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THE THERMODYNAMICS OF EVOLVING INTERFACES FAR FROM EQUILIBRIUM

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ABSTRACT We develop a general thermodynamical description of an evolving interface appropriate to situations far from equilibrium. The theory represents a broad departure from theories based on classical nonequilibrium thermodynamics, as we do not assume a linear relationship between fluxes and forces, and we do not limit our theory to small departures from equilibrium. Further, we allow for diffusion in both phases without an assumption of steady-state diffusion in the bulk material; we allow the composition of material transferred across the interface to differ from the compositions of either phase, with solute drag included as a special case; and we allow for heat flow in both phases. As an application of the general theory, we develop linearized interface conditions for an evolving interface.

1. INTRODUCTION

1.1. BACKGROUND. SCOPE

Understanding the thermodynamic conditions at an evolving interface between phases containing two or more chemical components has been a central issue in the study of phase transformations, as a knowledge of these conditions is crucial to the description of the growth kinetics and

morphological evolution of a phase. The principle used most frequently to determine the interface conditions is based on an assumption of local equilibrium in which the interfacial temperature and composition are presumed given by relations obtained by minimizing the total free energy of the system. As the interface is not stationary, such a variational approach can, at best, provide an approximate description; in fact, there are experiments involving large interfacial velocities in which the actual interface conditions are not consistent with this assumption of local equilibrium.

A number of theories have been proposed to describe the evolution of an interface that is not in local equilibrium. These theories fall into three broad categories. The first includes theories that determine the temperature and the ratio of the interfacial compositions of each phase. Here the temperature is determined using the energy dissipation-rate and the composition-ratio is determined using a detailed description of the energy changes accompanying the motion of atoms across an atomistically sharp interface [1-4]. The second category includes descriptions based upon linear combinations of generalized fluxes and forces linked through a condition on the production of entropy [5-7]. The final category considers the interface as having nonzero thickness within which certain of the thermodynamic variables—including, often, a phase-field—exhibit large gradients [8-10]. While the predictions of these theories are far from agreement, they generally conclude that, as the velocity of the interface increases, the composition jump across the interface goes to zero, while the temperature of the interface decreases.

Some theories predict that the solute present in an impure material will introduce a "drag" on the interface. The initial treatments of "solute drag" dealt with the motion of grain boundaries in single-phase two-component alloys [11-13], but these have been generalized to two-phase alloys [2,9,14,15]. Solute drag is also present implicitly in the phase-field models of solute trapping [10].

Underlying solute drag is the contention that the preferential adsorption of solute to a moving interface acts as a drag force. At sufficiently large velocities, however, the interface sheds this excess solute and there is no solute drag. Thus, there is a major difference between the behavior of the interface at low and high velocities. The effects of solute drag depend on the concentration profile through the interface and the distance dependence of the interaction energy between the adsorbing atoms and the phase boundary. Solute drag has been observed experimentally to influence the motion of grain boundaries [16] and antiphase-domain boundaries [17], although recent experiments indicate that solute drag may not be present during certain solid-liquid transformations [18].

A number of theories for the conditions at a moving interface have been developed for use in situations involving rapid solidification, but the diffusion of solute within the growing phase has usually been neglected. In fact, the effects of diffusion in the growing phase—for models with a sharp interface—remain controversial; for example, Caroli et al claim that diffusion in the solid is necessary for consistency with Onsagers symmetry-relations [7]. In contrast, Kaplan et al claim that Onsager's relations are then not valid [19]. Further, a theory that includes diffusion in both phases would be of particular importance in solid-state transformations, where the diffusivity of the two phases has roughly the same magnitude. An additional defect in the sharp-interface theories derived to date is an assumption of steady-state diffusion in the determination of the interface conditions.

In this paper we develop a general thermodynamical description of an evolving interface, a description that we believe to be appropriate in situations far from equilibrium. Our theory is a broad departure from those based on classical nonequilibrium thermodynamics, as we do not assume a linear relationship between fluxes and forces, and we do not limit our theory to small departures from equilibrium. Further: (i) we allow for diffusion in both phases without an assumption of steady-state diffusion in the bulk material; (ii) we allow the composition of material transferred across the interface to differ from the compositions of either phase, with solute drag included as a special case; (iii) we allow for heat flow in both phases, an extension that enables us to address the question of whether the large temperature gradients that accompany rapid solification influence the thermodynamic conditions at the interface.

1.2. PROCEDURE

We consider a two-phase system consisting of bulk regions separated by a sharp interface. We base our discussion on balance laws for mass, energy, and configurational forces in conjunction with an entropy growth inequality that we use to develop a suitable constitutive theory for the interface. We assume that mass transport is characterized by the bulk diffusion of a *single* independent species, an assumption we make to avoid notational complications; the generalization to multi-component systems involves neither conceptual nor analytical difficulty. What is most important, to model situations in which the evolution of the interface is rapid, we allow the chemical potential to have different limiting values on the two sides of the interface, although the temperature is presumed to be continuous everywhere. Finally, we neglect deformation.

Our proceedure is as follows:

1. We begin with balance laws for mass, energy, and configurational forces together with a dynamical version of the second law. Such basic laws, common to large classes of materials, are carefully kept distinct from specific constitutive assumptions, which differentiate between particular materials.

2. *Each* balance law is equipped with an external supply. These supplies are not specified by constitutive equations, but instead are allowed to be assignable in any way compatible with the basic laws, just as the body forces and the heat supply are often left assignable in the more standard theories of mechanics and heat conduction.

3. The second law is localized and the balance laws—in local form—are used to eliminate the external supplies. This yields one or more local dissipation inequalities.

4. Constitutive equations are introduced. The balance laws do not restrict the constitutive equations, instead they determine the external supplies needed to support processes related through the constitutive equations. On the other hand, the dissipation inequalities have no flexibility, as the supplies have been removed; for that reason the requirement that the second law hold in all constitutive processes severly restricts the constitutive equations. (This is the Coleman-Noll [20] procedure as generalized to multi-phase systems in [21,22].)

5. The basic laws supplemented by the thermodynamically restricted constitutive equations give the PDEs and interface conditions of the theory.

One might argue with the assumed availability of external supplies, since it is difficult to conceive of "real physical situations" in which such supplies are present and, what is more important, completely controllable. (For example, we allow for an external supply of mass to infinitesimally thin layers of bulk material immediately adjacent to the interface.) The availability of supplies is essential to our development: it allows for the arbitrary prescription of constitutive processes. In fact, this availibility of supplies is tacit in many other theories of mathematical physics, although the assumption is never made explicit. For example, the variational derivation of field equations or interface conditions from the condition that an "energy" be a minimum requires that the underlying variational statement hold for all possible variations of the basic fields; but such variations will generally not be consistent with the resulting balance laws unless suitable supplies are, in fact, introduced.

Since our basic approach to the development of a suitable constitutive theory differs from that common among material scientists, we begin with the classical theory of single-phase diffusion. This allows us to discuss, within a familiar context, our treatment of configurational forces as well as the manner in which we use thermodynamics to restrict constitutive equations. With this as background we turn toward our chief goal: the development of a general thermodyamical theory of evolving interfaces far from equilibrium, a study that occupies most of this paper. Finally, as an application of the general theory, we develop linearized interface conditions for an evolving interface, allowing for diffusion in both phases.

1.3. NOTATION

We use notation and terminology standard in continuum mechanics. $\mathbb{R}^3$ is the underlying three-dimensional space. *Vectors* are elements of $\mathbb{R}^3$ and are denoted by lower-case boldface letters. A *dot* denotes the *inner product*. *Tensors* are linear transformations of $\mathbb{R}^3$ into $\mathbb{R}^3$ and are denoted by upper-case boldface letters. Vectors may be viewed as 3×1 column vectors and tensors as 3×3 matrices. $\mathbf{1}$ denotes the *unit tensor* ($\mathbf{1}$ is diagonal with ones along the diagonal). For a function $F(a,b,\dots,c)$ of scalar or vector variables, we write, for example, $\partial_b F(a,b,\dots,c)$ for the partial derivative $F(a,b,\dots,c)$ with respect to b.

