy is standard. This form for  $z(\varphi)$  is discussed in [19,20,28].

<sup>18</sup>Cf. Fried and Gurtin [29]. See also Blowey and Elliott [30], who add to  $\Psi(\varphi)$  the indicator function  $I_{[0,1]}(\varphi)$  (which vanishes on  $[0,1]$  but is otherwise equal to  $+\infty$ ).

$$F(\theta_M) = F'(\theta_M) = 0 \quad \text{for } F = F^\alpha \text{ and } F = F^\beta. \quad (4.38)$$

Taking  $F^\alpha(\theta) = F^\beta(\theta) = cA(\theta)$  reduces (4.37) to (4.32). The general case in which  $c(\theta, \varphi)$  depends on both  $\theta$  and  $\varphi$  can involve inconsistencies if, as would be expected, the difference  $c(\theta, 1) - c(\theta, 0)$  in bulk specific heats has one sign for all  $\theta$ . Indeed, in this instance  $F^\beta(\theta) - F^\alpha(\theta)$  is either: (i)  $\geq 0$  and strictly convex; or (ii)  $\leq 0$  and strictly concave. In either case a spurious (equilibrium) phase change will occur at a temperature  $\theta$  if

$$F^\beta(\theta) - F^\alpha(\theta) = z(\varphi)(\theta - \theta_M)\lambda/\theta_M \quad (4.39)$$

(i.e.,  $\hat{\psi}^{bu}(\theta, 0) = \hat{\psi}^{bu}(\theta, 1)$ ). In view of (4.31)<sub>2</sub> and (4.38), for case (i) (4.39) is always satisfied for some  $\theta > \theta_M$ ; in case (ii) for  $\lambda$  sufficiently large (4.39) will be satisfied for some  $\theta \in (0, \theta_M)$ . One would generally expect the spurious change of phase to occur at temperatures outside the range of physical interest, but even so, from a computational viewpoint such instabilities could result in erroneous results. This can be avoided by requiring that the individual free energies be adjusted (in a manner consistent with (A2)) so that  $F^\beta(\theta) = F^\alpha(\theta)$  outside the range of interest.

#### 4.5. Remark on a more general form of the exchange energy

One might wish to consider a temperature-dependent exchange energy  $\Psi(\theta, \varphi)$ . In this case, the assumption that the exchange energy not have an associated specific heat (and hence not effect bulk dynamics) yields the specific form

$$\Psi(\theta, \varphi) = E(\varphi) - \theta S(\varphi), \quad (4.40)$$

where  $E(\varphi)$  and  $S(\varphi)$  represent exchange functions for the internal energy and entropy. The bulk internal energy and entropy then involve  $E(\varphi)$  and  $S(\varphi)$ , as do the excess internal energy and entropy. Arguments similar to those used to establish (4.16) and (4.19) yield analogous results

$$q^{kin} = \theta \eta^{xs} \nabla m, \quad \pi^{th} = \eta^{xs} |\nabla \varphi|^{-1} m \cdot \nabla \theta, \quad (4.41)$$

with  $\eta^{xs} = S(\varphi) + \frac{1}{2} \bar{\eta}(\theta, m) |\nabla \varphi|^2$  no longer  $O(|\nabla \varphi|^2)$  at  $|\nabla \varphi| = 0$ , at least for  $S(\varphi) \neq 0$ . In particular, for  $S(\varphi) \neq 0$ ,  $\pi^{th}$  is unbounded at  $|\nabla \varphi| = 0$ ; for that reason we reject this more general form of exchange energy. (Note that  $S(\varphi) = 0$  leads to a singular term  $|\nabla \varphi|^{-1} S(\varphi) m \cdot \nabla \theta$  in the phase-field equation (5.1)<sub>2</sub> of the next section.)

## 5. PHASE-FIELD EQUATIONS

### 5.1. General anisotropic equations

Substituting the expressions in (4.15) and (4.19) for  $\mathbf{d}$  and  $\mathbf{a}$  into (2.22) and (2.21)<sub>2</sub> and using (4.9), (4.10), and (4.30)<sub>1</sub> results in the *generalized phase-field equations*

$$\begin{aligned} c(\theta, \varphi)\theta' + \theta \{ \partial_\varphi \hat{\eta}^{bu}(\theta, \varphi)\varphi' + \frac{1}{2}(\ell^2 \bar{\eta}(\theta, m))' - \frac{1}{2} \operatorname{div}(\bar{\eta}(\theta, m)\varphi' \nabla \varphi) \} = \\ \operatorname{div}(K(\theta, \varphi) \nabla \theta) + \bar{b}(\theta, m)(\varphi')^2, \\ \bar{b}(\theta, m)\varphi' = \operatorname{div} \{ \bar{\psi}(\theta, m) \nabla \varphi + \frac{1}{2} \ell \partial_m \bar{\psi}(\theta, m) \} + \\ - \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) - \Psi'(\varphi) + \frac{1}{2} \bar{\eta}(\theta, m) \nabla \varphi \cdot \nabla \theta. \end{aligned} \quad (5.1)$$

These PDEs represent phase-field equations of great generality: they account for the internal energy and entropy of the interface; they allow for an interface with anisotropic and temperature dependent structure; and they allow for general nonlinear constitutive behavior for the bulk material of each phase.

Note that, by (3.3), (3.5)<sub>2</sub>, (3.6) and (3.8)<sub>2,4</sub>, (5.1)<sub>1</sub> has the alternative form

$$\begin{aligned} c(\theta, \varphi)\theta' + \theta \partial_\varphi \hat{\eta}^{bu}(\theta, \varphi)\varphi' + \frac{1}{2} \theta \{ \ell^2 \bar{\eta}(\theta, m)' + \frac{1}{2} \bar{\eta}(\theta, m)(\ell^2)' - \ell^2 \bar{\eta}(\theta, m)KV \} = \\ \operatorname{div}(K(\theta, \varphi) \nabla \theta) + \ell^2 \bar{b}(\theta, m)V^2, \end{aligned} \quad (5.2)$$

while, by (4.23), (4.28) reads

$$\begin{aligned} \ell \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) + \{ \Psi(\varphi) + \frac{1}{2} \ell^2 \bar{\psi}(\theta, m) \} K - \frac{1}{2} \operatorname{div} \{ \ell^2 \partial_m \bar{\psi}(\theta, m) \} \\ + \operatorname{div} \{ (\Psi(\varphi) - \frac{1}{2} \ell^2 \bar{\psi}(\theta, m)) m \} = \ell^2 \bar{b}(\theta, m)V. \end{aligned} \quad (5.3)$$

Together (5.2) and (5.3), which are equivalent to (5.1), form a basis for the comparison with the sharp-interface theory given in Section 9.

Finally, to help ensure reasonable behavior of the foregoing PDEs we assume that (cf. (4.31)):

- (A6) the kinetic and gradient-energy moduli  $\bar{b}(\theta, m)$  and  $\bar{\psi}(\theta, m)$  are strictly positive for all  $(\theta, m)$ ; the conductivity tensor  $K(\theta, \varphi)$  is positive-definite for all  $(\theta, \varphi)$ .

### 5.2. Isotropy

If the material is isotropic,

$$K(\theta, \varphi) = k(\theta, \varphi)1, \quad \bar{b}(\theta, m) = \bar{b}(\theta), \quad \bar{\psi}(\theta, m) = \bar{\psi}(\theta), \quad \bar{\eta}(\theta, m) = \bar{\eta}(\theta), \quad (5.4)$$

and, since  $\bar{\eta}(\theta) = -\bar{\psi}'(\theta)$ ,  $\text{div}\{\bar{\psi}(\theta)\nabla\varphi\} = \bar{\psi}(\theta)\Delta\varphi - \bar{\eta}(\theta)\nabla\theta \cdot \nabla\varphi$ ; hence (5.1) reduce to

$$\begin{aligned} c(\theta, \varphi)\theta' + \theta \{ \partial_\varphi \hat{\eta}^{bu}(\theta, \varphi)\varphi' + \frac{1}{2} (\ell^2 \bar{\eta}(\theta))' - \frac{1}{2} \text{div}(\bar{\eta}(\theta)\varphi' \nabla\varphi) \} = \\ \text{div}(k(\theta, \varphi)\nabla\theta) + \bar{b}(\theta)(\varphi')^2, \end{aligned} \quad (5.5)$$

$$\bar{b}(\theta)\varphi' = \bar{\psi}(\theta)\Delta\varphi - \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) - \Psi'(\varphi) - \frac{1}{2} \bar{\eta}(\theta)\nabla\theta \cdot \nabla\varphi.$$

These PDEs, while restricted to isotropic materials, are otherwise quite general.

Standard simplifying assumptions are that the specific heat  $c$  and conductivity  $k$  are constant and independent of phase. Granted these assumptions, (5.5) take the simple form

$$\begin{aligned} c\theta' - \theta \{ z(\varphi)' \lambda / \theta_M - \frac{1}{2} (\ell^2 \bar{\eta}(\theta))' + \frac{1}{2} \text{div}(\bar{\eta}(\theta)\varphi' \nabla\varphi) \} = k\Delta\theta + \bar{b}(\theta)(\varphi')^2, \\ \bar{b}(\theta)\varphi' = \bar{\psi}(\theta)\Delta\varphi - \Psi'(\varphi) - z'(\varphi)(\theta - \theta_M)\lambda / \theta_M - \frac{1}{2} \bar{\eta}(\theta)\nabla\theta \cdot \nabla\varphi, \end{aligned} \quad (5.6)$$

where we have used (4.32).

## 6. REVIEW OF THE SHARP-INTERFACE THEORY. ROUGH COMPARISON OF THE DIFFUSE- AND SHARP-INTERFACE THEORIES

We here present a rough comparison of the the basic laws of the diffuse-interface theory developed here with those arising in the sharp-interface theory of Gurtin [22] (see also [23-26]). For convenience, we rely on the abbreviations

DT = diffuse-interface theory,      ST = sharp-interface theory.

### 6.1. Review of the sharp-interface theory

We consider a body whose phases  $\alpha$  and  $\beta$  occupy regions separated by a sharp interface  $\mathcal{S}=\mathcal{S}(t)$  that evolves with scalar normal-velocity  $V_{\mathcal{S}}$  in the direction of its unit normal field  $\mathbf{m}_{\mathcal{S}}$ . Let  $R$ , with outward unit normal  $\mathbf{n}$ , be a stationary control volume, write

$$Q(t) = \mathcal{S}(t) \cap R \tag{6.1}$$

for the portion of  $\mathcal{S}$  in  $R$ , and let

$$\begin{aligned} \mathbf{P}_{\mathcal{S}} &= \mathbf{1} - \mathbf{m}_{\mathcal{S}} \otimes \mathbf{m}_{\mathcal{S}}, \\ \boldsymbol{\nu}_{\partial Q} &= (1 - (\mathbf{n} \cdot \mathbf{m}_{\mathcal{S}})^2)^{-\frac{1}{2}} \mathbf{P}_{\mathcal{S}} \mathbf{n}, \\ U_{\partial Q} &= -(1 - (\mathbf{n} \cdot \mathbf{m}_{\mathcal{S}})^2)^{-\frac{1}{2}} (\mathbf{n} \cdot \mathbf{m}_{\mathcal{S}}) V_{\mathcal{S}} \end{aligned} \tag{6.2}$$

(cf. (3.9), (3.13)), so that  $\mathbf{P}_{\mathcal{S}}$  is the projection onto  $\mathcal{S}$ ,  $\boldsymbol{\nu}_{\partial Q}$ , a vector field tangent to  $\mathcal{S}$ , is the outward unit normal to the boundary curve  $\partial Q$ , and  $U_{\partial Q}$  is the scalar normal velocity of  $\partial Q$  in the direction  $\boldsymbol{\nu}_{\partial Q}$ . Then balance of energy and growth of entropy for  $R$  have the form

$$\begin{aligned} \left\{ \int_R \varepsilon dv + \int_Q e da \right\}' - \int_{\partial Q} e U_{\partial Q} dl &= - \int_{\partial R} \mathbf{q} \cdot \mathbf{n} da + \int_{\partial Q} V_{\mathcal{S}} \mathbf{c} \cdot \boldsymbol{\nu}_{\partial Q} dl, \\ \left\{ \int_R \eta dv + \int_Q s da \right\}' - \int_{\partial Q} s U_{\partial Q} dl &\geq - \int_{\partial R} (\mathbf{q}/\theta) \cdot \mathbf{n} da. \end{aligned} \tag{6.3}$$

Here  $\theta$  is the temperature with

$$\theta \text{ assumed continuous across } \mathcal{S} \text{ (local equilibrium);} \tag{6.4}$$

$\varepsilon$ ,  $\eta$ , and  $\mathbf{q}$  are the bulk energy, entropy, and heat flux;  $e$  and  $s$  are the energy and entropy of the interface; and  $\mathbf{c}$ , a vector field tangent to  $\mathcal{S}$ , is the surface

shear. These laws are supplemented by a configurational force balance: writing

$$\psi = \varepsilon - \theta\eta, \quad f = e - \theta s \quad (6.5)$$

for the bulk and interfacial free energies and<sup>19</sup>

$$\mathbf{C} = f\mathbf{P}_g + \mathbf{m}_g \otimes \mathbf{c} \quad (6.6)$$

for the interfacial stress, this force balance has the form

$$\int_{\partial Q} \mathbf{C}\nu_{\partial Q} dl + \int_Q \pi da = 0, \quad (6.7)$$

with  $\pi$  the total configurational force on the interface. A consequence of (6.7) is the identity

$$\int_{\partial Q} V_g \mathbf{c} \cdot \nu_g dl = - \int_Q (fK_g V_g + \mathbf{c} \cdot \mathbf{m}_g^\circ + V_g \pi \cdot \mathbf{m}_g) da \quad (6.8)$$

for the working term in the energy balance, where  $g^\circ$  represents differentiation with respect to time following the normal trajectories of the interface (cf. (3.6)).