2. REVIEW OF SINGLE-PHASE DIFFUSION

To illustrate our approach to nonequilibrium thermodynamics, before discussing interfaces we first consider the simpler case of diffusion in a single-phase crystalline solid, which we suppose to be a binary substitutional alloy with no vacancies.

2.1. BALANCE OF MASS

We consider two species of diffusing atoms in a nondeformable crystalline solid that occupies a region Ω in three-dimensional space. We label the species by $i=1,2$, and write $\rho_i(\mathbf{x},t)$ for the molar density, per unit volume, of species i, $\bar{\mathbf{h}}_i(\mathbf{x},t)$ for the molar flux of species i, per unit area, and $\bar{h}_i(\mathbf{x},t)$ for the molar supply of species i, per unit volume. The molar densities must be compatible with the constraint imposed by the crystal lattice; namely, $\rho_1+\rho_2=\rho$, with ρ, a *constant*, the number of lattice points per unit volume; consistent with this, we assume that $\bar{\mathbf{h}}_1=-\bar{\mathbf{h}}_2$ and $\bar{h}_1=-\bar{h}_2$.

We formulate basic balance laws using an arbitrary subregion D of Ω, which we will refer to as a *control volume*. Balance of mass for D has the form

$$\{\int_D \rho_i\, dv\}^{\cdot} = -\int_{\partial D} \bar{\mathbf{h}}_i\cdot d\mathbf{a} + \int_D \bar{h}_i\, dv, \tag{2.1}$$

for i=1,2, where $d\mathbf{a}$ is a vector element of area such that $\mathbf{f}\cdot d\mathbf{a}=\mathbf{f}\cdot\mathbf{m}\,da$ with $\mathbf{m}$ the outward unit normal to the boundary ∂D of D. Here and in what follows we use a superscript dot to denote the derivative of a function of t or the partial derivative with respect to t of a function of $\mathbf{x}$ and t.

To simplify the theory, we work with concentrations (molar fractions) $c_i=\rho_i/\rho$ rather than molar densities. Then, defining $\mathbf{h}_i=\bar{\mathbf{h}}_i/\rho$ and $h_i=\bar{h}_i/\rho$, it follows that

$$c_1+c_2=1, \qquad \mathbf{h}_1=-\mathbf{h}_2, \qquad h_1=-h_2, \tag{2.2}$$

and, since ρ is constant, balance of mass becomes

$$\{\int_D c_i\, dv\}^{\cdot} = -\int_{\partial D} \mathbf{h}_i\cdot d\mathbf{a} + \int_D h_i\, dv. \tag{2.3}$$

The lattice constraints (2.2) allow us to drop one of the balance laws (2.3), but a more symmetric treatment may be obtained by defining

$$c = (c_1 - c_2)/2, \qquad \mathbf{h} = \mathbf{h}_1, \qquad \mathbf{h} = \mathbf{h}_1, \tag{2.4}$$

in which case (2.3) yields

$$\{\int_D c\,dv\}^{\cdot} = -\int_{\partial D} \mathbf{h}\cdot\mathbf{da} + \int_D h\,dv. \tag{2.5}$$

Using the divergence theorem and the fact that D is arbitrary leads to the local mass balance

$$c^{\cdot} = -\mathrm{div}\,\mathbf{h} + h. \tag{2.6}$$

2.2. BALANCE OF ENERGY. GROWTH OF ENTROPY

To describe the thermodynamics we introduce the internal energy $\varepsilon(\mathbf{x},t)$, the entropy $\eta(\mathbf{x},t)$, the heat flux $\mathbf{q}(\mathbf{x},t)$, the heat supply $q(\mathbf{x},t)$, the temperature $T(\mathbf{x},t)$, and the chemical potentials $\mu_i(\mathbf{x},t)$, with ε, η, and q measured per unit volume, and $\mathbf{q}$ measured per unit area. At this point in the development the temperature and chemical potential are primitive concepts: μ_i represents energy per unit transported mass, so that $\mu_i\mathbf{h}_i$ and $\mu_i h_i$ represent energy carried with the mass flux $\mathbf{h}_i$ and the mass supply h_i; analogously, $\mathbf{q}/T$ and q/T represent entropy transported with the heat flux $\mathbf{q}$ and the heat supply q. In particular, the relationship between μ_i and derivatives of an energy has not yet been established.

The first two laws for a control volume D express balance of energy

$$\{\int_D \varepsilon\,dv\}^{\cdot} = -\int_{\partial D}(\mathbf{q} + \Sigma_i\,\mu_i\mathbf{h}_i)\cdot\mathbf{da} + \int_D (r + \Sigma_i\,\mu_i h_i)\,dv \tag{2.7}$$

and growth of entropy

$$\{\int_D \eta\,dV\}^{\cdot} \geq -\int_{\partial D}(\mathbf{q}/T)\cdot\mathbf{da} + \int_D (q/T)\,dv. \tag{2.8}$$

In view of (2.2) and (2.4), the definition

$$\mu = \mu_1 - \mu_2 \tag{2.9}$$

allows us to rewrite the energy balance as

$$\{\int_D \varepsilon\, dv\}^{\cdot} = -\int_{\partial D} (\mathbf{q} + \mu\mathbf{h})\cdot d\mathbf{a} + \int_D (q + \mu h)\, dv, \tag{2.10}$$

showing that the sum $\mu_1 + \mu_2$ of chemical potentials does not contribute to the energetics, a result consistent with the fact that, due to the lattice constraint, $\rho_1 + \rho_2$ does not contribute to the mass balance. We will refer to μ as the *(effective) chemical potential.*

The relations (2.5) and (2.10) are also appropriate starting points for the diffusion of a single interstitial species, with c the concentration and μ the chemical potential of the interstitial; our results are therefore applicable also in that case.

It is convenient to introduce the free energy

$$\psi = \varepsilon - T\eta. \tag{2.11}$$

Then, using the divergence theorem and the mass balance (2.5), we can rewrite (2.8) and (2.10) in the form of a local energy balance

$$\varepsilon^{\cdot} = -\mathrm{div}(\mathbf{q} + \mu\mathbf{h}) + q + \mu h \tag{2.12}$$

and a *bulk dissipation inequality*

$$\psi^{\cdot} + \eta T^{\cdot} - \mu c^{\cdot} + T^{-1}\mathbf{q}\cdot\nabla T + \mathbf{h}\cdot\nabla\mu \leq 0. \tag{2.13}$$

Note that neither the mass supply nor the heat supply appear in (2.13).

2.3. CONSTITUTIVE EQUATIONS. THERMODYNAMIC RESTRICTIONS

We view the balance laws for mass and energy and the law of entropy growth as basic laws, common to large classes of materials; we carefully keep such laws distinct from specific constitutive equations, which differentiate between particular materials.

We consider constitutive equations giving ψ, μ, η, $\mathbf{h}$, and $\mathbf{q}$ at a point $\mathbf{x}$ and time t when c, T, ∇c, and ∇T are known at $(\mathbf{x},t)$; we denote by $\hat{\psi}$ the constitutive response function delivering the free energy,

$$\psi(\mathbf{x},t) = \hat{\psi}(c(\mathbf{x},t),T(\mathbf{x},t),\nabla c(\mathbf{x},t),\nabla T(\mathbf{x},t)); \tag{2.14}$$

similarly $\hat{\mu}$, $\hat{\eta}$, $\hat{\mathbf{h}}$, and $\hat{\mathbf{q}}$ denote the response functions for μ, η, $\mathbf{h}$, and $\mathbf{q}$. We do not write a constitutive equation for the external supplies h and q, but instead allow h and q to be assignable in any way compatible with the basic laws.

Given smooth time-dependent fields c and T, the constitutive equations may be used to compute fields ψ, μ, η, $\mathbf{h}$, and $\mathbf{q}$; balance of mass and energy, (2.6) and (2.12), then determine the mass h and heat q that must be supplied to the body to support this constitutive process. The presence of nonzero supplies h and q are essential in this regard, as they allow for arbitrary prescription of the fields c and T *without violating the basic balance laws.* The second law remains to be satisfied in all such constitutive processes, a requirement we will use to restrict the constitutive equations. In particular, we assume that

> *the bulk dissipation inequality* (2.13) *is satisfied in all constitutive processes.*

Note that we allow all smooth prescriptions of the concentration and temperature; we add no constraints regarding their temporal or spatial rates of change.

Let

$$\mathbf{z} = (c,T,\mathbf{p},\mathbf{g}), \quad \mathbf{p} = \nabla c, \quad \mathbf{g} = \nabla T. \tag{2.15}$$

Substituting the constitutive equations into the dissipation inequality yields the inequality

$$\partial_{\mathbf{p}}\hat{\psi}(\mathbf{z})\cdot\mathbf{p}^{\cdot} + \partial_{\mathbf{g}}\hat{\psi}(\mathbf{z})\cdot\mathbf{g}^{\cdot} + \{\partial_c\hat{\psi}(\mathbf{z}) - \hat{\mu}(\mathbf{z})\}c^{\cdot} + \{\partial_T\hat{\psi}(\mathbf{z}) + \hat{\eta}(\mathbf{z})\}T^{\cdot} +$$
$$T^{-1}\hat{\mathbf{q}}(\mathbf{z})\cdot\nabla T + \hat{\mathbf{h}}(\mathbf{z})\cdot\nabla\{\hat{\mu}(\mathbf{z})\} \le 0, \tag{2.16}$$

where, e.g., $\partial_{\mathbf{p}}$ represents the partial derivative with respect to $\mathbf{p}$. We can always find fields c and T such that $\mathbf{z}$, $c^{\cdot}$, $T^{\cdot}$, $p^{\cdot}$, $g^{\cdot}$, ∇p, and ∇g have arbitrarily prescribed values at some chosen $\mathbf{x}$ and t. Therefore, for the inequality (2.16) to be satisfied by all constitutive processes, we must have $\partial_p\hat{\psi}(\mathbf{z})=\partial_g\hat{\psi}(\mathbf{z})=0$, $\partial_c\hat{\psi}(\mathbf{z})=\hat{\mu}(\mathbf{z})$, $\partial_T\hat{\psi}(\mathbf{z})=-\hat{\eta}(\mathbf{z})$. Therefore:

1. The free energy, the chemical potential, and the entropy are independent of the gradients of concentration and temperature and, moreover, are related through

$$\hat{\mu}(c,T) = \partial_c\hat{\psi}(c,T), \qquad \hat{\eta}(c,T) = -\partial_T\hat{\psi}(c,T). \tag{2.17}$$

2. The dissipation inequality assumes the form

$$T^{-1}\hat{\mathbf{q}}(c,T,\mathbf{p},\mathbf{g})\cdot\nabla T + \hat{\mathbf{h}}(c,T,\mathbf{p},\mathbf{g})\cdot\nabla\mu \le 0. \tag{2.18}$$

An immediate consequence of (2.17) is that in this nonequilibrium system

$$\psi^{\cdot} = \mu c^{\cdot} - \eta T^{\cdot}. \tag{2.19}$$

Gibbs relations of this form are typically *assumed* to hold in the more standard treatments of the thermodynamics of nonequilibrium processes (cf., e.g., DeGroot and Mazur [23]).

Note that by (2.11) and (2.17), the internal energy is also given by a function

$$\varepsilon = \hat{\varepsilon}(c,T) = \hat{\psi}(c,T) - T\partial_T\hat{\psi}(c,T). \tag{2.20}$$

We shall assume throughout that $\partial_c\hat{\mu}(c,T)>0$ for all (c,T), thereby limiting the theory to systems that are isothermally metastable or stable. This assumption allows us to consider c as a function

$$c = \tilde{c}(\mu,T), \tag{2.21}$$

and to consider the mass flux and heat flux as functions

$$\mathbf{q} = \tilde{\mathbf{q}}(\mu,T,\nabla\mu,\nabla T), \qquad \mathbf{h} = \tilde{\mathbf{h}}(\mu,T,\nabla\mu,\nabla T) \tag{2.22}$$

subject to

$$T^{-1}\tilde{\mathbf{q}}(\mu,T,\nabla\mu,\nabla T)\cdot\nabla T + \tilde{\mathbf{h}}(\mu,T,\nabla\mu,\nabla T)\cdot\nabla\mu \le 0. \tag{2.23}$$

The next lemma [24,25] facilitates the study of inequalities of the form (2.23).

Lemma. *Let* $\mathbf{u}(\mathbf{w},\mathbf{y})$ *in* $\mathbb{R}^n$ *be a smooth function of* $\mathbf{w}$ *in* $\mathbb{R}^m$ *and* $\mathbf{y}$ *in* $\mathbb{R}^n$, *and suppose that*

$$\mathbf{u}(\mathbf{w},\mathbf{y})\cdot\mathbf{y} \le 0$$

for all $\mathbf{w}$ *and* $\mathbf{y}$. *Then for each* $(\mathbf{w},\mathbf{y})$ *there is an* $n\times n$ *matrix* $\mathbf{K}(\mathbf{w},\mathbf{y})$, *with* $\mathbf{K}(\mathbf{w},0)$ *positive semi-definite, such that*

$$\mathbf{u}(\mathbf{w},\mathbf{y}) = -\mathbf{K}(\mathbf{w},\mathbf{y})\mathbf{y}.$$

To prove this lemma we fix the argument $\mathbf{w}$ and suppress it in what follows. Then $\varphi(\mathbf{y})=\mathbf{u}(\mathbf{y})\cdot\mathbf{y}\le 0$ has a maximum at $\mathbf{y}=0$, so that $\nabla\varphi(0)=\mathbf{u}(0)=0$ and $\nabla\nabla\varphi(0)=\nabla\mathbf{u}(0)$ is negative semi-definite. Since $\mathbf{u}(0)=0$, we have the identity

$$\mathbf{u}(\mathbf{y}) = \Big\{\int_0^1 \nabla\mathbf{u}(s\mathbf{y})\,ds\Big\}\mathbf{y}, \tag{2.24}$$

and the desired conclusions follow upon setting $\mathbf{K}(\mathbf{y})=-\{\ldots\}$.

This lemma with $\mathbf{u}=(\hat{\mathbf{h}},T^{-1}\hat{\mathbf{q}})$, $\mathbf{w}=(\mu,T)$, and $\mathbf{y}=(\nabla\mu,\nabla T)$ yields the following reduced constitutive equations for the fluxes:

$$\begin{aligned} \mathbf{h} &= -\mathbf{K}_{11}\nabla\mu - \mathbf{K}_{12}\nabla T,\\ \mathbf{q} &= -\mathbf{K}_{21}\nabla\mu - \mathbf{K}_{22}\nabla T, \end{aligned} \tag{2.25}$$

with coefficient matrices $\mathbf{K}_{ij}=\mathbf{K}_{ij}(\mu,T,\nabla\mu,\nabla T)$ consistent with (2.23), and with the matrix (of matrices) with rows $\mathbf{K}_{1j}(\mu,T,0,0)$ and $T^{-1}\mathbf{K}_{2j}(\mu,T,0,0)$

positive semi-definite. These relations allow for mass transport due to a temperature gradient (Soret effect) and for heat flow due to a concentration gradient (Dufour effect).

In the absence of external supplies, the balance equations for mass and force take the form

$$c^{\cdot} = -\mathrm{div}\,\mathbf{h}, \qquad \varepsilon^{\cdot} = -\mathrm{div}(\mathbf{q} + \mu\mathbf{h}), \tag{2.26}$$

and these with the thermodynamically restricted constitutive equations (2.17) and (2.20) form the basic partial differential differential equations of the theory. These are the most general equations consistent with the second law and the underlying constitutive assumptions. Particular problems would then dictate what further simplifications are appropriate.

2.4. CONFIGURATIONAL FORCES[1]

Configurational forces are irrelevant when discussing defect-free single-phase materials, but their study within that context provides essential information regarding their nature.