Using (6.5) and (6.6), we can express (6.3) alternatively as (cf. [25])

$$\begin{aligned} \left\{ \int_R \varepsilon dv + \int_Q \varepsilon da \right\}' &= - \int_{\partial Q} \mathbf{q} \cdot \mathbf{n} da + \int_{\partial R} Q U_{\partial Q} dl + \int_{\partial Q} \mathbf{C}\nu_{\partial Q} \cdot \mathbf{u}_{\partial Q} dl, \\ \left\{ \int_R \eta dv + \int_Q s da \right\}' &\geq - \int_{\partial R} (\mathbf{q}/\theta) \cdot \mathbf{n} da + \int_{\partial Q} (Q/\theta) U_{\partial Q} dl, \end{aligned} \quad (6.9)$$

in which  $Q = \theta s$  is a scalar configurational heating for the interface (cf. (2.37)) and  $\mathbf{u}_{\partial Q} = V_g \mathbf{m}_g + U_{\partial Q} \nu_{\partial Q}$  is the intrinsic velocity of  $\partial Q$ .

The constitutive theory for the interface begins with  $f$ ,  $s$ ,  $\mathbf{c}$ , and  $\pi \cdot \mathbf{m}_g$  as functions of  $\theta$ ,  $\mathbf{m}_g$ , and  $V_g$ ; compatibility with the local dissipation inequality that follows from (6.3) and (6.7) then yields reduced constitutive relations, which, when restricted to linear transition kinetics, have the form

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<sup>19</sup> $\mathbf{C}$  is a surface tensor and hence a linear transformation from tangent vectors into  $\mathbb{R}^3$ ; we extend  $\mathbf{C}$  to  $\mathbb{R}^3$  by requiring that  $\mathbf{C}\mathbf{m}_g = 0$ .

$$\begin{aligned}
 f &= \hat{f}(\theta, m_{\mathcal{S}}), \\
 s &= -\partial_{\theta} \hat{f}(\theta, m_{\mathcal{S}}), \\
 c &= -\partial_{m_{\mathcal{S}}} \hat{f}(\theta, m_{\mathcal{S}}), \\
 \pi \cdot m_{\mathcal{S}} &= [\psi] - b(\theta, m_{\mathcal{S}}) V_{\mathcal{S}},
 \end{aligned} \tag{6.10}$$

with  $b = b(\theta, m_{\mathcal{S}}) \geq 0$ . (More generally,  $b = b(\theta, m_{\mathcal{S}}, V_{\mathcal{S}})$ ; we neglect the dependence of  $b$  on  $V_{\mathcal{S}}$  to be consistent with our assumption (A5), which precludes a nonlinear dependence of the kinetic modulus  $\bar{b}$  of DT on  $\varphi$ . (Cf. footnote 13.))

The integral balance laws and reduced constitutive equations yield the local interface conditions

$$\begin{aligned}
 \theta \{-[\eta] V_{\mathcal{S}} + s^{\circ} - s K_{\mathcal{S}} V_{\mathcal{S}}\} &= -[q] \cdot m + b V_{\mathcal{S}}^2, \\
 [\psi] + f K_{\mathcal{S}} + \operatorname{div}_{\mathcal{S}} c &= b V_{\mathcal{S}},
 \end{aligned} \tag{6.11}$$

where  $K_{\mathcal{S}}$  is the total curvature of  $\mathcal{S}$ ,  $\operatorname{div}_{\mathcal{S}}$  is the surface divergence on  $\mathcal{S}$ , and  $[g]$  denotes the jump in a field  $g$  across  $\mathcal{S}$  ( $\beta$ -side minus  $\alpha$ -side). The relations (6.11) represent the free-boundary conditions of ST; standard approximations reduce (6.11) to the more conventional conditions (1.1) (cf. [22]).

The bulk theory is classical. Constitutive equations are given for each phase  $\gamma = \alpha, \beta$ :

$$\psi = \hat{\psi}^{\gamma}(\theta), \quad \eta = -\partial_{\theta} \hat{\psi}^{\gamma}(\theta), \quad \mathbf{q} = -\mathbf{K}^{\gamma}(\theta) \nabla \theta, \tag{6.12}$$

with  $\hat{\psi}^{\gamma}$  strictly concave and  $\mathbf{K}^{\gamma}$  positive-definite. These with the energy equation in the form

$$\theta \eta^{\circ} = -\operatorname{div} \mathbf{q} \tag{6.13}$$

yield parabolic PDEs to be satisfied in the separate regions occupied by phase  $\alpha$  and phase  $\beta$ .

The production of entropy in this theory consists of bulk contributions  $\Gamma^{\alpha}$  and  $\Gamma^{\beta}$  arising from heat conduction in each phase and an interfacial contribution  $\Gamma_{\mathcal{S}}$  generated by accretion, with

$$\Gamma^{\gamma} = \theta^{-2} \nabla \theta \cdot \mathbf{K}^{\gamma}(\theta) \nabla \theta, \quad \Gamma_{\mathcal{S}} = \theta^{-1} b(\theta, m_{\mathcal{S}}) (V_{\mathcal{S}})^2. \tag{6.14}$$

## 6.2. Preliminary comparison of DT and ST based on intuitive considerations

Proceeding without the benefit of precise assumptions concerning the relative magnitudes of the various quantities appearing in DT, we now compare the basic laws of DT with those of ST. In Section 8, formal asymptotics will be used to make these identifications more rigorous.

Consider DT. Let  $R$  be a stationary control volume. Then, by (3.3), the last of (4.10), and (4.23)<sub>1</sub>,

$$\varphi' \xi \cdot n = -\ell^2 \bar{\psi}(\theta, m) V m \cdot n + V \tau \cdot n. \quad (6.15)$$

Thus (4.10), (4.16), and (4.23) imply that

$$\begin{aligned} -q^{kin} \cdot n + \varphi' \xi \cdot n &= -(\epsilon^{xs} - J) V m \cdot n + V \tau \cdot n, \\ -(q^{kin}/\theta) \cdot n &= -\eta^{xs} V m \cdot n, \end{aligned} \quad (6.16)$$

and, since  $\tau$  is tangent to uniformity surfaces (cf. (4.23)), we may use (3.13) to rewrite the basic laws (2.1) and (2.2) for DT in the form

$$\begin{aligned} \left\{ \int_R (\epsilon^{bu} + \epsilon^{xs}) dv \right\}' - \int_{\partial R} \epsilon^{xs} U dA &= - \int_{\partial R} q^{th} \cdot n da + \int_{\partial R} V \tau \cdot \nu dA - \int_{\partial R} J U dA, \\ \left\{ \int_R (\eta^{bu} + \eta^{xs}) dv \right\}' - \int_{\partial R} \eta^{xs} U dA &\geq - \int_{\partial R} (q^{th}/\theta) \cdot n da, \end{aligned} \quad (6.17)$$

where

$$dA = (n \cdot \nu) da, \quad n \cdot \nu = (1 - (n \cdot m)^2)^{\frac{1}{2}}, \quad (6.18)$$

with  $\nu$ , defined in (3.9), the outward unit normal to the curves  $\mathcal{U}$  that mark the intersection of the uniformity surfaces with  $\partial R$ . The measure  $dA$  represents the area on  $\partial R$  projected onto the plane perpendicular to  $\nu$ . For a thin interfacial layer consisting of closely packed uniformity surfaces,  $dA$  may be written as the product of a measure  $dl$  representing arc length on the curves  $\mathcal{U}$  and a measure representing integration across the layer. Thus the basic laws (6.17) of DT have the same structure as the corresponding laws (6.3) for ST provided:

- (i)  $\epsilon^{bu}$ ,  $\eta^{bu}$ , and  $q^{th}$  are identified with the corresponding bulk fields of ST;
- (ii) the integrals of  $\epsilon^{xs}$ ,  $\eta^{xs}$ , and  $\tau$  across the layer are identified with  $e$ ,  $s$ , and

c of ST;

- (iii)  $V$ ,  $U$ , and  $\nu$  are approximately constant across the layer and identified with  $V_s$ ,  $U_{\partial\mathcal{G}}$ , and  $\nu_{\partial\mathcal{G}}$  of ST;
- (iv) the integrals of  $\varepsilon^{bu}$ ,  $\eta^{bu}$ ,  $q^{th}$ , and  $J$  across the layer are "small"; and
- (v)  $\varepsilon^{xs}$ ,  $\eta^{xs}$ ,  $\tau$ , and  $J$  are "small" away from the layer.

Consider next the working term involving the integral of  $V\tau \cdot \nu dA = V\tau \cdot n da$ . Since  $\tau$  is tangent to uniformity surfaces, (3.8) yields

$$\int_{\partial R} V\tau \cdot n da = \int_R (V \operatorname{div} \tau + \tau \cdot m^\circ) dv. \quad (6.19)$$

Further, by (3.5) and (4.26), we may write the normal configurational force balance (4.28) in the form

$$\psi^{xs} K + \operatorname{div} \tau + m \cdot f^{xs} + \operatorname{div} (Jm) = 0. \quad (6.20)$$

Since  $(\nabla m)^T m = 0$ , (3.8) and last two results yield the power identity

$$\int_{\partial R} V\tau \cdot \nu dA - \int_{\partial R} JU dA = - \int_R (\psi^{xs} KV + \tau \cdot m^\circ + Vf^{xs} \cdot m + J\ell^\circ/\ell) dv, \quad (6.21)$$

which has the same structure as its counterpart (6.8) of ST if, in addition to (i)-(v),

- (vi)  $m$  and  $K$  are approximately constant across the layer and identified with  $m_s$  and  $K_s$  of ST;
- (vii) the integral of  $f^{xs}$  across the layer is identified with  $\pi$  in ST;
- (viii) the integral of  $J(\ell^\circ/\ell)$  across the layer is "small"; and
- (ix)  $f^{xs}$  and  $J(\ell^\circ/\ell)$  are "small" away from the layer.

The conclusions based on (i)-(ix) are reinforced by a comparison of (4.22) and (6.6), which motivates:

- (x) identifying the integral of  $C^{xs}$  across the layer with the interfacial stress  $C$  of ST.

## 7. SCALED EQUATIONS. MATCHED ASYMPTOTICS (PRELIMINARIES)

### 7.1. Scaling

Our goal is a simple scaling with a single small parameter  $\delta$  such that the gradient free-energy and kinetic modulus are  $O(\delta)$ , the bulk free-energy and conductivity are  $O(1)$ , and the exchange energy is  $O(\delta^{-1})$ .