We capture the mechanics associated with the addition and deletion of material at the boundary of a portion of the body using *control volumes* D(t) *that evolve with time.* The boundry $\partial D = \partial D(t)$ of such a control volume is an evolving surface and hence may be parametrized by a function of the form $\mathbf{x} = \mathbf{X}(u_1,u_2,t)$; the field $\mathbf{v}(\mathbf{x},t) = \partial\hat{\mathbf{X}}(u_1,u_2,t)/\partial t$ then represents a *velocity field* for $\partial D(t)$. Of course, $\mathbf{v}$ depends on the parametrization chosen for $\partial D(t)$, but the normal velocity

$$\mathcal{V} = \mathbf{v}\cdot\mathbf{m} \qquad (\mathbf{m} = \text{outward unit normal to } \partial D) \tag{2.27}$$

does not. For $\boldsymbol{\Phi}(\mathbf{x},t)$ a smooth field,

$$(d/dt)\{\int_D \boldsymbol{\Phi}\} = \int_D \boldsymbol{\Phi}^{\cdot}dv + \int_{\partial D} \boldsymbol{\Phi}\mathcal{V}\,da, \tag{2.28}$$

---

[1] This section is taken from [26]. Standard forces associated with continua arise as a response to deformation. That additional *configurational* forces may be needed to describe the internal structure of the material is clear from Eshelby's work on lattice defects [27,28].

where

$$(d/dt)\{\int_{D}\Phi\, dv\} \quad \text{denotes} \quad (d/dt)\{\int_{D(t)}\Phi(\mathbf{x},t)\, dv(\mathbf{x})\}. \qquad (2.29)$$

To the classical fields discussed thus far we add four configurational fields: a stress field $\mathbf{S}$, an internal body force $\mathbf{e}$, a scalar mass flux $\mathcal{H}$, and a scalar heating Q. The stress $\mathbf{S}$ represents forces that expend power when material is added or removed from $D = D(t)$ through the motion of $\partial D = \partial D(t)$; we presume this power to be of the form

$$\int_{\partial D}\mathbf{S}\mathbf{m}\cdot\mathbf{v}\, da. \qquad (2.30)$$

(The body force $\mathbf{e}$ does not expend power on D, since it acts *internally* to D.) Similarly, the integrals

$$\int_{\partial D}\mathcal{H}\mathcal{V}\, da, \quad \int_{\partial D}\mu\mathcal{H}\mathcal{V}\, da, \quad \int_{\partial D}Q\mathcal{V}\, da, \quad \int_{\partial D}(Q/\theta)\mathcal{V}\, da, \qquad (2.31)$$

represent flows of mass, energy, heat, and entropy into D associated with the motion of ∂D.

We now write the form we propose for the basic laws, taking into account the motion of $\partial D(t)$. To focus on the role of the terms (2.30) and (2.31), we write RMassBal(D), REnergyBal(D), and REntropyIneq(D), respectively, for the right-hand sides of the (more standard) mass balance (2.5), energy balance (2.10), and entropy inequality (2.8). The basic laws, for each evolving control volume $D = D(t)$, are then *balance of mass*

$$(d/dt)\{\int_{D}c\, dv\} = \mathrm{RMassBal}(D) + \int_{\partial D}\mathcal{H}\mathcal{V}\, da, \qquad (2.32)$$

balance of energy

$$(d/dt)\{\int_{D}\varepsilon\, dv\} = \mathrm{REnergyBal}(D) + \int_{\partial D}(Q + \mu\mathcal{H})\mathcal{V}\, da + \int_{\partial D}\mathbf{S}\mathbf{m}\cdot\mathbf{v}\, da, \qquad (2.33)$$

growth of entropy

$$(d/dt)\{\int_D \eta\, dv\} \geq \mathrm{REntropyIneq}(D) + \int_{\partial D} (Q/T)\mathcal{V}\, da, \tag{2.34}$$

and a *balance law for configurational forces*

$$\int_{\partial D} \mathbf{S}\, da + \int_D \mathbf{e}\, dv = \mathbf{0}, \tag{2.35}$$

with the stipulation that balance of energy *be independent of the particular local parametrizations used to determine the velocity field* $\mathbf{v}$ *for* ∂D. Note that, for D stationary (2.32) - (2.34) reduce to (2.5), (2.10), and (2.8), demonstrating consistency with the more standard formulation of these laws.

Because of (2.27), changes in parametrization affect the tangential component of $\mathbf{v}$, but leave the normal component unaltered. In fact, invariance of (2.33) under reparametrization is equivalent to the requirement that $\mathbf{Sm}\cdot\mathbf{t} = 0$ on ∂D for all tangential vector fields $\mathbf{t}$ on ∂D; thus, since D is arbitrary, $\mathbf{Sm}$ is parallel to $\mathbf{m}$ for all $\mathbf{m}$, so that $\mathbf{S}$ is a pure tension τ $(\mathbf{S} = \tau\mathbf{1})$. Further, given a time s, it is possible to find a second referential control volume $D'(t)$ with $D'(s) = D(s)$, but with $\mathcal{V}'(\mathbf{x},s)$, the normal velocity of $\partial D'(s)$, an *arbitrary* scalar field on $\partial D'(s)$; therefore, applying (2.28) to c, ε, and η in (2.32)-(2.34) and using the fact that $\mathcal{V}'$ is arbitrary, we conclude that

$$c = \mathcal{H}, \qquad \varepsilon = \tau + Q + \mu\mathcal{H}, \qquad \eta = Q/T, \tag{2.36}$$

relations that, when multiplied by $\mathcal{V}$, express balance of mass, energy, and entropy associated with the addition of material to D. A trivial but important corollary of these relations is that the bulk tension τ coincides with the grand canonical free energy ω:

$$\mathbf{S} = \omega\mathbf{1} \tag{2.37}$$

with

$$\omega = \psi - \mu c. \tag{2.38}$$

The relation (2.37) and the configurational force balance will be crucial to our discussion of interface conditions for a two-phase system. It is important to note that our derivation of the relation (2.37) for the configurational stress was accomplished without recourse to constitutive equations or to a variational principle; the derivation was based on versions of the mass and energy balances and entropy inequality appropriate to control volumes whose boundaries evolve with time.

The divergence theorem applied to to (2.35) yields the local balance

$$\operatorname{div}\mathbf{S} + \mathbf{e} = 0; \tag{2.39}$$

therefore, using (2.37), (2.38), and the constitutive equations (2.17),

$$\mathbf{e} = \eta\nabla T + c\nabla\mu, \tag{2.40}$$

showing that internal configurational forces arise as a response to inhomogenieties induced by nonuniformities in the temperature and chemical potential.

2.5. THEORY WHEN THE MATERIAL DOES NOT DIFFUSE MASS

Often in problems involving a solid in a liquid melt, diffusion in the solid is negligible compared to diffusion in the liquid. To model the solid phase in such situations we consider a class of materials consistent with the constraint

$$\mathbf{h} = 0. \tag{2.41}$$

In this case the local expressions for balance of mass and energy and the bulk dissipation inequality take the forms (2.6), (2.12), and (2.13) with $\mathbf{h}=0$. The constitutive theory does not involve an equation for $\mathbf{h}$, but otherwise is not essentially different from that of the previous section. In the absence of external supplies the resulting equations are

$$\varepsilon^{\cdot} = -\operatorname{div}\mathbf{q}, \qquad c^{\cdot} = 0, \tag{2.42}$$

in conjunction with the constitutive equations (2.17), (2.20), and

$$q = -K\nabla T, \qquad (2.43)$$

with coefficient matrix $K = K(T, \nabla T)$ consistent with $q \cdot \nabla T \le 0$, so that, in particular, $K(T,0)$ is positive semi-definite.

3. TWO-PHASE SYSTEMS

We now consider a two-phase system consisting of bulk phases α and β separated by a sharp interface, with the motion of the interface accompanied by mass and heat transport in the bulk material. Surface transport along the interface as well as deformation in the bulk phases will be neglected.

3.1. THE INTERFACE

We model the interface $s(t)$ as an infinitesimally thin two-dimensional surface that divides the body into two regions, $\Omega_\alpha(t)$ and $\Omega_\beta(t)$, the former occupied by α, the latter by β. We orient $s(t)$ by choosing its unit normal field $n(x,t)$ to point into β, and we denote by $V(x,t)$ the normal velocity of $s(t)$ in the direction $n(x,t)$. (Cf. [21,22] for a discussion of the geometry of evolving interfaces.)

Our theory is characterized by: (1) bulk fields defined in $\Omega_\alpha(t)$ and $\Omega_\beta(t)$ for all t, and allowed to suffer jump discontinuities across the interface; and (2) interfacial fields defined on $s(t)$ for all t. For Φ a bulk field, we write Φ^- and Φ^+, respectively, for the limits of Φ as the interface is approached from the α and β phase regions, and $[\Phi]$ for the jump in Φ across the interface:

$$[\Phi] = \Phi^+ - \Phi^-. \qquad (3.1)$$

We will again make use of an arbitrary control volume D, which, in this case, is fixed in Ω. When D contains material in both phases, the portions $D_\alpha(t)$, $D_\beta(t)$, and $d(t)$ of D that lie, respectively, in the α phase, in the β phase, and on the interface, will be functions of time. We will refer to $D_\alpha(t)$ and $D_\beta(t)$ as interactive control volumes. For $\gamma = \alpha$ or $\gamma = \beta$ the boundary of $D_\gamma(t)$ will have two components: the portion $d(t)$ that lies on the interface and the portion $(\partial D)_\gamma(t)$ that lies in the bulk material of phase γ (Figure 1).

3.2. BALANCE OF MASS.

Basic to our discussion of the interface is a scalar field $C(\mathbf{x},t)$ that represents the composition of bulk material currently situated in the interface, or equivalently, the composition of bulk material currently being transferred across the interface. (Consistent with (2.2), for a binary system $C=(C_1-C_2)/2$, $C_1+C_2=1$.) It may happen that $C=c^-$ or $C=c^+$, but this need not be so, although one might assume that C lies between c^- and c^+.

We also introduce, in addition to the bulk mass flows of Section 2, interfacial fluxes $j_\gamma(\mathbf{x},t)$ and interfacial external mass supplies $H_\gamma(\mathbf{x},t)$, where, for $\gamma=\alpha,\beta$, j_γ represents the mass flow per unit area *by diffusion* out of the interface and into phase γ, while H_γ represents an external supply of mass per unit area to an infinitesimal layer of phase γ adjacent to the interface. Thus there are net mass flows into an interactive control volume $D_\gamma(t)$, from the bulk material of γ,

$$-\int_{(\partial D)_\gamma} \mathbf{h}\cdot d\mathbf{a}\,, \tag{3.2}$$

from the interface by diffusion,

$$-\int_{d} j_\gamma \, da\,, \tag{3.3}$$

from the interface due solely to its motion,

$$\pm\int_{d} CV \, da \tag{3.4}$$

with the plus of minus chosen according as $\gamma=\alpha$ or $\gamma=\beta$, and from the external supplies,

$$\int_{d} H_\gamma da + \int_{D_\gamma} h \, dv. \tag{3.5}$$

We will formulate balance of mass for the control volume D as well as for the interactive control volumes $D_\gamma(t)$; the latter will help to characterize the interaction between phases. Balance of mass for D is the requirement that

$$\{\int_D c\,dv\}^{\cdot} = -\int_{\partial D} h\cdot da + \int_D h\,dv + \int_d (H_\alpha + H_\beta)\,da, \tag{3.6}$$

while balance of mass for each interactive control volume $D_\gamma(t)$ yields

$$\{\int_{D_\gamma} c\,dv\}^{\cdot} = -\int_{(\partial D)_\gamma} h\cdot da + \int_{D_\gamma} h\,dv + \int_d (j_\gamma \pm CV + H_\gamma)\,da. \tag{3.7}$$

The mass flows $j_\alpha + CV$ and $j_\beta - CV$ do not appear in (3.6) as they are internal to D.

Applying (3.6) to control volumes D that exclude the interface leads to the the bulk mass balance (2.6), which is now required to hold in each of the bulk regions for all time. On the other hand, if we shrink D to the interface, the left side of (3.6) approaches the integral over d of $-[c]V$, the first term on the right tends to the integral over d of $-[h]\cdot n$, and the second term gives no contribution; we are therefore led to the interfacial mass balance

$$[c]V = [h]\cdot n - H_\alpha - H_\beta. \tag{3.8}$$

If we apply the same procedure to (3.7) with $\gamma = \alpha$, we find that the left side approaches the integral over d of $c^- V$, while the first term on the right tends to the integral over d of $h^-\cdot n$; similarly, for $\gamma = \beta$ the analogous terms become $-c^+ V$ and $-h^+\cdot n$. Thus we are led to the additional balances

$$j_\alpha + CV = c^- V - h^-\cdot n - H_\alpha, \qquad j_\beta - CV = -c^+ V + h^+\cdot n - H_\beta; \tag{3.9}$$

hence, by (3.8),

$$j_\beta = -j_\alpha \equiv j. \tag{3.10}$$

The interfacial field j represents the mass flow by diffusion across the interface in the direction $\mathbf{n}$. We envisage the interface as modelling an actual interface having a small but nonzero thickness, with j the diffusive mass flux through this thickness. By (3.9) and (3.10),

$$j = (C - c^-)V + \mathbf{h}^-\cdot\mathbf{n} + H_\alpha = (C - c^+)V + \mathbf{h}^+\cdot\mathbf{n} - H_\beta, \tag{3.11}$$

so that, for

$$H_\alpha = H_\beta = 0, \tag{3.12}$$

an assumption we will make for the remainder of the section,

$$j = (C - c^-)V + \mathbf{h}^-\cdot\mathbf{n} = (C - c^+)V + \mathbf{h}^+\cdot\mathbf{n}. \tag{3.13}$$

The concentration C can always be written as a weighted average of c^- and c^+; indeed, λ defined by

$$\lambda = (C - c^-)/[c] \tag{3.14}$$

yields $C = \lambda c^+ + (1 - \lambda)c^-$, and, interestingly, by (3.13),

$$j = \lambda\mathbf{h}^+\cdot\mathbf{n} + (1 - \lambda)\mathbf{h}^-\cdot\mathbf{n}. \tag{3.15}$$

Thus j is a weighted average of the bulk diffusive fluxes at each side of the interface with weight equal to that giving C in terms of c^+ and c^-.

Consider the limit, relevant to rapid solidification, in which the growing phase, say phase α, does not diffuse mass; then V must be positive and $\mathbf{h}^-\cdot\mathbf{n} = 0$. In this limit, (3.13) becomes

$$j = (C - c^-)V. \tag{3.16}$$

Since the composition of the α phase is c^-, and since α does not diffuse mass, the mass flux into α is c^-V. By (3.16), if the composition C of the material passing across the interface is equal to c^-, then the diffusive flux j within the interface vanishes:

$$j = 0 \text{ when } C = c^{-}. \tag{3.17}$$

Similarly,

$$j = [c]V \text{ when } C = c^{+}. \tag{3.18}$$

Summarizing: when $C=c^{-}$ there is no diffusion in the interface; when $C=c^{+}$ there is maximal diffusion within the interface. Here it is important to note that (3.16) is a consequence of balance of mass; it does not involve constitutive assumptions other than the presumption that phase α not diffuse mass.

4. BALANCE OF FORCES AND ENERGY. GROWTH OF ENTROPY

4.1. FORCES

We now generalize the configurational force balance to account for the interface. We consider, in addition to the bulk stress $\mathbf{S}$ and bulk internal force $\mathbf{e}$ defined in Section 2.4, an internal force $\boldsymbol{\pi}$ and an external force $\mathbf{f}$, per unit area, applied to the interface. The force $\boldsymbol{\pi}$ is an interfacial counterpart of the bulk configurational force $\mathbf{e}$, and, while $\mathbf{e}$ is generally unimportant, $\boldsymbol{\pi}$ is essential as it represents dissipative forces associated with the kinetics of the interface. We will refer to

$$\pi = \mathbf{n}\cdot\boldsymbol{\pi} \tag{4.1}$$

as the normal internal force. The external force $\mathbf{f}$ is an analog of the supplies introduced previously.

We neglect other configurational forces, such as surface tension, that act within the interface. Balance of forces therefore requires that

$$\int_{\partial D}\mathbf{S}\,da + \int_{D}\mathbf{e}\,dv + \int_{d}\boldsymbol{\pi}\,da + \int_{d}\mathbf{f}\,da = 0 \tag{4.2}$$

for all control volumes D. We do not write a force balance for interactive control volumes. To do this would require additional structure; the resulting theory would be unchanged.