In scaling the basic equations it is most convenient to *label the unscaled fields (all of which, aside from  $\varphi$ , carry dimensions) with an asterisk and to reserve letters without asterisks for dimensionless quantities*. In particular, we now write  $\mathbf{x}^*$  and  $t^*$  for the position vector and the time,  $\theta^*(\mathbf{x}^*, t^*)$  and  $\varphi^*(\mathbf{x}^*, t^*)$  for the temperature and the order parameter,  $\psi^{bu*} = \hat{\psi}^{bu*}(\theta^*, \varphi^*)$  for the bulk free-energy, and so forth. We let  $\mu$  and  $\kappa$  denote scale factors for the bulk and gradient constitutive functions, respectively; for example,

$$\mu = \lambda^* = \varepsilon^{bu*}(\theta_M, 1) - \hat{\varepsilon}^{bu*}(\theta_M, 0), \quad \kappa = \max_m \bar{\psi}^*(\theta_M, m). \quad (7.1)$$

We consider a process and write  $L$  for a characteristic length and  $T$  for a characteristic time associated with that process, we assume that  $\mu$  and  $\kappa$  scale with dimensionless modulus

$$\delta = \kappa / \mu L^2 > 0 \quad (7.2)$$

small, and we introduce the dimensionless independent and dependent variables

$$\mathbf{x} = \mathbf{x}^*/L, \quad t = t^*/T, \quad \theta(\mathbf{x}, t) = \theta^*(\mathbf{x}^*, t^*)/\theta_M, \quad \varphi(\mathbf{x}, t) = \varphi^*(\mathbf{x}^*, t^*), \quad (7.3)$$

and the constitutive functions

$$\begin{aligned} \hat{\psi}^{bu}(\theta, \varphi) &= \hat{\psi}^{bu*}(\theta^*, \varphi^*)/\mu, \\ \bar{\Psi}(\varphi) &= \delta \bar{\Psi}^*(\varphi^*)/\mu, \\ \bar{\psi}(\theta, m) &= \bar{\psi}^*(\theta^*, m)/\delta \mu L^2, \\ \bar{\eta}(\theta, m) &= -\partial_\theta \bar{\psi}(\theta, m) = \theta_M \bar{\eta}^*(\theta^*, m)/\delta \mu L^2, \\ K(\theta, \varphi) &= \theta_M T K^*(\theta^*, \varphi^*)/\mu L^2, \\ \bar{b}(\theta, m) &= \bar{b}^*(\theta^*, m)/\delta \mu T, \end{aligned} \quad (7.4)$$

where the quantities without asterisks in (7.3) and (7.4) are of  $O(1)$  in  $\delta$ . This scaling yields

$$\varepsilon^{bu*} = \mu \varepsilon^{bu}, \quad \eta^{bu*} = \mu \eta^{bu} / \theta_M, \quad \psi^{xs*} = \mu \psi^{xs}, \quad \varepsilon^{xs*} = \mu \varepsilon^{xs}, \quad (7.5)$$

where

$$\begin{aligned} \varepsilon^{bu} &= \hat{\varepsilon}^{bu}(\theta, \varphi) = \hat{\psi}^{bu}(\theta, \varphi) - \theta \partial_\theta \hat{\psi}^{bu}(\theta, \varphi), \\ \eta^{bu} &= \hat{\eta}^{bu}(\theta, \varphi) = -\partial_\theta \hat{\psi}^{bu}(\theta, \varphi), \\ \psi^{xs} &= \delta^{-1} \Psi(\varphi) + \frac{1}{2} \delta \ell^2 \bar{\psi}(\theta, m), \\ \varepsilon^{xs} &= \delta^{-1} \Psi(\varphi) + \frac{1}{2} \delta \ell^2 \{ \bar{\psi}(\theta, m) - \theta \partial_\theta \bar{\psi}(\theta, m) \}, \\ \eta^{xs} &= -\frac{1}{2} \delta \ell^2 \partial_\theta \bar{\psi}(\theta, m), \end{aligned} \quad (7.6)$$

and

$$\mathbf{q}^{th} = -K(\theta, \varphi) \nabla \theta, \quad \tau = -\frac{1}{2} \delta \ell^2 \delta \partial_m \bar{\psi}(\theta, m), \quad J = \delta^{-1} \Psi(\varphi) - \frac{1}{2} \delta \ell^2 \bar{\psi}(\theta, m). \quad (7.7)$$

The basic laws (6.17) were written for the original quantities, which were dimensional, so that the terms in (6.13) now carry asterisks. If we use (7.3) - (7.5) to convert these laws to nondimensional form we find, with the aid of the relations  $V^* = LV/T$  and  $U^* = LU/T$ , that, after a common factor of  $\mu L^3/T$  has been cancelled from each term, (6.17) remain valid as is (i.e., without asterisks), but with the underlying fields given by (7.6) and (7.7).

## 7.2. Scaled PDEs

Granted our scaling, the PDEs (5.1) have the form

$$\begin{aligned} \theta \hat{\eta}^{bu}(\theta, \varphi)^* + \frac{1}{2} \delta \theta \{ (\ell^2 \bar{\eta}(\theta, m))^* - \text{div}(\bar{\eta}(\theta, m) \varphi^* \nabla \varphi) \} = \\ \text{div}(K(\theta, \varphi) \nabla \theta) + \delta \bar{b}(\theta, m) (\varphi^*)^2, \\ \delta \bar{b}(\theta, m) \varphi^* = \delta \text{div} \{ \bar{\psi}(\theta, m) \nabla \varphi + \frac{1}{2} \ell \partial_m \bar{\psi}(\theta, m) \} + \\ - \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) - \delta^{-1} \Psi'(\varphi) + \frac{1}{2} \delta \bar{\eta}(\theta, m) \nabla \varphi \cdot \nabla \theta, \end{aligned} \quad (7.8)$$

while (5.2) and (5.3) can be written as

$$\begin{aligned}
 \theta \hat{\eta}^{bu}(\theta, \varphi) + \frac{1}{2} \delta \theta \{ \ell^2 \bar{\eta}(\theta, m)^\circ + \frac{1}{2} \bar{\eta}(\theta, m) (\ell^2)^\circ - \ell^2 \bar{\eta}(\theta, m) K V \} = \\
 \text{div}(K(\theta, \varphi) \nabla \theta) + \delta \ell^2 \bar{b}(\theta, m) V^2, \\
 \ell \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) + \delta^{-1} \{ \Psi(\varphi) + \frac{1}{2} \delta^2 \ell^2 \bar{\psi}(\theta, m) \} K - \frac{1}{2} \delta \text{div} \{ \ell^2 \partial_m \bar{\psi}(\theta, m) \} \\
 + \delta^{-1} \text{div} \{ (\Psi(\varphi) - \frac{1}{2} \delta^2 \ell^2 \bar{\psi}(\theta, m)) m \} = \delta \ell^2 \bar{b}(\theta, m) V.
 \end{aligned} \tag{7.9}$$

Our goal is to obtain the asymptotic form of the theory for small  $\delta$ . In this regard, the PDEs (7.8) are convenient away from the layer, but within the layer (7.9) are generally more useful, as they contain explicit information regarding the geometric structure of the layer.

### 7.3. Equivalent sharp-interface constitutive equations

In Sections 8 and 9 we will show that the diffuse-interface theory is asymptotic to the sharp-interface theory defined by the following constitutive functions:

#### bulk constitutive functions

$$\begin{aligned}
 \hat{\psi}^\alpha(\theta) &= \hat{\psi}^{bu}(\theta, 0) & \hat{\psi}^\beta(\theta) &= \hat{\psi}^{bu}(\theta, 1), \\
 \hat{\eta}^\alpha(\theta) &= \hat{\eta}^{bu}(\theta, 0), & \hat{\eta}^\beta(\theta) &= \hat{\eta}^{bu}(\theta, 1), \\
 \hat{\varepsilon}^\alpha(\theta) &= \hat{\varepsilon}^{bu}(\theta, 0), & \hat{\varepsilon}^\beta(\theta) &= \hat{\varepsilon}^{bu}(\theta, 1), \\
 K^\alpha(\theta) &= K(\theta, 0), & K^\beta(\theta) &= K(\theta, 1),
 \end{aligned} \tag{7.10}$$

#### interface constitutive functions

$$\begin{aligned}
 \hat{f}(\theta, m) &= (\bar{\psi}(\theta, m))^{\frac{1}{2}} \int_0^1 (2\Psi(\varphi))^{\frac{1}{2}} d\varphi, \\
 \hat{s}(\theta, m) &= -\partial_\theta \hat{f}(\theta, m), \\
 \hat{c}(\theta, m) &= -\partial_m \hat{f}(\theta, m), \\
 \hat{e}(\theta, m) &= \hat{f}(\theta, m) - \theta \partial_\theta \hat{f}(\theta, m), \\
 b(\theta, m) &= \bar{b}(\theta, m) \hat{f}(\theta, m) / \bar{\psi}(\theta, m).
 \end{aligned} \tag{7.11}$$

The bulk relations are motivated by our previous discussion and are consistent with the bulk thermodynamic requirements  $\hat{\eta}^\nu(\theta) = -\partial_\theta \hat{\psi}^\nu(\theta)$ ,  $\hat{\varepsilon}^\nu(\theta) = \hat{\psi}^\nu(\theta) + \theta \partial_\theta \hat{\psi}^\nu(\theta)$ . Our choice of interfacial free-energy  $\hat{f}(\theta, m)$  and kinetic modulus  $b(\theta, m)$ , while not at all obvious, will be clear from the ensuing

asymptotics; given  $\hat{f}(\theta, m)$ , the choices of  $\hat{s}(\theta, m)$ ,  $\hat{c}(\theta, m)$ , and  $\hat{e}(\theta, m)$  are predicated upon (6.10)<sub>1-3</sub> and (6.5)<sub>2</sub>.

An essential ingredient in the conversion of gradient moduli in the diffuse interface theory to interfacial quantities in the sharp interface theory is the function

$$F(\theta, m) = (\bar{\psi}(\theta, m))^{-\frac{1}{2}} \int_0^1 (2\Psi(\varphi))^{\frac{1}{2}} d\varphi; \quad (7.12)$$

indeed

$$\begin{aligned} \hat{f}(\theta, m) &= F(\theta, m) \bar{\psi}(\theta, m); \\ \hat{s}(\theta, m) &= -\frac{1}{2} F(\theta, m) \partial_\theta \bar{\psi}(\theta, m), \\ \hat{c}(\theta, m) &= -\frac{1}{2} F(\theta, m) \partial_m \bar{\psi}(\theta, m), \\ \hat{e}(\theta, m) &= F(\theta, m) \left\{ \bar{\psi}(\theta, m) - \frac{1}{2} \theta \partial_\theta \bar{\psi}(\theta, m) \right\}, \\ b(\theta, m) &= F(\theta, m) \bar{b}(\theta, m). \end{aligned} \quad (7.13)$$

We will refer to  $F(\theta, m)$  as the *conversion modulus*; the dimensional counterpart of  $F(\theta, m)$  carries units of (length)<sup>-1</sup>.

Note that, since  $\bar{\eta} = -\partial_\theta \bar{\psi}$  and  $\bar{\epsilon} = \bar{\psi} + \theta \bar{\eta}$ , the conversions for entropy and internal energy are  $\hat{s} = \frac{1}{2} F \bar{\eta}$  and  $\hat{e} = F(\bar{\epsilon} + \frac{1}{2} \theta \bar{\eta})$ ; thus, surprisingly, the interfacial internal energy depends on the gradient moduli for both internal energy and entropy.

#### 7.4. Expansions

We assume that the process under consideration consists, at each time  $t$ , of an interfacial layer  $\mathcal{L}(t, \delta)$  and regions  $\mathcal{P}^\alpha(t, \delta)$  and  $\mathcal{P}^\beta(t, \delta)$  composed, respectively, of bulk material in phase  $\alpha$  ( $\varphi \approx 0$ ) and bulk material in phase  $\beta$  ( $\varphi \approx 1$ ). We assume that  $\mathcal{L}(t, \delta)$  contains the set of  $\mathbf{x}$  with  $\varphi(\mathbf{x}, t)$  in the spinodal interval for  $\Psi$  (cf. Section 4.1), and that the thickness of  $\mathcal{L}(t, \delta)$  tends to zero with  $\delta$ ; precisely, we assume that the limit

$$\mathcal{S}(t) = \mathcal{L}(t, 0+) \quad (7.14)$$

exists with  $\mathcal{S}(t)$  a smooth surface contained in  $\mathcal{L}(t, \delta)$  for all small  $\delta$ .

We focus on a stationary control volume  $R$  that—over the course of some time interval—contains material from both phases, and we let

$$G(t) = R \cap \delta(t), \quad R^\gamma(t) = R \cap \mathcal{P}^\gamma(t, 0+), \quad (\partial R)^\gamma(t) = \partial R \cap R^\gamma(t), \quad \gamma = \alpha, \beta. \quad (7.15)$$

When we compare the asymptotic form of the basic laws for DT with those of ST,  $\delta$  will play the role of the interface,  $G$  the portion of the interface in  $R$ , and  $R^\gamma(t)$  and  $(\partial R)^\gamma$  the portions of  $R$  and  $\partial R$  occupied by phase- $\gamma$  material.

The diffuse nature of DT precludes a definitive boundary between the interfacial layer and the bulk regions, and for that reason  $R \cap \mathcal{L}$  is not presumed disjoint from  $R \cap \mathcal{P}^\gamma$  ( $\gamma = \alpha, \beta$ ). In the asymptotics we will consider inner and outer expansions of the basic fields, with the outer expansion valid in the regions  $R \cap \mathcal{P}^\gamma$ , the inner expansion in  $R \cap \mathcal{L}$ ; the regions  $(R \cap \mathcal{L}) \cap (R \cap \mathcal{P}^\gamma)$  of overlap will represent sets in which the inner and outer expansions agree, a requirement that gives rise to matching conditions.<sup>20</sup> Of course,  $R$  is the union of  $R \cap \mathcal{L}$  and the regions  $R \cap \mathcal{P}^\gamma$ , and therefore

$$R \setminus \mathcal{L} \subset R \cap (\mathcal{P}^\alpha \cup \mathcal{P}^\beta). \quad (7.16)$$

We write  $d(\mathbf{x}, t)$  for the signed distance between  $\mathbf{x}$  and  $G(t)$  with  $d(\mathbf{x}, t) < 0$  in  $R^\alpha(t)$  and  $d(\mathbf{x}, t) > 0$  in  $R^\beta(t)$ . Then

$$\mathbf{m}_\delta = \nabla d, \quad \mathbf{V}_\delta = -\dot{d} \quad (7.17)$$

represent a unit normal and corresponding normal velocity for  $\delta$ . It is convenient to define a function  $\xi(\mathbf{x}, t)$  through

$$\xi(\mathbf{x}, t) = \mathbf{x} - d(\mathbf{x}, t)\mathbf{m}_\delta(\mathbf{x}, t), \quad (7.18)$$

so that  $\xi(\mathbf{x}, t) \in \delta(t)$ . We assume that  $d(\mathbf{x}, t)$  is smooth within  $R \cap \mathcal{L}(t, \delta)$ ; then, for fixed  $t$ , the mapping  $\mathbf{x} \mapsto (\xi(\mathbf{x}, t), d(\mathbf{x}, t))$  is one-to-one. Further,  $\mathbf{m}_\delta$  and  $\mathbf{V}_\delta$  are well defined and, as functions of  $(d, \xi)$ , are independent of  $d$ :  $\mathbf{m}_\delta = \mathbf{m}_\delta(\xi, t)$ ,  $\mathbf{V}_\delta = \mathbf{V}_\delta(\xi, t)$ .

Within the layer we stretch the coordinate normal to  $G(t)$  by letting

$$\mathbf{r}(\mathbf{x}, t) = \delta^{-1}d(\mathbf{x}, t), \quad (7.19)$$

and, consistent with this, we assume that within  $R$  the thickness  $h(\delta)$  of  $\mathcal{L}(t, \delta)$  approaches zero with  $\delta$ , but at a slightly slower rate; precisely, we require that

$$h(\delta) \rightarrow 0, \quad \delta^{-1}h(\delta) \rightarrow +\infty, \quad \delta^{-1}h^2(\delta) \rightarrow 0 \quad (7.20)$$

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<sup>20</sup>Cf. the discussion of Penrose and Fife [31], Section 3.

as  $\delta \rightarrow 0$ , so that the stretched coordinate  $r$  varies from  $-\infty$  to  $+\infty$  within the layer.

For the fields  $u = \theta$  and  $u = \varphi$  we introduce an *outer expansion*

$$u(\mathbf{x}, t) = \tilde{u}_0(\mathbf{x}, t) + \delta \tilde{u}_1(\mathbf{x}, t) + O(\delta^2) \quad (7.21)$$

assumed valid in  $R \cap \mathcal{P}^\alpha(t, \delta)$  and  $R \cap \mathcal{P}^\beta(t, \delta)$ , and an *inner expansion*

$$u(\mathbf{x}, t) = u_0(r(\mathbf{x}, t), \xi(\mathbf{x}, t), t) + \delta u_1(r(\mathbf{x}, t), \xi(\mathbf{x}, t), t) + O(\delta^2) \quad (7.22)$$

assumed valid within  $R \cap \mathcal{L}(t, \delta)$ . Defining  $\tilde{u}_0^\pm(\xi, t)$  and  $u_0^\pm(\xi, t)$  on  $\mathcal{G}(t)$  by

$$\tilde{u}_0^\pm(\xi(\mathbf{x}, t), t) = \lim_{r(\mathbf{x}, t) \rightarrow 0^\pm} \tilde{u}_0(\mathbf{x}, t), \quad u_0^\pm(\xi(\mathbf{x}, t), t) = u_0(\pm\infty, \xi(\mathbf{x}, t), t), \quad (7.23)$$

and writing  $[g] = g^+ - g^-$ , we then have the  $O(1)$  matching conditions

$$\tilde{u}_0^\pm = u_0^\pm, \quad [\tilde{u}_0] = [u_0]. \quad (7.24)$$

We write  $\nabla_{\mathcal{S}}$  for the gradient on  $\mathcal{S}$ ; in the variables  $(\xi, r)$ , the derivative with respect to  $\xi$  holding  $r$  fixed may be identified with  $\nabla_{\mathcal{S}}$ . For  $\Phi$  a scalar function and  $\mathbf{v}$  a vector function,  $\nabla_{\mathcal{S}}\Phi = P_{\mathcal{S}}\nabla\Phi$ ,  $\nabla_{\mathcal{S}}\mathbf{v} = (\nabla\mathbf{v})P_{\mathcal{S}}$ , where  $P_{\mathcal{S}}$  is defined by (6.2)<sub>1</sub>. In particular, by (7.17),  $(\nabla m_{\mathcal{S}})m_{\mathcal{S}} = (\nabla\nabla d)\nabla d = \frac{1}{2}\nabla(|\nabla d|^2) = 0$ , so that the curvature tensor  $L_{\mathcal{S}} = L_{\mathcal{S}}(\xi, t) = -\nabla_{\mathcal{S}}m_{\mathcal{S}}$  for  $\mathcal{S}$  is also given by

$$L_{\mathcal{S}} = -\nabla m_{\mathcal{S}}. \quad (7.25)$$

Further, by (7.17) and (7.18),

$$\nabla\xi = P_{\mathcal{S}} - dL_{\mathcal{S}}; \quad (7.26)$$

and therefore

$$\begin{aligned} \nabla\Phi &= \delta^{-1}(\partial_r\Phi)m_{\mathcal{S}} + (1 - dL_{\mathcal{S}})(\nabla_{\mathcal{S}}\Phi), \\ \nabla\mathbf{v} &= \delta^{-1}(\partial_r\mathbf{v})\otimes m_{\mathcal{S}} + (\nabla_{\mathcal{S}}\mathbf{v})(1 - dL_{\mathcal{S}}). \end{aligned} \quad (7.27)$$

### 7.5. Preliminary estimates

Within the layer  $|d| \leq 2h(\delta)$ ; thus

$$d = O(h(\delta)), \quad (7.28)$$

and, appealing to (7.22) and (7.27), we have the estimates

$$\begin{aligned} u^* &= -\delta^{-1} \nabla_{\delta} \partial_r u_0 + O(1), \\ \nabla u &= \delta^{-1} (\partial_r u_0) m_{\delta} + \nabla_{\delta} u_0 + (\partial_r u_1) m_{\delta} + O(h(\delta)), \\ \nabla \nabla u &= \delta^{-2} (\partial_r \partial_r u_0) m_{\delta} \otimes m_{\delta} + O(\delta^{-1}) \end{aligned} \quad (7.29)$$

for  $u = \varphi$  and  $u = \theta$ . (Some care is needed in establishing the first estimate. The partial derivative of  $u(r, \xi, t)$  with respect to  $t$  is not defined, as  $\xi \in \delta(t)$ , but we can still write  $u^*(r, \xi, t)$  as  $\delta^{-1}(\partial_r u)$  plus an  $O(1)$  term; namely the derivative of  $u(r, \xi(x, t), t)$  with respect to  $t$  holding  $x$  and  $r$  fixed.)

Using the outer expansions of  $\theta$  and  $\varphi$  in (7.8)<sub>2</sub>, we find that  $\tilde{\varphi}_0$  must satisfy

$$\Psi'(\tilde{\varphi}_0) = 0, \quad (7.30)$$

and hence must be constant in  $R \cap \mathcal{P}^{\alpha}$  and  $R \cap \mathcal{P}^{\beta}$ . By hypothesis, the constant values of  $\tilde{\varphi}_0$  on either side of the layer lie outside the spinodal; we therefore conclude from (4.3) and (7.30) that

$$\tilde{\varphi}_0 = 0 \text{ in } R \cap \mathcal{P}^{\alpha}, \quad \tilde{\varphi}_0 = 1 \text{ in } R \cap \mathcal{P}^{\beta}, \quad (7.31)$$

and  $\Psi(\tilde{\varphi}_0) = 0$ ; thus and by (7.6), (7.7), and (7.30), we have the following estimates in  $R \cap \mathcal{P}^{\alpha}$  and  $R \cap \mathcal{P}^{\beta}$ :

$$\Psi(\varphi) = O(\delta^2), \quad \psi^{x_s}, \varepsilon^{x_s}, \eta^{x_s}, \tau, J = O(\delta). \quad (7.32)$$

Further, by virtue of (7.31), the matching condition (7.24) requires that  $\varphi_0$  satisfy

$$\varphi_0 \rightarrow 0 \text{ as } r \rightarrow -\infty, \quad \varphi_0 \rightarrow 1 \text{ as } r \rightarrow +\infty. \quad (7.33)$$

A tacit assumption of the analysis presented thus far is that  $\nabla \varphi$  not vanish within  $\mathcal{L}$ , for otherwise  $m$  and  $V$  would be undefined therein. Bearing in mind (7.33),  $\varphi_0$  must therefore be strictly increasing on  $(-\infty, +\infty)$ , so that

$$\ell = \delta^{-1} (\partial_r \varphi_0) + O(1) > 0; \quad (7.34)$$

we may therefore conclude from (3.3) that

$$\mathbf{m} = \mathbf{m}_\delta + O(\delta), \quad \mathbf{V} = \mathbf{V}_\delta + O(\delta), \quad (7.35)$$

and hence, by (3.4) and (6.2)<sub>1</sub>, that

$$\mathbf{P} = \mathbf{P}_\delta + O(\delta). \quad (7.36)$$

Our next step will be to establish the estimates

$$\mathbf{L} = \mathbf{L}_\delta + O(h(\delta)), \quad \mathbf{m}^\circ = \mathbf{m}_\delta^{\circ(\delta)} + O(h(\delta)), \quad (7.37)$$

with  $\mathbf{L}_\delta$  and  $\mathbf{L}$ , respectively, the curvature tensors for  $\delta$  and for uniformity surfaces,  $\mathbf{m}^\circ$  the normal time-derivative of  $\mathbf{m}$  following uniformity surfaces, and  $\mathbf{m}_\delta^{\circ(\delta)} = -\nabla_\delta \mathbf{V}_\delta$  the normal time-derivative of  $\mathbf{m}_\delta$  following  $\delta$ . A consequence of (7.37)<sub>1</sub> is the estimate

$$\mathbf{K} = \mathbf{K}_\delta + O(h(\delta)). \quad (7.38)$$

To verify (7.37) we note first that, since  $\partial_r \mathbf{m}_\delta = 0$  and  $\partial_r \mathbf{V}_\delta = 0$ , (7.24) with  $\mathbf{v} = \mathbf{m}_\delta$  and  $\Phi = \mathbf{V}_\delta$  yields

$$-\nabla d^\circ = \nabla \mathbf{V}_\delta = (1 - d\mathbf{L}_\delta)(\nabla_\delta \mathbf{V}_\delta) = \nabla_\delta \mathbf{V}_\delta + O(h(\delta)) = -\mathbf{m}_\delta^{\circ(\delta)} + O(h(\delta)). \quad (7.39)$$

On the other hand, by (7.27)<sub>2</sub> with  $\mathbf{v} = \nabla \varphi$  and (7.25),

$$\mathbf{P}_\delta(\nabla \nabla \varphi) \mathbf{P}_\delta = -\delta^{-1}(\partial_r \varphi) \mathbf{L}_\delta + O(\delta^{-1}h(\delta)). \quad (7.40)$$

The result (7.37)<sub>1</sub> follows from (3.8)<sub>1</sub>, (7.38), (7.36), and (7.40).