Applying (4.2) to control volumes that exclude the interface yields the bulk relation (2.39), while (4.2) applied to control volumes that include the interface yields the interfacial balance

$$[\mathbf{S}]\mathbf{n} + \boldsymbol{\pi} + \mathbf{f} = \mathbf{0}. \qquad (4.3)$$

Since $\mathbf{S}$ has the specific form (2.38), the normal part of (4.3) is therefore given by

$$[\omega] + \pi + \mathbf{f}\cdot\mathbf{n} = 0. \qquad (4.4)$$

As we shall see, only the normal component of $\boldsymbol{\pi}$ will enter the dissipation inequality for the interface; consistent this, we leave as *indeterminate* the tangential component of $\boldsymbol{\pi}$, and therefore concern ourselves only with π, $\mathbf{f}\cdot\mathbf{n}$, and the *normal component* (4.4) of the configurational force balance (4.3).

Basic to the theory is the manner in which forces expend power. Consider a fixed control volume D that contains a portion of the interface. The stress $\mathbf{S}$ does not expend power on D, because it acts on ∂D, which is stationary, and the forces $\boldsymbol{\pi}$ and $\mathbf{e}$ do not expend power on D, as they act *internally* to D. On the other hand, the external force $\mathbf{f}$ acts on the interface, which evolves with time, and a basic assumption of the theory is that $\mathbf{f}$ expends power over the velocity of the interface. We are therefore led to the following expression for the power expended on D:

$$\int_{d} \mathbf{f}\cdot\mathbf{n}\,V\,da. \qquad (4.5)$$

4.2. BALANCE OF ENERGY. GROWTH OF ENTROPY

We add to the (bulk) thermodynamic fields described in Section 2.2 an interfacial heat supply $Q(\mathbf{x},t)$, which represents an external supply of heat per unit area to the interface. A basic assumption of our theory is that

the temperature T *is continuous across the interface,* (4.6)

but we do not make a similar assumption for the effective chemical potential, as we are interested in situations in which there is "local equilibrium" for heat transfer, but not for mass transfer. Then, arguing as before, we are led to the following versions of balance of energy and growth of entropy for a stationary control volume D:

$$\begin{aligned}\Big\{\int_D \varepsilon\, dv\Big\}^{\cdot} = -\int_{\partial D}(\mathbf{q} + \mu\mathbf{h})\cdot d\mathbf{a} + \int_D (q + \mu h)\, dv \,+ \\ \int_d (Q + \mu^- H_\alpha + \mu^+ H_\beta + V\mathbf{f}\cdot\mathbf{n})\, da,\end{aligned} \tag{4.7}$$

$$\Big\{\int_D \eta\, dV\Big\}^{\cdot} \geq -\int_{\partial D}(\mathbf{q}/T)\cdot d\mathbf{a} + \int_D (q/T)\, dv + \int_d (Q/T)\, dv. \tag{4.8}$$

The first two integrals on the right sides of (4.7) and (4.8) are identical to those of (2.10) and (2.8), as they represent heat, energy, and entropy flows in the bulk material. Thus using control volumes that exclude the interface allows us to recover the results (2.12) and (2.13). The presence of an interface results in the remaining terms on the right sides of (4.7) and (4.8); these represent energy, heat, and entropy supplied to the interface and power expended on the interface.

If we shrink D to the interface using (4.4), (4.6), and an argument analogous to that leading to (3.8), we arrive at expressions for balance of energy and growth of entropy at the interface:

$$\begin{aligned}-[\varepsilon]V &= -[\mathbf{q} + \mu\mathbf{h}]\cdot\mathbf{n} + Q + \mu^- H_\alpha + \mu^+ H_\beta - (\pi + [\omega])V, \\ -[\eta]V &\geq -([\mathbf{q}]\cdot\mathbf{n} - Q)/T.\end{aligned} \tag{4.9}$$

If we combine (4.9) using the free energy (2.11), we find that

$$(\pi - [c\mu])V + [\mu\mathbf{h}]\cdot\mathbf{n} - \mu^- H_\alpha - \mu^+ H_\beta \leq 0. \tag{4.10}$$

This and (3.11) yield the *interfacial dissipation inequality*

$$(\pi - C[\mu])V + j[\mu] \leq 0. \tag{4.11}$$

It is convenient when choosing constitutive laws to define an auxiliary field

$$\Pi = \pi - C[\mu]; \tag{4.12}$$

(4.11) then becomes

$$\Pi V + j[\mu] \le 0. \tag{4.13}$$

As before, the external supplies of heat and mass are not present in the dissipation inequality.

An alternative form of the dissipation inequality follows from (4.11):

$$\pi V + J[\mu] \le 0, \tag{4.14}$$

where

$$J = j - CV \tag{4.15}$$

is the net mass flux across the interface. The constitutive relations that follow from (4.14) are not as transparent as those which can be derived from (4.13), chiefly because the flux J is not purely diffusive: it involves an accretive component CV.

4.3. EFFECTIVE DRIVING FORCE

When the external force f vanishes, the normal configurational force balance takes the form

$$[\omega] - C[\mu] + \Pi = 0, \tag{4.16}$$

where we have used (4.12). Thus, writing

$$E = \psi^{+} - \psi^{-} + \mu^{+}(C - c^{+}) - \mu^{-}(C - c^{-}). \tag{4.17}$$

and appealing to (2.38), we see that

$$E = \omega^{+} - \omega^{-} + C(\mu^{+} - \mu^{-}), \tag{4.18}$$

and hence the normal force balance takes the simple form

$$E + \Pi = 0. \tag{4.19}$$

In the dissipation inequality (4.13) the force Π is conjugate to the normal velocity V and, as we shall see, is purely dissipative. The relation (4.19) balances configurational forces represented by E, which work to equilibrate the system, with dissipative forces represented by Π. We will refer to E as the *effective driving force.* The relation (4.19) for the driving force is general; in particular, it is independent of specific constitutive assumptions.

An assumption of local equilibrium with respect to mass transport would yield the continuity of μ across the interface, in which case E is simply the jump in ω across the interface. The additional term $C(\mu^+ - \mu^-)$ is a direct consequence of a lack of local equilibrium. Since μ represents energy per unit transported mass, $(\mu^+ - \mu^-)C$ gives the additional energy required to transfer (a unit volume of) material of composition C from α of composition c^- to β of composition c^+.

5. CONSTITUTIVE EQUATIONS. THERMODYNAMIC RESTRICTIONS

We consider bulk constitutive equations for each phase γ of the form described in Section 4.2, so that, in particular,

$$\psi(\mathbf{x},t) = \hat{\psi}_\gamma(c(\mathbf{x},t),T(\mathbf{x},t),\nabla c(\mathbf{x},t),\nabla T(\mathbf{x},t)) \tag{5.1}$$

gives the free energy at an arbitrary point $\mathbf{x}$ in phase γ at time t. Similarly, $\hat{\mu}_\gamma$, $\hat{\eta}_\gamma$, $\hat{\mathbf{h}}_\gamma$, and $\hat{\mathbf{q}}_\gamma$ denote the remaining response functions for phase γ.

To these bulk relations we add interfacial constitutive equations giving the composition C of material currently at the interface, the diffusive mass flow j, and the normal configurational force π as functions of the normal $\mathbf{n}$, the normal velocity V, the limiting values $c^\pm$ of the concentration, and the temperature T (cf. (4.6)):

$$C = \hat{C}(\mathfrak{z}), \qquad j = \hat{j}(\mathfrak{z}), \qquad \pi = \hat{\pi}(\mathfrak{z}), \tag{5.2}$$

where $\zeta = (n, V, c^-, c^+, T)$. Note that, by (4.17) and (4.12), the bulk and interfacial constitutive equations yield an auxiliary constitutive relation $\Pi = \hat{\Pi}(\zeta)$.

We do not write constitutive equations for the external fields h, H_α, H_β, q, Q, and f, nor for the stress S, but instead allow them to be assignable in any way compatible with the basic balance laws.

An important special case of these constitutive relations occurs when $\zeta = (V, c^-, c^+, T)$ and defines an isotropic interface; another special case is when $\zeta = (n, c^-, c^+, T)$ and defines a weakly kinetic interface. Note that, by (3.11), this latter definition does not yield interface conditions that are independent of V.