Consider (7.37)<sub>2</sub>. In view of (3.3), (3.7)<sub>1</sub>, and (3.8),

$$\mathbf{m}^\circ = \ell^{-2} \mathbf{P} \{ \ell \nabla \varphi^\circ - \varphi^\circ (\nabla \nabla \varphi) \mathbf{m} \}, \quad (7.41)$$

and, by (7.27)<sub>1</sub>,

$$\begin{aligned} \mathbf{P}_\delta(\nabla \nabla \varphi) \mathbf{m}_\delta &= \delta^{-1}(\nabla_\delta \partial_r \varphi) + O(\delta^{-1}h(\delta)), \\ \mathbf{P}_\delta \nabla \varphi^\circ &= \delta^{-1}(\partial_r \varphi) \nabla d^\circ + \delta^{-1}(\nabla_\delta \partial_r \varphi) d^\circ + O(\delta^{-1}h(\delta)). \end{aligned} \quad (7.42)$$

Since  $V = -\varphi'/\ell$  and  $d' = -V_{,\delta}$ , we may use (7.39)<sub>2</sub>, (7.35)<sub>2</sub>, and (7.42)<sub>2</sub> to conclude that

$$P_{\delta}\nabla\varphi' = \delta^{-1}(\partial_r\varphi)m_{\delta}^{\circ(\delta)} + \delta^{-1}(\nabla_{\delta}\partial_r\varphi)\ell^{-1}\varphi' + O(\delta^{-1}h(\delta)); \quad (7.43)$$

(7.34), (7.35), (7.42)<sub>1</sub>, and (7.43) yield the desired estimate (7.37)<sub>2</sub>.

Two additional estimates that we will find useful are

$$\ell^{\circ}/\ell = O(1), \quad \Phi^{\circ} = \Phi^{\circ(\delta)} + O(\delta), \quad (7.44)$$

provided  $\Phi$  is independent of  $r$ . To verify the first of (7.44), we precede as in the proof of (7.37)<sub>2</sub> using, in place of (7.41), the identity

$$\ell^{\circ}/\ell = \ell^{-2}m \cdot \{ \ell\nabla\varphi' - \varphi'(\nabla\nabla\varphi)m \} \quad (7.45)$$

(cf. (3.3)<sub>2</sub> and (3.8)<sub>4</sub>). The second of (7.44) follows from (7.35) and the identities

$$\Phi^{\circ} = \Phi' + Vm \cdot \nabla\Phi, \quad \Phi^{\circ(\delta)} = \Phi' + V_{,\delta}m_{\delta} \cdot \nabla\Phi. \quad (7.46)$$

Finally, we assume that  $\delta(t)$  crosses  $\partial R$  transversely; then, granted smoothness,

$$|m_{\delta} \cdot n| \text{ is bounded away from } 1 \quad (7.47)$$

and the outward unit normal  $\nu_{\partial Q}$  to  $\partial Q$  and the scalar normal velocity  $U_{\partial Q}$  of  $\partial Q$  in the direction  $\nu_{\partial Q}$  are well defined and, in fact, given by the relations (6.2). Further, in view of the discussion in the paragraph containing (7.47), the fields  $\nu$  and  $U$  defined in (3.9) and (3.13) and used in (6.17) are well defined in  $\partial R \cap \mathcal{L}$  and there satisfy

$$\nu(\mathbf{x},t) = \nu_{\partial Q}(\xi(\mathbf{x},t),t) + O(\delta), \quad U(\mathbf{x},t) = U_{\partial Q}(\xi(\mathbf{x},t),t) + O(\delta). \quad (7.48)$$

### 7.6. Sharper estimates

The coordinates  $(r, \xi, t)$  are not convenient, as  $\xi$  must lie on  $\delta(t)$ , a constraint that precludes differentiation with respect to  $t$  holding  $\xi$  fixed. This difficulty may be circumvented by fixing a time  $\check{t}$  and using  $\check{\xi} \in \delta(\check{t})$  as reference coordinates for the interface. Precisely, we define a function  $\mathbf{z}(\check{\xi}, t)$  that associates with each time  $t$  and each  $\check{\xi} \in \delta(\check{t})$  the point  $\xi = \mathbf{z}(\check{\xi}, t)$  on  $\delta(t)$  obtained, at time  $t$ , by following the normal trajectory emanating from  $\check{\xi}$  at  $\check{t}$ . Then, defining  $\mathbf{v}(\xi, t) = V_{,\delta}m_{\delta}$ ,  $\mathbf{z}(\check{\xi}, t)$  is

the solution of the system

$$\partial_t z(\check{\xi}, t) = v(z(\check{\xi}, t), t), \quad z(\check{\xi}, \check{t}) = \check{\xi}. \quad (7.49)$$

For our purposes it suffices to construct the function  $z$  locally in the variables  $(\xi, t)$ . Granted this and granted sufficient smoothness,  $\xi = z(\check{\xi}, t)$  will be, for  $t$  fixed, smoothly invertible in  $\check{\xi}$ ; we write  $\check{\xi} = \check{z}(\xi, t)$  to describe the corresponding inverse function.

Let  $\mathcal{T}(\xi, t)$  denote the tangent plane to  $\mathcal{S}(t)$  at  $\xi \in \mathcal{S}(t)$ . We write  $\check{V}$  for the surface gradient on  $\mathcal{S}(t)$ . Then  $\check{V}z(\check{\xi}, t)$  is an invertible linear transformation from  $\mathcal{T}(\check{\xi}, \check{t})$  onto  $\mathcal{T}(\xi, t)$ ,  $\xi = z(\check{\xi}, t)$ ; and  $\nabla_{\mathcal{S}} \check{z}(\xi, t) = \{\check{V}z(\check{\xi}, t)\}^{-1}$ .

Finally, using the function  $z$  we can express any function  $\Phi(r, \xi, t)$  as a function  $\check{\Phi}(r, \check{\xi}, t)$ :

$$\check{\Phi}(r, \check{\xi}, t) = \Phi(r, z(\check{\xi}, t), t). \quad (7.50)$$

Since  $\xi$  can be considered a function of  $(x, t)$  through (7.18), so also can  $\check{\xi}$ :

$$\check{\xi}(x, t) = \check{z}(\xi(x, t), t). \quad (7.51)$$

Using the functions  $\xi(x, t)$  and  $\check{\xi}(x, t)$  we can define, via (3.6), the time-derivatives  $\xi^\circ$  and  $\check{\xi}^\circ$  following the normal trajectories of uniformity surfaces. By (3.6), (7.17), (7.18), (7.26), and (7.51),

$$\begin{aligned} \xi^\circ &= V_{\mathcal{S}} m_{\mathcal{S}} - d(m_{\mathcal{S}})' + VP_{\mathcal{S}} m - dVL_{\mathcal{S}} m, \\ \check{\xi}^\circ &= (\nabla_{\mathcal{S}} \check{z}) \xi^\circ + \partial_t \check{z}. \end{aligned} \quad (7.52)$$

Thus, since  $(\nabla_{\mathcal{S}} \check{z}) \xi^\circ = (\nabla_{\mathcal{S}} \check{z}) P_{\mathcal{S}} \xi^\circ$ , and, since  $m_{\mathcal{S}}$  is independent of  $r$  so that  $(m_{\mathcal{S}})' = O(1)$ , we may use (7.28) and (7.36) to conclude that

$$\xi^\circ = V_{\mathcal{S}} m_{\mathcal{S}} + O(h(\delta)), \quad \check{\xi}^\circ = O(h(\delta)). \quad (7.53)$$

It is convenient to extend the normal time-derivative  $\Phi^{\circ(\mathcal{S})}$  following  $\mathcal{S}$  to functions  $\Phi(r, \xi, t)$  that depend nontrivially on  $r$ , by considering this derivative as a partial derivative holding  $r$  fixed; in view of the transformation (7.50) and the definition of  $z$ :

$$\Phi^{\circ(\mathcal{S})}(r, \xi, t) = \partial_t \check{\Phi}(r, \check{\xi}, t), \quad \check{\xi} = \check{z}(\xi, t). \quad (7.54)$$

The derivative  $\Phi^\circ$  following uniformity surfaces is more complicated:

$$\Phi^\circ = \delta^{-1}(\partial_r \check{\Phi})d^\circ + (\check{\nabla} \check{\Phi}) \cdot \check{\xi}^\circ + \partial_t \check{\Phi}. \quad (7.55)$$

As we shall see, if  $\Phi$  is an  $O(1)$  field, then (7.55) leads to the estimate

$$\Phi^\circ = \partial_t \check{\Phi} - (\partial_r \check{\Phi})(\partial_r \check{\varphi}_0)^{-1}(\partial_t \check{\varphi}_0) + O(h(\delta)), \quad (7.56)$$

so that, in particular,  $\Phi^\circ = O(1)$ .

Our verification of (7.56) begins with the estimates

$$\begin{aligned} \ell &= \delta^{-1}(\partial_r \varphi_0)\{1 + \delta(\partial_r \varphi_0)^{-1}(\partial_r \varphi_1)\} + O(\delta^2), \\ m &= m_\delta + \delta(\partial_r \varphi_0)^{-1}(\nabla_\delta \varphi_0) + O(\delta h(\delta)), \\ V &= V_\delta - \delta(\partial_r \check{\varphi}_0)^{-1}(\partial_t \check{\varphi}_0) + O(\delta h(\delta)). \end{aligned} \quad (7.57)$$

The first of (7.57) follows from (7.27)<sub>1</sub>, while (7.57)<sub>1</sub> and (7.27)<sub>1</sub> yield (7.57)<sub>2</sub>. Note that, as a consequence of (7.57)<sub>2</sub>,

$$m \cdot m_\delta = 1 + O(\delta^2). \quad (7.58)$$

To establish (7.57)<sub>3</sub>, we note that, by (7.58) and since  $d^\circ = d^\circ + Vm \cdot \nabla d$ ,

$$d^\circ = (m \cdot m_\delta)V - V_\delta = V - V_\delta + O(\delta^2). \quad (7.59)$$

Next, since  $\varphi^\circ$  represents a time derivative following level sets of  $\varphi$ ,  $\varphi^\circ = 0$ ; thus

$$0 = \varphi^\circ = \delta^{-1}(\partial_r \check{\varphi})d^\circ + (\check{\nabla} \check{\varphi}) \cdot \check{\xi}^\circ + \partial_t \check{\varphi}; \quad (7.60)$$

(7.53)<sub>2</sub>, (7.59), and (7.60) yield (7.57)<sub>3</sub>.

The estimate (7.56) follows from (7.55), (7.53)<sub>2</sub>, (7.57)<sub>3</sub>, and (7.59).

Next, by (7.27)<sub>1</sub>,

$$\ell^2 = \delta^{-2}(\partial_r \varphi)^2 + O(1) = \delta^{-2}(\partial_r \varphi_0)^2 + 2\delta^{-1}(\partial_r \varphi_0)(\partial_r \varphi_1) + O(1) \quad (7.61)$$

and, in view of the comment following (7.56),

$$(\ell^2)^\circ = \delta^{-2}\{(\partial_r \varphi_0)^2\}^\circ + O(\delta^{-1}). \quad (7.62)$$

### 7.6. Asymptotic continuity of temperature across the interface

We now show that:

$$[\theta] = O(\delta). \quad (7.63)$$

Consider the energy balance (7.9)<sub>1</sub> and restrict attention to the layer. By (7.27) and (7.56), for  $O(1)$  fields  $\mathbf{v}$  and  $\bar{\Phi}$ ,  $\text{div} \mathbf{v} = \delta^{-1}(\partial_r \mathbf{v}) \cdot \mathbf{m}_g + O(1)$  and  $\bar{\Phi}^\circ = O(1)$ . Thus, since  $\ell = O(\delta^{-1})$ , while  $\mathbf{m}$ ,  $V$ ,  $K$ , and  $\ell^\circ/\ell$  are  $O(1)$  (cf. Section 7.5), we may use the inner expansions for  $\theta$  and  $\varphi$  in conjunction with (7.29) to conclude that  $\partial_r \{k(\theta_0, \varphi_0, \mathbf{m}_g) \partial_r \theta_0\} = 0$ , where  $k(\theta_0, \varphi_0, \mathbf{m}_g) = \mathbf{m}_g \cdot \mathbf{K}(\theta_0, \varphi_0) \mathbf{m}_g$ . Thus

$$k(\theta_0, \varphi_0, \mathbf{m}_g) \partial_r \theta_0 = \bar{\Phi} \quad (7.64)$$

with  $\bar{\Phi}$  independent of  $r$ . Assume that  $\bar{\Phi} > 0$ . By (A6),  $\mathbf{K}(\theta_0, \varphi_0)$  is positive definite; thus  $k(\theta_0, \varphi_0, \mathbf{m}_g) > 0$  and  $\partial_r \theta_0 > 0$ . It is tacit that  $\theta_0(r, \xi, t)$  and  $\varphi_0(r, \xi, t)$  are bounded functions of  $r$  (cf. (7.23)). Thus so also is  $k(\theta_0, \varphi_0, \mathbf{m}_g)$  and we may conclude from (7.23) that the integral of the left side of (7.64) from  $r = -\infty$  to  $r = +\infty$  is bounded by the maximum of  $k(\theta_0, \varphi_0, \mathbf{m}_g)$  times  $[\theta_0]$ . But the same integral applied to the right side of (7.64) is  $+\infty$ , as  $\bar{\Phi}$  independent of  $r$ . A similar contradiction arises when  $\bar{\Phi} < 0$ . Thus  $\bar{\Phi} = 0$  and

$$\partial_r \theta_0 = 0, \quad (7.65)$$

whereby  $\theta_0$  must be independent of  $r$ . Therefore,  $[\theta_0] = [\bar{\theta}_0] = 0$ , and (7.63) follows.

By virtue of (7.65), we note that

$$\theta^\circ = (\theta_0)^\circ(\delta) + O(h(\delta)) = \theta^\circ(\delta) + O(h(\delta)). \quad (7.66)$$

### 7.7. Form of $\varphi_0$ within the layer

Using the inner expansions of  $\theta$  and  $\varphi$  in (7.8)<sub>2</sub>, we find, with the aid of (7.29), (7.35), and (7.65), that

$$\bar{\Psi}(\theta_0, \mathbf{m}_g) \partial_r \partial_r \varphi_0 - \Psi'(\varphi_0) = 0. \quad (7.67)$$

In view of the assumed nature of  $\bar{\Psi}$  and  $\Psi$  (cf. (A6) and the discussion containing

(4.2)), we may conclude that the system (7.33), (7.67) has a unique solution. Further, this solution satisfies the *energy-partition relation*

$$\Psi(\varphi_0) = \frac{1}{2} \bar{\Psi}(\theta_0, m_g) |\partial_r \varphi_0|^2 \quad (7.68)$$

and is hence of the form

$$\varphi_0(r, \xi, t) = \phi(y), \quad y = r / (\bar{\Psi}(\theta_0, m_g))^{\frac{1}{2}}, \quad (7.69)$$

with  $\phi$  the solution of

$$\phi' = (2\Psi(\phi))^{\frac{1}{2}}, \quad \phi(-\infty) = 0, \quad \phi(+\infty) = 1, \quad (7.70)$$

so that

$$\partial_r \varphi_0 > 0 \quad (7.71)$$

and, consistent with the discussion immediately preceding (7.34),  $\varphi_0$  increases monotonically from 0 to 1 as  $r$  varies between  $-\infty$  and  $+\infty$ . Further, (7.69), (7.70), the conditions  $\phi'(\pm\infty) = 0$ , and the fact that  $\Psi(\phi)$  and  $\Psi'(\phi)$  vanish at  $\phi=0,1$  imply there is a constant  $A > 0$  such that

$$\partial_r \varphi_0(r, \xi, t) = O(e^{-A|r|}) \quad \text{as } |r| \rightarrow \infty; \quad (7.72)$$

$\partial_r \varphi_0(r, \xi, t)$ , as a function of  $r$ , therefore belongs to  $L^2(-\infty, \infty)$ . In fact,

$$\int_{-\infty}^{+\infty} |\partial_r \varphi_0|^2 dr = F(\theta_0, m_g), \quad (7.73)$$

an identity that follows from (7.12), (7.69), and (7.70).

### 7.8. Estimates for the conversion modulus

In this section we will establish two estimates for the conversion modulus: let

$$g = |\partial_r \varphi_0|^2; \quad (7.74)$$

then, as  $\delta \rightarrow 0$ ,

$$F(\theta_0, m_\delta) = \int_{-h(\delta)/\delta}^{h(\delta)/\delta} g \, dr + o(1), \quad (7.75)$$

$$F(\theta_0, m_\delta)^{\circ(\delta)} = \frac{1}{2} \int_{-h(\delta)/\delta}^{h(\delta)/\delta} g^\circ \, dr + o(1),$$

The first of (7.75) is a direct consequence of (7.20) and (7.73).

To verify (7.75)<sub>2</sub> we first note that an argument similar to that following (7.72) shows that  $(\partial_t \check{g})$ , as a function of  $r$ , belongs to  $L^2(-\infty, \infty)$ , and that, by (7.73) and (7.50),

$$F(\theta_0, m_\delta)^{\circ(\delta)} = \int_{-\infty}^{+\infty} (\partial_t \check{g}) \, dr. \quad (7.76)$$

Let  $u = \partial_r \{(\partial_r \check{\psi}_0)(\partial_t \check{\psi}_0)\}$  so that, by (7.33),

$$\int_{-\infty}^{+\infty} u \, dr = 0; \quad (7.77)$$

then, using (7.56),

$$\begin{aligned} \partial_t \check{g} &= 2(\partial_r \check{\psi}_0)(\partial_r \partial_t \check{\psi}_0) = (\partial_r \check{\psi}_0)(\partial_r \partial_t \check{\psi}_0) - (\partial_r \partial_r \check{\psi}_0)(\partial_t \check{\psi}_0) + u \\ &= \frac{1}{2} \{ \partial_t \check{g} - (\partial_r \check{g})(\partial_r \check{\psi}_0)^{-1}(\partial_t \check{\psi}_0) \} + u \\ &= \frac{1}{2} g^\circ + u + O(h(\delta)). \end{aligned} \quad (7.78)$$

The result (7.75) follows upon integrating (7.78) from  $-h(\delta)/\delta$  to  $h(\delta)/\delta$  and using (7.20)<sub>2,3</sub>, (7.76), and (7.77).

## 8. STRUCTURAL CONSONANCE OF THE BASIC LAWS IN THE DIFFUSE- AND SHARP-INTERFACE THEORIES

We now show that

*the basic laws (6.17) of energy balance and entropy growth for the diffuse-interface theory are formally asymptotic to their counterparts (6.3) of the sharp-interface theory*

provided we use, for ST constitutive equations, the response functions defined in (7.10) and (7.11). In fact, we will show that, as  $\delta \rightarrow 0$ :

- (i) our definitions of bulk and excess free-energy, internal energy, and entropy yield the correct asymptotic form for the free energy, internal energy, and entropy of  $R$ :

$$\int_R \omega^{bu} dv = \int_{R^\alpha} \hat{\omega}^\alpha(\theta) dv + \int_{R^\beta} \hat{\omega}^\beta(\theta) dv + o(1) \quad \text{for } \omega = \psi, \epsilon, \eta, \quad (8.1)$$

$$\int_R \omega^{xs} dv = \int_G \hat{w}(\theta, m_s) da + o(1) \quad \text{for } \omega = \psi, \epsilon, \eta, \quad w = f, e, s;$$

- (ii) our identification of  $q^{th}$  as the bulk heat-flux yields the correct asymptotic form for the heat and entropy flow into  $R$ :

$$\int_{\partial R} q^{th} \cdot n da = - \int_{(\partial R)^\alpha} K^\alpha(\theta) \nabla \theta \cdot n da - \int_{(\partial R)^\beta} K^\beta(\theta) \nabla \theta \cdot n dv + o(1), \quad (8.2)$$

$$\int_{\partial R} \theta^{-1} q^{th} \cdot n da = - \int_{(\partial R)^\alpha} \theta^{-1} K^\alpha(\theta) \nabla \theta \cdot n da - \int_{(\partial R)^\beta} \theta^{-1} K^\beta(\theta) \nabla \theta \cdot n dv + o(1);$$

- (iii) the forms proposed for the kinetic heat-flux  $q^{kin}$  and for the working of the microforces yield the correct asymptotic forms for the working on—and the fluxes of free energy, internal energy, and entropy into—the control volume  $R$ :

$$\int_{\partial R} V \tau \cdot \nu dA = \int_{\partial G} V_s \hat{c}(\theta, m_s) \cdot \nu_{\partial G} dl + o(1) \quad (8.3)$$

$$\int_{\partial R} \omega^{xs} U dA = \int_{\partial G} \hat{w}(\theta, m_s) U_{\partial G} dl + o(1) \quad \text{for } \omega = \psi, \epsilon, \eta, \quad w = f, e, s;$$

- (iv) the field  $J$  is asymptotically insignificant:

$$\int_{\partial R} JU \, dA = o(1). \quad (8.4)$$

Further, not only is the total working of DT asymptotic to that of ST (in the sense of (iii) and (iv)) but, in addition:

(v) each term of the decomposition (6.21) of the DT working is formally asymptotic to its ST counterpart in (6.8):

$$\begin{aligned} \int_R \psi^{xs} KV \, dv &= \int_G \hat{f}(\theta, m_\delta) K_\delta V_\delta \, da + o(1), \\ \int_R \tau \cdot m^\circ \, dv &= \int_G \hat{c}(\theta, m_\delta) \cdot m_\delta^\circ \, da + o(1), \\ \int_R V f^{xs} \cdot m \, dv &= \int_G V_\delta \pi \cdot m_\delta \, da + o(1), \\ \int_R J(\ell^\circ/\ell) \, dv &= o(1), \end{aligned} \quad (8.5)$$

where  $m_\delta^\circ$  is the a normal time-derivative of  $m_\delta$  following  $\delta$ , while  $m^\circ$  and  $\ell^\circ$  are normal time-derivatives of  $m$  and  $\ell$  following uniformity surfaces.

The result (8.5)<sub>3</sub> motivates the choice (7.11)<sub>5</sub> for the kinetic modulus.

To establish the bulk estimates (8.1)<sub>1</sub> and (8.2), we use the outer expansion of  $\varphi$  in the relations (7.6)<sub>1,2</sub> and (7.7)<sub>1</sub> giving

$$\omega^{bu} = \hat{\omega}^{bu}(\theta, \tilde{\varphi}_0) + O(\delta), \quad q^{th} = -K(\theta, \tilde{\varphi}_0) \nabla \tilde{\theta}_0 + O(\delta) \quad (8.6)$$

in  $R \cap \mathcal{P}^\alpha(t, \delta)$  and in  $R \cap \mathcal{P}^\beta(t, \delta)$ ; thus, since  $\theta$ ,  $\nabla \theta$ , and  $\varphi$  are bounded on  $R$  uniformly in  $\delta$  (cf. (7.65)), and since the volume of  $R \cap \mathcal{L}(t, \delta)$  and the area of  $\partial R \cap \mathcal{L}(t, \delta)$  are bounded by the thickness  $h(\delta)$  of the layer, we may conclude from (7.15), (7.20), and (7.30) that (8.1)<sub>1</sub> and (8.2) are valid.

Next, by (7.6), (7.7), (7.29), (7.68), and (7.35),

$$\begin{aligned} \omega^{xs} &= (\delta F(\theta_0, m_\delta))^{-1} \hat{w}(\theta_0, m_\delta) |\partial_r \varphi_0|^2 + O(1) \quad \text{for } \omega = \psi, \varepsilon, \eta, \quad w = f, e, s, \\ \tau &= (\delta F(\theta_0, m_\delta))^{-1} \hat{c}(\theta_0, m_\delta) |\partial_r \varphi_0|^2 + O(1), \\ J &= O(1) \end{aligned} \quad (8.7)$$

within  $R \cap \mathcal{L}$ , and (7.35), (7.32), and (8.7) imply (8.4).