Suppose we are given a smooth motion of the interface together with compatible prescriptions of the fields c and T representing the concentration and temperature. Then the bulk and interfacial constitutive equations may be used to compute the bulk fields μ, ψ, and h, and the interfacial fields C, j, and π; the balance laws for force, mass, and energy can then be used to determine the fields h, H_α, H_β, q, Q, and f needed to support the process. The second law remains to be satisfied in all such constitutive processes, a requirement that will result in restrictions on the constitutive equations. We assume that:

> *the bulk and interfacial dissipation inequalities* (2.13) *and* (4.11) *are satisfied in all constitutive processes.*

For the bulk material we recover the results shown previously for a single-phase material: for each phase γ, the functions $\hat{\psi}_\gamma$, $\hat{\eta}_\gamma$, and $\hat{\mu}_\gamma$, are independent of ∇c and ∇T,

$$\hat{\mu}_\gamma(c,T) = \partial_c \hat{\psi}_\gamma(c,T), \qquad \hat{\eta}_\gamma(c,T) = -\partial_T \hat{\psi}_\gamma(c,T), \tag{5.3}$$

and, assuming as before that $\partial_c \hat{\mu}_\gamma(c,T) > 0$ so that $c = \tilde{c}_\gamma(\mu,T)$,

$$\begin{aligned} \mathbf{h} &= -\mathbf{K}_{\gamma 11}\nabla\mu - \mathbf{K}_{\gamma 12}\nabla T, \\ \mathbf{q} &= -\mathbf{K}_{\gamma 21}\nabla\mu - \mathbf{K}_{\gamma 22}\nabla T, \end{aligned} \tag{5.4}$$

where the coefficient matrices $K_{\gamma ij} = K_{\gamma ij}(\mu,T,\nabla\mu,\nabla T)$ in (5.4) are consistent with the assertions following (2.25).

If we substitute the interfacial constitutive equations into the dissipation inequality (4.13), we find that

$$\hat{\Pi}(\xi)V + \hat{J}(\xi)[\mu] \le 0. \tag{5.5}$$

Since $c = \tilde{c}_\gamma(\mu,T)$, we can replace the constitutive variables c^- and c^+ by μ^- and μ^+. Thus, since a knowledge of μ^- and μ^+ is equivalent to a knowledge of the jump $[\mu]$ and the average[2] $\langle\mu\rangle = (\mu^+ + \mu^-)/2$, we may consider $\hat{J}(\xi)$ and $\hat{\Pi}(\xi)$ as functions $\tilde{J}(n,\langle\mu\rangle,T,V,[\mu])$ and $\tilde{\Pi}(n,\langle\mu\rangle,T,V,[\mu])$; hence (5.5) becomes

$$\tilde{\Pi}(n,\langle\mu\rangle,T,V,[\mu])V + \tilde{J}(n,\langle\mu\rangle,T,V,[\mu])[\mu] \le 0. \tag{5.6}$$

We can always find a motion of the interface and compatible concentration and temperature fields c and T such that n, $\langle\mu\rangle$, T, V, and $[\mu]$ have arbitrarily prescribed values at some chosen point of the interface and some chosen time. Therefore applying the lemma of Section 2.3 to (5.6) with $u = (\tilde{\Pi},\tilde{J})$, $w = (n,\langle\mu\rangle,T)$, and $y = (V,[\mu])$, and then converting back to the constitutive variable ξ, we conclude that there are functions $b(\xi)$, $B(\xi)$, $a(\xi)$, and $A(\xi)$ such that

$$\begin{aligned} \hat{\Pi}(\xi) &= -A(\xi)V - a(\xi)[\mu], \\ \hat{J}(\xi) &= -b(\xi)V - B(\xi)[\mu], \end{aligned} \tag{5.7}$$

where the diagonal coefficients are given by capital letters and the cross-coupling coefficients are given by lower case letters. Moreover, the coefficient matrix

$$\mathbb{B}(\xi) = \begin{pmatrix} A(\xi) & a(\xi) \\ b(\xi) & B(\xi) \end{pmatrix} \tag{5.8}$$

must satisfy the inequality found by substituting (5.7) into (5.5):

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[2] In Section 7 we will use the symbol $\langle\,\rangle$ to denote a certain weighted average.

$$\mathbf{y}\mathbb{B}(\zeta)\mathbf{y}^T \leq 0, \tag{5.9}$$

where the superscript T denotes the transpose. If $\mathbb{B}(\zeta)$ is independent of $\mathbf{y}$, or for small deviations about equilibrium where $\mathbf{y} = \mathbf{0}$, $\mathbb{B}(\zeta)$ must be positive semi-definite to be consistent with the second law. Our thermodynamical development does not require that $\mathbb{B}(\zeta)$ be symmetric, although other physical hypotheses might.

Note that thermodynamics places no restrictions on the constitutive equation $C = \hat{C}(\zeta)$. In particular, the theory does not rule out a dependence of C on velocity (cf., e.g., the model of Eckler et al [29]).

For a weakly kinetic interface the argument ζ is independent of V; thus, since V is arbitrary, we may conclude from (5.5) that

$$\hat{\Pi}(\zeta) = 0, \tag{5.10}$$

and, since $\hat{j}(\zeta)[\mu] \leq 0$, we must have $b(\zeta) = 0$ and

$$j = -B(\zeta)[\mu] \tag{5.11}$$

with $B(\zeta) \geq 0$, so that diffusion across the interface is driven by a jump in chemical potential.

For most problems of interest there are no external supplies of mass, energy, or force. In this case

$$h = H_\alpha = H_\beta = q = Q = 0, \quad f = 0, \tag{5.12}$$

and, by (4.19), the interfacial constitutive equations (5.7) assume the form

$$\begin{aligned} E &= A(\zeta)V + a(\zeta)[\mu], \\ j &= -b(\zeta)V - B(\zeta)[\mu] \end{aligned} \tag{5.13}$$

(or $E = 0$, $j = -B(\zeta)[\mu]$, for a weakly kinetic interface). The relations (5.13), the central results of our theory, are valid in the general case in which there is diffusion in both phases. Here A characterizes the mobility of the interface, while B is the mobility of atoms within the interface. What is interesting and important about (5.13) is that—even though we do *not* assume isothermal conditions—the temperature T appears in (5.13) only as a parameter. Tracing back the steps leading to (5.13), we conclude that, granted (5.12), the entropy Γ produced by the interface per unit area is given by

$$\Gamma = (EV - j[\mu])/T \geq 0. \tag{5.14}$$

Thus, in general, both the mobility of the interface and diffusion across the interface dissipate energy.

In view of the bulk constitutive equations we can express E in the form

$$E = \psi^+ - \psi^- + \partial_C \hat{\psi}_\beta(c^+,T)(C - c^+) - \partial_C \hat{\psi}_\alpha(c^-,T)(C - c^-). \tag{5.15}$$

This yields the tangent-to-tangent construction of Baker and Cahn [30]. For $[\mu]<0$, which might be expected during rapid solidification with α the growing phase, the magnitude of E decreases as the composition C of material being transferred increases. The effects of this decrease are easy to see in the limit where A is a constant and $a=0$. Using (5.13) we see that, in this case, the velocity of the interface must decrease. This decrease in velocity induced by an increase in material being transferred corresponds to what has been termed, in other contexts, "solute drag".

Assume now that the external supplies of mass and energy and the external force vanish. Then the free-boundary problem of the general theory consists of the bulk balance equations (2.26) and the bulk constitutive equations (5.3) and (5.4) in each phase in conjunction with the interface conditions

$$\begin{aligned}
[\varepsilon]V &= [\mathbf{q} + \mu\mathbf{h}]\cdot\mathbf{n}, \\
E &= -A(\varrho)V - a(\varrho)[\mu], \qquad (5.16)\\
(C - c^-)V + \mathbf{h}^-\cdot\mathbf{n} = (C - c^+)V + \mathbf{h}^+\cdot\mathbf{n} &= -b(\varrho)V - B(\varrho)[\mu],
\end{aligned}$$

supplemented by the constitutive equation $C = \hat{C}(\varrho)$. The more standard condition $[c]V = [\mathbf{h}]\cdot\mathbf{n}$ is a consequence of $(5.16)_3$.

These conditions along with (2.11), (4.11), and (5.10) yield the interfacial entropy balance (cf. the second of (4.9)):

$$[\eta]V = T^{-1}[\mathbf{q}]\cdot\mathbf{n} - \Gamma, \tag{5.17}$$

with Γ the interfacial entropy production (5.14).