The estimates (8.1)<sub>2</sub> and (8.3) remain to be verified. With this in mind, we establish two identities:

$$\delta^{-1} \int_{R \cap \mathcal{L}} |\partial_r \varphi_0|^2 \rho \, dv = \int_{\mathcal{G}} F(\theta_0, m_g) \rho \, da + o(1), \quad (8.8)$$

$$\delta^{-1} \int_{(\partial R) \cap \mathcal{L}} |\partial_r \varphi_0|^2 \rho \, dA = \int_{\partial \mathcal{G}} F(\theta_0, m_g) \rho \, dl + o(1),$$

in which  $dA$  is the measure (6.18)<sub>1</sub>,  $F$  is the conversion modulus (7.12), and  $\rho$  is a scalar-valued field independent of  $r$  and of  $O(1)$  in  $\delta$ . (Bear in mind that  $m_g$  and  $\theta_0$  are independent of  $r$ .)

Since the integrand  $g = |\partial_r \varphi_0|^2 \rho$  of (8.8) is bounded, we may use (7.20) and (7.72) to conclude that

$$\int_{R \cap \mathcal{L}} g \, dv = \int_{\mathcal{G}} \int_{-h}^h g \, d(\delta r) \, da + O(h^2) = \delta \int_{\mathcal{G}} \int_{-\infty}^{+\infty} g \, dr \, da + o(\delta), \quad (8.9)$$

$$\int_{(\partial R) \cap \mathcal{L}} g \, dA = \int_{\partial \mathcal{G}} \int_{-h}^h g \, d(\delta r) \, dl + O(h^2) = \delta \int_{\partial \mathcal{G}} \int_{-\infty}^{+\infty} g \, dr \, dl + o(\delta),$$

and (8.8) follow from (7.73).

Next, by (7.16) and (7.32),

$$\int_R \omega^{xs} \, dv = \int_{R \cap \mathcal{L}} \omega^{xs} \, dv + o(1), \quad (8.10)$$

and (8.1)<sub>2</sub> follows from (8.7) and (8.8)<sub>1</sub>.

Consider (8.3). On the subset of  $\partial R$  outside of  $\mathcal{L}$  we use (3.13), (6.18), and the fact that  $\tau \cdot m = 0$  to write  $\omega^{xs} U \, dA = -\omega^{xs} V m \cdot n \, da$  and  $V \tau \cdot \nu \, dA = V \tau \cdot n \, da$ ; then since  $V$  and  $m$  are there  $O(1)$ , while  $\tau$  and  $\omega^{xs}$  are  $O(\delta)$  (cf. (7.32)),

$$\int_{\partial R} \omega^{xs} U \, dA = \int_{(\partial R) \cap \mathcal{L}} \omega^{xs} U_{\partial \mathcal{G}} \, dA + o(1), \quad \int_{\partial R} V \tau \cdot \nu \, dA = \int_{(\partial R) \cap \mathcal{L}} V_g c \cdot \nu_{\partial \mathcal{G}} \, dA + o(1), \quad (8.11)$$

where we have used (7.35) and (7.48). The estimates (8.3) follow from (8.7), (8.8)<sub>2</sub>, and (8.11).

Finally, to establish (8.5)<sub>1-3</sub> we use the inner and outer expansions appropriately in (7.6)<sub>3</sub>, (7.7)<sub>2,3</sub>, (4.26), (7.6)<sub>1,2</sub>, (7.4)<sub>6</sub>, and rely on (8.8)<sub>1</sub>; (8.5)<sub>4</sub> follows similarly upon noting that  $\ell^\circ / \ell = O(1)$  (cf. (7.44)<sub>1</sub>).

9. ASYMPTOTIC CONSONANCE OF THE PDES OF THE DIFFUSE-INTERFACE THEORY WITH THE PDES AND INTERFACE CONDITIONS OF THE SHARP-INTERFACE THEORY

We now show that

*the PDEs (7.8) (or equivalently, (7.9)) of the diffuse-interface theory are formally asymptotic to the bulk PDE (6.13) and the interface conditions (6.11) of the sharp-interface theory*

provided we use, for ST constitutive equations, the response functions defined in (7.10) and (7.11).

Our analysis will use the framework of Section 7.4, but with  $R$  replaced by the region  $\Omega$  under consideration. Thus, as the thickness  $h(\delta)$  of the layer  $\mathcal{L}(t, \delta)$  decreases to zero with  $\delta$ :

$$\mathcal{S}(t) = \mathcal{L}(t, 0+), \quad \Omega^\gamma(t) = \mathcal{P}^\gamma(t, 0+), \quad (9.1)$$

so that  $\mathcal{S}(t)$  and  $\Omega^\gamma(t)$ , respectively, represent, for the asymptotic sharp-interface theory, the interface and the portion of  $\Omega$  occupied by bulk material of phase  $\gamma$ .

Specifically, we will show that the PDEs of DT yield, asymptotically as  $\delta \rightarrow 0$ :

(i) the bulk energy-balance

$$\theta \hat{\eta}^\gamma(\theta)^\circ = \text{div}(\mathbf{K}^\gamma(\theta) \nabla \theta) + o(1) \quad (9.2)$$

in  $\Omega^\gamma$  for each phase  $\gamma = \alpha, \beta$ ;

(ii) the interfacial energy-balance<sup>21</sup>

$$\begin{aligned} \theta \{ -[\hat{\eta}^\gamma(\theta)] V_\delta + \hat{s}(\theta, m_\delta)^\circ - \hat{s}(\theta, m_\delta) K_\delta V_\delta \} = \\ [\mathbf{K}^\gamma(\theta) \nabla \theta] \cdot m_\delta + b(\theta, m_\delta) V_\delta^2 + o(1) \end{aligned} \quad (9.3)$$

and the normal configurational force-balance

$$[\hat{\psi}^\gamma(\theta)] + \hat{f}(\theta, m_\delta) K_\delta + \text{div}_\delta \{ \hat{c}(\theta, m_\delta) \} = b(\theta, m_\delta) V_\delta + o(1) \quad (9.4)$$

on  $\mathcal{S}$ , where the normal time-derivative in (9.3) is that following  $\mathcal{S}$ .

To establish (9.2), we restrict attention to  $\Omega \cap \mathcal{P}^\gamma(t, \delta)$  and observe that, by (7.30) and (7.10), the bulk terms of (7.8)<sub>1</sub> satisfy

<sup>21</sup>Here  $[\hat{\eta}^\gamma(\theta)] = \hat{\eta}^\beta(\theta) - \hat{\eta}^\alpha(\theta)$ , and so forth.

$$\theta \hat{\eta}^{bu}(\theta, \varphi)^\circ = \theta \hat{\eta}^v(\theta)^\circ + O(\delta), \quad \text{div}(K(\theta, \varphi)\nabla\theta) = \text{div}(K^v(\theta)\nabla\theta) + O(\delta), \quad (9.5)$$

while the remaining terms of (7.8)<sub>1</sub> are  $O(\delta)$ ; hence (9.2) follows.

We turn now to the derivation of the interface conditions (9.3) and (9.4), which are derived by integrating (7.9) across the layer. The estimates

$$\begin{aligned} m &= m_\delta + O(\delta), \\ V &= V_\delta + O(\delta), \\ L &= L_\delta + O(h(\delta)), \\ K &= K_\delta + O(h(\delta)), \\ \varrho^2 &= \delta^{-2}g + 2\delta^{-1}(\partial_r\varphi_0)(\partial_r\varphi_1) + O(1), \quad g = (\partial_r\varphi_0)^2, \\ (\varrho^2)^\circ &= \delta^{-2}g^\circ + O(\delta^{-1}), \end{aligned} \quad (9.6)$$

which were established in Section 7, will be used repeatedly, often without reference, as will the conditions  $\varphi_0(-\infty, \xi, t) = 0$ ,  $\varphi_0(+\infty, \xi, t) = 1$  and the  $r$ -independence of  $\theta_0$ ,  $V_\delta$ ,  $m_\delta$ , and  $K_\delta$ .

Consider (7.9)<sub>1</sub>. Using the inner expansions of  $\theta$  and  $\varphi$ , (7.29), (7.27)<sub>2</sub>, and (7.65), we have the estimates

$$\begin{aligned} \theta \hat{\eta}^{bu}(\theta, \varphi)^\circ &= -\delta^{-1}\theta_0 V_\delta \partial_r \{ \hat{\eta}^{bu}(\theta_0, \varphi_0) \} + O(1), \\ \text{div}(K(\theta, \varphi)\nabla\theta) &= \delta^{-1}m_\delta \cdot \partial_r \{ K(\theta_0, \varphi_0)(\nabla_\delta\theta_0 + (\partial_r\theta_1)m_\delta) \} + O(\delta^{-1}h(\delta)), \end{aligned} \quad (9.7)$$

so that, by virtue of (7.10) and (7.29),

$$\begin{aligned} \int_{-h(\delta)}^{h(\delta)} \theta \hat{\eta}^{bu}(\theta, \varphi)^\circ d(\delta r) &= -\theta [\hat{\eta}^v(\theta)] V_\delta + o(1), \\ \int_{-h(\delta)}^{h(\delta)} \text{div}(K(\theta, \varphi)\nabla\theta) d(\delta r) &= [K^v(\theta)\nabla\theta] \cdot m_\delta + o(1). \end{aligned} \quad (9.8)$$

Next, (7.46)<sub>2</sub> and (7.65) yield

$$\begin{aligned} \bar{\eta}(\theta, m)^\circ &= \partial_\theta \bar{\eta}(\theta, m)\theta^\circ + \partial_m \bar{\eta}(\theta, m) \cdot m^\circ \\ &= \partial_\theta \bar{\eta}(\theta_0, m_\delta)\theta_0^{\circ(\delta)} + \partial_m \bar{\eta}(\theta_0, m_\delta) \cdot m_\delta^{\circ(\delta)} + O(h(\delta)) \\ &= \bar{\eta}(\theta_0, m_\delta)^{\circ(\delta)} + O(h(\delta)). \end{aligned} \quad (9.9)$$

Thus and by (7.75),

$$\int_{-h(\delta)}^{h(\delta)} \delta \theta \ell^2 \bar{\eta}(\theta, m)^\circ d(\delta r) = \theta_0 \bar{\eta}(\theta_0, m_\delta)^\circ(\delta) F(\theta_0, m_\delta) + o(1), \quad (9.10)$$

$$\int_{-h(\delta)}^{h(\delta)} \delta \theta \bar{\eta}(\theta, m)(\ell^2)^\circ d(\delta r) = 2 \theta_0 \bar{\eta}(\theta_0, m_\delta) F(\theta_0, m_\delta)^\circ(\delta) + o(1),$$

and an argument analogous to (9.9) allows us to replace  $\theta_0$  on the right sides of (9.10) with  $\theta$ . Thus, recalling (7.13)<sub>2</sub> and the relation  $\bar{\eta} = -\partial_\theta \bar{\psi}$ ,

$$\int_{-h(\delta)}^{h(\delta)} \delta \theta \{ \ell^2 \bar{\eta}(\theta, m)^\circ + \bar{\eta}(\theta, m)(\ell^2)^\circ \} d(\delta r) = 2 \theta \hat{s}(\theta, m_\delta)^\circ + o(1), \quad (9.11)$$

where, as in (9.3), the time derivative on the right side of (9.11) is that following  $\delta$ . Further, (7.75)<sub>1</sub>, (9.6), and the relation  $\bar{\eta} = -\partial_\theta \bar{\psi}$  yield

$$\int_{-h(\delta)}^{h(\delta)} \delta \theta \ell^2 \bar{\eta}(\theta, m) K V d(\delta r) = 2 \theta \hat{s}(\theta, m_\delta) K_\delta V_\delta + o(1), \quad (9.12)$$

$$\int_{-h(\delta)}^{h(\delta)} \delta \ell^2 \bar{b}(\theta, m) V^2 d(\delta r) = b(\theta, m_\delta) V_\delta^2 + o(1).$$

Together, (7.9)<sub>1</sub>, (9.8), (9.11), and (9.12) imply (9.3).

Consider (9.4), whose derivation involves integrating (7.9)<sub>2</sub> across the layer. Note first that

$$\begin{aligned} \ell \partial_\varphi \hat{\psi}^{bu}(\theta, \varphi) &= \delta^{-1} \partial_r \{ \hat{\psi}^{bu}(\theta_0, \varphi_0) \} + O(1), \\ \delta^{-1} \{ \bar{\Psi}(\varphi) + \frac{1}{2} \delta^2 \ell^2 \bar{\psi}(\theta, m) \} K &= \delta^{-1} |\partial_r \varphi_0|^2 \bar{\psi}(\theta_0, m_\delta) K_\delta + O(\delta^{-1} h(\delta)), \end{aligned} \quad (9.13)$$

where the second estimate is based on the energy-partition relation (7.68). With a view toward estimating the remaining terms in (7.9)<sub>2</sub>, we use (3.5), (7.45), and (7.29) to obtain

$$\begin{aligned} \operatorname{div} \{ \partial_m \bar{\psi}(\theta, m) \} &= \partial_\theta \partial_m \bar{\psi}(\theta, m) \cdot \nabla \theta + \partial_m \partial_m \bar{\psi}(\theta, m) \cdot \nabla m \\ &= \partial_\theta \partial_m \bar{\psi}(\theta, m) \cdot \nabla \theta - \partial_m \partial_m \bar{\psi}(\theta, m) \cdot L \\ &= \partial_\theta \partial_m \bar{\psi}(\theta_0, m_\delta) \cdot \nabla_\delta \theta_0 - \partial_m \partial_m \bar{\psi}(\theta_0, m_\delta) \cdot L_\delta + O(h(\delta)) \\ &= \operatorname{div}_\delta \{ \partial_{m_\delta} \bar{\psi}(\theta_0, m_\delta) \} + O(h(\delta)). \end{aligned} \quad (9.14)$$

The estimates (9.13) and (9.14) in conjunction with (7.75)<sub>1</sub> and (7.13)<sub>1,3</sub> yield

$$\int_{-h(\delta)}^{h(\delta)} \ell \partial_\varphi \hat{\psi}^{bu}(\vartheta, \varphi) d(\delta r) = [\hat{\psi}^v(\vartheta)] + o(1),$$

$$\int_{-h(\delta)}^{h(\delta)} \delta^{-1} \{ \Psi(\varphi) + \frac{1}{2} \delta^2 \ell^2 \bar{\Psi}(\vartheta, m) \} K d(\delta r) = \hat{f}(\vartheta, m_\delta) K_\delta + o(1), \quad (9.15)$$

$$\int_{-h(\delta)}^{h(\delta)} -\frac{1}{2} \delta \operatorname{div} \{ \ell^2 \partial_m \bar{\Psi}(\vartheta, m) \} d(\delta r) = \operatorname{div}_\delta \{ \hat{c}(\vartheta, m_\delta) \} + o(1),$$

Similarly,

$$\int_{-h(\delta)}^{h(\delta)} \delta \ell^2 \bar{b}(\vartheta, m) V d(\delta r) = b(\vartheta, m_\delta) V_\delta + o(1). \quad (9.16)$$

Next, under the scaling introduced in Section 7.1 the field  $J$  defined by (4.23)<sub>2</sub> has the form

$$J = \Psi(\varphi) - \frac{1}{2} \delta^2 \ell^2 \bar{\Psi}(\vartheta, m). \quad (9.17)$$

The term in (7.9)<sub>2</sub> yet to be considered is

$$\delta^{-1} \operatorname{div}(Jm) = \delta^{-1}(JK + m \cdot \nabla J) \quad (9.18)$$

(cf. (3.5), (3.7)<sub>3</sub>). By (7.68),

$$\delta^{-1} JK = O(1), \quad (9.19)$$

so its integral across the layer will be  $o(1)$ . The treatment of  $\delta^{-1} m \cdot \nabla J$  is more delicate. Since  $\partial_r J$  and  $\nabla_\delta J$  are  $O(1)$ , we may use (7.27)<sub>1</sub> to conclude that

$$\delta^{-1} m \cdot \nabla J = \delta^{-2} (\partial_r J) m \cdot m_\delta + \delta^{-1} m \cdot (1 - dL_\delta) (\nabla_\delta J) = \delta^{-2} \partial_r J + O(1). \quad (9.20)$$

The results (9.18)-(9.20) imply that, for  $\rho = h(\delta)/\delta$ ,

$$\int_{-h(\delta)}^{h(\delta)} \delta^{-1} \operatorname{div}(Jm) d(\delta r) = \delta^{-2} \int_{-h(\delta)}^{h(\delta)} \partial_r J d(\delta r) + o(1) = \delta^{-1} \{ J(\rho) - J(-\rho) \} + o(1), \quad (9.21)$$

where we have suppressed the arguments  $(\xi, t)$ . By (9.6),

$$J(\rho) = \Psi(\varphi_0) + \delta\Psi'(\varphi_0) + O(\delta^2) - \frac{1}{2}\{g + 2\delta(\partial_r\varphi_0)(\partial_r\varphi_1) + O(\delta^2)\}\{\bar{\Psi}(\theta_0, m_\delta) + O(\delta)\} \quad (9.22)$$

with the fields on the right evaluated at  $r=\rho$ . Since  $\rho = h(\delta)/\delta$ , (7.68) and (7.72) imply that  $\partial_r\varphi_0(\rho)$  and  $g(\rho)$  tend to zero as  $\delta \rightarrow 0$ . Further, since  $\varphi_0(\rho) \rightarrow 1$  as  $\delta \rightarrow 0$  and  $\Psi'(1)=0$ , it follows that  $\Psi'(\varphi_0(\rho)) \rightarrow 0$  as  $\delta \rightarrow 0$ . Thus, since, by (7.68),  $\Psi(\varphi_0) - \frac{1}{2}g\bar{\Psi}(\theta_0, m_\delta) \equiv 0$ , (9.22) yields the estimate

$$\delta^{-1}J(\rho) = o(1). \quad (9.23)$$

Similarly,  $\delta^{-1}J(-\rho) = o(1)$  and we may conclude that

$$\int_{-h(\delta)}^{h(\delta)} \delta^{-1} \operatorname{div}(Jm) d(\delta r) = o(1). \quad (9.24)$$

Integrating (7.9)<sub>1</sub> across the layer and using the estimates (9.15), (9.16), and (9.24), we are led to (9.4).

A more standard argument leading to (9.4) involves working with (7.8)<sub>2</sub> in place of (7.9)<sub>2</sub>. Inserting the inner expansions of  $\theta$  and  $\varphi$  in (7.8), this approach leads to an equation of the form

$$\delta^{-1}\{\bar{\Psi}(\theta_0, m_\delta)\partial_r\partial_r\varphi_1 - \Psi''(\varphi_0)\varphi_1\} = \delta^{-1}Z + O(\delta^{-1}h(\delta)), \quad (9.25)$$

with  $Z = Z(\theta_0, \partial_r\varphi_0, m_\delta, V_\delta, K_\delta) = O(1)$ . Hence, recognizing that  $\partial_r\varphi_0$  satisfies the homogeneous equation

$$\bar{\Psi}(\theta_0, m_\delta)\partial_r\partial_r(\partial_r\varphi_0) - \Psi''(\varphi_0)\partial_r\varphi_0 = o(1) \quad (9.26)$$

(which results directly upon differentiating (7.67) with respect to  $r$ ),  $Z$  and  $\partial_r\varphi_0$  must be orthogonal in the sense that

$$\int_{-\infty}^{+\infty} Z \partial_r\varphi_0 dr = O(h(\delta)). \quad (9.27)$$

Evaluating the integral in (9.27) then yields (9.4). Our derivation of (9.4) using the configurational force balance obviates the need to use such an orthogonality condition.

Finally, we note that the entropy production  $\Gamma = \theta_M T \Gamma^*/\mu$  of DT (cf. (4.20)<sub>1</sub>), which due to the scaling is now given by

$$\theta^2\Gamma = \nabla\theta \cdot K(\theta, \varphi)\nabla\theta + \delta\ell^2\theta\bar{b}(\theta, m)V^2, \quad (9.28)$$

has, in agreement with (6.14), the asymptotic form

$$\begin{aligned} \epsilon^{-2} \nabla \epsilon \cdot K^\gamma(\epsilon) \nabla \epsilon + o(1) & \quad \text{in } \Omega^\gamma \text{ for each phase } \gamma = \alpha, \beta, \\ \epsilon^{-1} b(\epsilon, m_\delta) (V_\delta)^2 + o(1) & \quad \text{on } \delta. \end{aligned} \tag{9.29}$$

This result follows from arguments similar to those used in deriving (9.3) and (9.4).

## 10. Discussion

The results of Sections 8 and 9 show that given a sharp-interface theory with constitutive functions  $\hat{\psi}^\alpha(\theta)$  and  $K^\alpha(\theta)$  for the bulk material and  $\hat{f}(\theta, m_s)$  and  $b(\theta, m_s)$  for the interface, corresponding response functions  $\hat{\psi}^{bu}(\theta, \varphi)$ ,  $K(\theta, \varphi)$ ,  $\bar{\psi}(\theta, m)$ ,  $\bar{b}(\theta, m)$ , and  $\Psi(\varphi)$  for a diffuse-interface theory can be selected so that, in the asymptotic limit of decreasing layer thickness,

*the basic laws of the diffuse-interface theory are asymptotic to the basic laws of the sharp-interface theory,*

and

*the PDEs of the diffuse-interface theory are asymptotic to the bulk PDEs and interface conditions of the sharp-interface theory.*

In selecting  $\hat{\psi}^{bu}(\theta, \varphi)$ ,  $K(\theta, \varphi)$ ,  $\bar{\psi}(\theta, m)$ ,  $\bar{b}(\theta, m)$ , one must only adhere to the following guidelines:<sup>22</sup>

(i) the bulk free-energy  $\hat{\psi}^{bu}(\theta, \varphi)$  and conductivity  $K(\theta, \varphi)$  must obey

$$\begin{aligned}\hat{\psi}^{bu}(\theta, 0) &= \hat{\psi}^\alpha(\theta), & K(\theta, 0) &= K^\alpha(\theta); \\ \hat{\psi}^{bu}(\theta, 1) &= \hat{\psi}^\beta(\theta), & K(\theta, 1) &= K^\beta(\theta);\end{aligned}\tag{10.1}$$

(ii) the gradient energy modulus  $\bar{\psi}(\theta, m)$  must obey

$$\bar{\psi}(\theta, m) = \{\hat{f}(\theta, m) / \int_0^1 (2\Psi(\varphi))^{\frac{1}{2}} d\varphi\}^2;\tag{10.2}$$

(iii) the kinetic modulus  $\bar{b}(\theta, m)$  must obey

$$\bar{b}(\theta, m) = \hat{f}(\theta, m)b(\theta, m) / \left\{ \int_0^1 (2\Psi(\varphi))^{\frac{1}{2}} d\varphi \right\}^2.\tag{10.3}$$

The specific form of the exchange energy  $\Psi(\varphi)$  as well as the behavior of  $\hat{\psi}^{bu}(\theta, \varphi)$  and  $K(\theta, \varphi)$  for  $\varphi$  away from  $\varphi=0,1$  remain unrestricted by these requirements. In fact, the exchange energy effects the limiting constitutive equations only in the integral of its square-root from well to well across the spinodal. Hence  $\Psi(\varphi)$  can be chosen based on practical considerations, motivated, say, by the desire for computational simplicity. One might, for example, select the exchange energy to

<sup>22</sup>In addition to the relevant portions of assumptions (A1) and (A5).

be of the form (3.34) with the constant  $\nu$  chosen to approximate a desired interface thickness  $\mathcal{T}$ . For example,  $\mathcal{T}$  may be defined to be the value of  $d = r\delta$  corresponding to  $\phi = \rho$  minus that corresponding to  $\phi = 1 - \rho$ , with  $\rho$  small,<sup>23</sup> so that, by (7.19), (7.69), and (7.70),

$$\mathcal{T} = \mathcal{T}(\theta, m) = \delta(\bar{\psi}(\theta, m))^{\frac{1}{2}} / \int_{\rho}^{1-\rho} (2\Psi(\varphi))^{\frac{1}{2}} d\varphi; \quad (10.4)$$

in general, this thickness may vary with both interfacial temperature and orientation.

We emphasize that with these prescriptions our diffuse interface theory is capable of generating any sharp interface theory that falls within the general framework discussed in Section 6.1.

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<sup>23</sup>Wang et al. [19] take  $\rho \approx .05$ .

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