6. THEORY WHEN ONE PHASE DOES NOT DIFFUSE MASS

We now consider the limit, relevant to rapid solidification, in which the growing phase, say phase α, does not diffuse mass. Then, assuming there are no external supplies of mass, energy, or force (cf. (5.12)), the interface equations consist of (5.16) with $\mathbf{h}^{-}\cdot\mathbf{n} = 0$:

$$\begin{aligned}
[\varepsilon]V &= [\mathbf{q}]\cdot\mathbf{n} + [\mu]\mathbf{h}^{+}\cdot\mathbf{n},\\
[c]V &= \mathbf{h}^{+}\cdot\mathbf{n},\\
E &= -A(\zeta)V - a(\zeta)[\mu],\\
(C - c^{-})V &= -b(\zeta)V - B(\zeta)[\mu].
\end{aligned} \tag{6.1}$$

Here $C = \hat{C}(\zeta)$, with no thermodynamic restrictions placed on this relation. A number of consitutive assumptions have been employed for C, ranging from a constant with the value $c-$ or $c+$ [2], to a continuous function of the velocity V [29]. A simple generalization of the former, ensuring that C lie between c^{-} and c^{+}, is furnished by the relation

$$C = \lambda c^{+} + (1 - \lambda)c^{-}, \qquad \lambda = \text{constant},\ 0 \le \lambda \le 1. \tag{6.2}$$

Here λ is a constitutive modulus characterizing the degree of solute drag: $\lambda = 0$ corresponds to $C = c^{-}$ and no solute drag, while increasing λ corresponds to increasing solute drag, with $\lambda = 1$ associated with $C = c^{+}$.

In standard formulations of rapid solidification problems, the interfacial temperature follows from $(6.1)_3$ and the velocity dependence of the distribution coefficient, $c-/c+$, from $(6.1)_4$. As is clear from (5.15), the temperature of the interface will depend on the degree of solute drag, as E

depends on C. In addition, for $a(\xi)$ nonzero, $(6.1)_3$ yields a kinetic influence on the driving force. As with most other sharp-interface models for rapid solidification, the velocity dependence of the distribution coefficient will depend on the mobility $B(\xi)$ of the atoms within the interface and the jump in the chemical potential across the interface. However, it is clear from $(6.1)_4$ that the distribution coefficient can also depend on the degree of solute drag, due to the presence of C on the left hand side of $(6.1)_4$. In fact, it is therefore possible to construct a general model for the interfacial temperature and distribution coefficient using $(6.1)_{3,4}$; some progress has been made along these lines [31].

7. ISOTHERMAL THEORY IN WHICH BOTH PHASES DIFFUSE MASS; SMALL DEPARTURES FROM EQUILIBRIUM

We now restrict attention to *isothermal* situations and develop an approximate theory—appropriate to small departures from equilibrium—that accounts for diffusion in both phases. The bulk fields of the equilibrium state are denoted by a superscript e and are constant in each phase. Further,

$$[\omega_e] = 0, \qquad [\mu_e] = 0, \tag{7.1}$$

and the constant values of the equilibrium concentration c_e are related to μ_e through the general expression (2.21) for each phase γ:

$$c_e = \tilde{c}_\gamma(\mu_e). \tag{7.2}$$

(Here and in what follows we omit mention of the temperature.)

As we have restricted attention to a theory valid close to equilibrium, we compute the concentration away from equilibrium using the linear approximation

$$c - c_e = \kappa_\gamma u, \tag{7.3}$$

where $\kappa = d\tilde{c}_\gamma(\mu)/d\mu$ at $\mu = \mu_e$ (or equivalently, $\kappa = \{d^2\hat{\psi}_\gamma(c)/dc^2\}^{-1}$ at $c = c_e$) and

$$u = \mu - \mu_e. \tag{7.4}$$

Finally, we assume that the composition C has the form (6.2) with λ a prescribed constitutive modulus.

For convenience, we introduce, for any function φ defined near the interface, the (λ-weighted) interfacial average $\langle\varphi\rangle$ and its conjugate $\langle\varphi\rangle^*$:

$$\langle\varphi\rangle = \lambda\varphi^+ + (1-\lambda)\varphi^-, \qquad \langle\varphi\rangle^* = \lambda\varphi^- + (1-\lambda)\varphi^+; \tag{7.5}$$

we then have the useful identity

$$[\varphi\beta] = \langle\varphi\rangle[\beta] + [\varphi]\langle\beta\rangle^*, \tag{7.6}$$

and, what is more important, (6.2) yields

$$C = \langle c\rangle, \qquad C_e = \langle c_e\rangle. \tag{7.7}$$

(In our discussion of constitutive equations, for example in (5.6), $\langle\varphi\rangle$ was used to denote $(7.5)_1$ with $\lambda = 1/2$.)

Our first step will be to obtain an approximate expression for the effective driving force E; for this calculation it is most convenient to write the expression (4.18) for E in the form

$$E = [\psi] + [(C-c)\mu]. \tag{7.8}$$

Expanding $[\psi]$ about equilibrium we conclude, with the aid of (5.3) that

$$[\psi] = [\psi_e] + [\mu_e(c-c_e)] + \text{h.o.t.}, \tag{7.9}$$

where "h. o. t." is shorthand for terms of order higher than one in $|c^\pm - c_e^\pm|$. Thus, by (7.1) and (7.4),

$$E = [u(C_e - c_e)] + \text{h.o.t.} \tag{7.10}$$

Therefore, writing

$$\nu = [c_e] \tag{7.11}$$

and using (7.5)-(7.7), we may conclude that

$$E = -\nu\langle u\rangle^{*} + \text{h.o.t.} \tag{7.12}$$

Since we have restricted attention to isothermal situations, we omit the interface condition $(5.16)_1$ expressing balance of energy. Further, because of the specific form (6.2) for C, the interface conditions $(5.16)_{2,3}$ are best expressed in terms of $\langle \mathbf{h}\cdot\mathbf{n}\rangle$ and $[\mathbf{h}\cdot\mathbf{n}]$. Thus, neglecting higher-order terms in (7.12), and assuming that the moduli A, a, b, and B are constant, we are led to the following approximate form for $(5.16)_{3,4}$:

$$\begin{aligned} \nu\langle u\rangle^{*} &= AV + a[u], \\ \langle \mathbf{h}\cdot\mathbf{n}\rangle &= -bV - B[u], \\ [\mathbf{h}\cdot\mathbf{n}] &= \nu V, \end{aligned} \tag{7.13}$$

where $(7.13)_2$ follows upon using (6.2) and $(5.16)_2$ in (5.13), and where, in writing $(7.13)_3$, we have approximated $[c]V$ by νV.

Note that these linearized interface conditions, which allow for diffusion in both phases, do not include an explicit expression for the velocity dependence of the distribution coefficient $k = c^{-}/c^{+}$. The usual expression for k is replaced by an expression for the average value of the bulk fluxes at the interface. Further, although C does not appear explicitly in the interface conditions, solute drag still influences the interfacial conditions through the λ dependence of the averages $\langle u\rangle^{*}$ and $\langle \mathbf{h}\cdot\mathbf{n}\rangle$.

For the bulk material, we take the constitutive relation (5.4) for the flux $\mathbf{h}$ in the form

$$\mathbf{h} = -\mathbf{K}_{\gamma}\nabla u \tag{7.14}$$

for each phase $\gamma = \alpha, \beta$, where the tensors $\mathbf{K}_{\gamma}$ are constant. Thus, neglecting the external supply of mass, the diffusion equation to be satisfied by u in bulk follows from (7.3) and the local mass balance (2.6):

$$\kappa_{\gamma}\dot{u} = \operatorname{div}(\mathbf{K}_{\gamma}\nabla u) \tag{7.15}$$

in each of the bulk phases $\gamma = \alpha, \beta$.

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Figure Caption

Figure 1. The control volume D, which contains material in both the α and β phases. The intersection of D with the interface is a surface d with boundary curve ∂d. Also noted are: the interactive control volumes D_α and D_β, which are the portions of D in α and β; the boundary ∂D of D; and the portions $(\partial D)_\alpha$ and $(\partial D)_\beta$ of ∂D that lie in α and β.