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THE CONTINUUM MECHANICS OF COHERENT TWO-PHASE ELASTIC SOLIDS WITH MASS TRANSPORT

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1. Introduction.

Diffusional phase transitions in crystalline solids are often isothermal and accompanied by deformation induced by a difference in lattice parameters between the two phases. Examples of such transformations are the Ostwald ripening of two-phase mixtures, and the growth of second-phase domains from a supersaturated matrix. The influence of deformation on the evolution of microstructure during Ostwald ripening is clear: in its absence the microstructure is statistically asymptotically time-invariant when scaled by the average particle size (Lifschitz and Slyozov 1961), but in the presence of deformation this scaled time-invariant structure no longer exists. Indeed, as noted in the reviews of Johnson and Voorhees (1992) and Voorhees (1992), the morphology and spatial distribution of the particles change during ripening, and the theoretical studies of Enomoto and Kawasaki (1989), Nishimori and Onuki (1990, 1991), Leo, Mullins, Sekerka and Vinals (1990), and Abinandanan (1991) and the experiments of Miyazaki, Doi and Kozakai (1988) and Miyazaki and Doi (1989) show that deformation can alter the temporal power-law for the average particle size during ripening. Thus central to understanding the kinetics of coarsening is a description of the dynamics of an interface driven by mass transport and stress.

Deformation also has a pronounced effect on the equilibrium shape of a particle in a matrix. For an isolated particle in the absence of deformation this shape minimizes interfacial energy under the constraint of fixed volume (Wulff's problem); as proved by Taylor (1978) and Fonseca (1991), the minimizing shape is necessarily convex and independent of particle size. In contrast, the equilibrium shape of a misfitting particle (a particle with nonzero stress-free transformation strain) can depend on its size. This size dependence is illustrated by the particle morphologies shown in Figure 1. In this case the Ni_3Al particles can be nearly spherical at small sizes, cuboidal at intermediate sizes, and plate-like at large sizes. Further, the recent experiments of Maheshwari and Ardell (1992) show that the equilibrium shape of a particle may be nonconvex. In addition, the literature is replete with examples of the strong effect an applied stress has on the shape of a particle (cf. Johnson and Voorhees 1992); for example, an applied uniaxial stress can cause an array of particles to transform to plates oriented parallel or perpendicular to the applied stress. Unfortunately, there has been little work on the derivation of variational principles that define the equilibrium shape of a particle of variable composition in the presence of deformation due to either a misfit or an applied stress.

It is our purpose here to develop a theory for the dynamics of an interface in a two-phase elastic solid with kinetics driven by mass transport and stress. Typically, such theories have been based on an approximation of local equilibrium, wherein the thermodynamical conditions at an interface are determined as Euler-Lagrange equations for a global Gibbs function to be stationary and then used to describe a moving interface not in equilibrium. While this description is of great utility, we show that it is possible to develop a dynamical description of a moving interface directly, thus circumventing the assumption of local equilibrium.

We follow the theoretical framework developed by Gurtin (1988) and Gurtin and Struthers (1990). We consider a two-phase system consisting of bulk regions separated by a sharp interface endowed with energy and capable of supporting force. We base our discussion on balance laws for mass and force in conjunction with a version of the second law — appropriate to a mechanical system out of equilibrium —

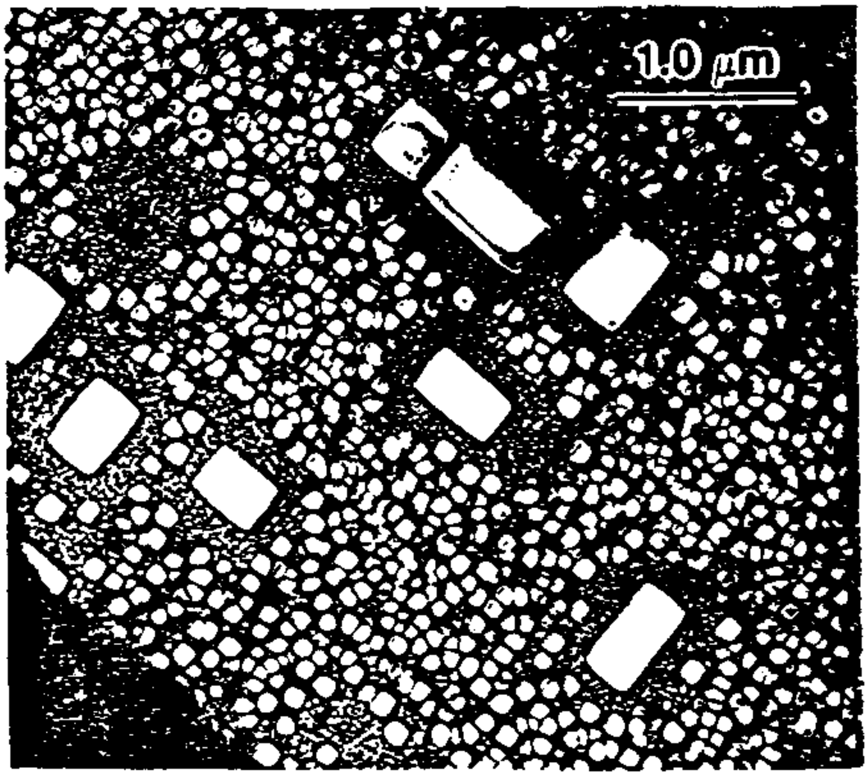

Figure 1. A dark-field transmission-microscope picture of NI$_3$A1 particles in a disordered NiAl matrix. The nonzero stress-free transformation strain between the Ni,A1 and Ni lattices induces an elastic stress which, in turn, results In a size dependence of the equilibrium particle-shapes (Kaufman, Voorhees, and Biancanieiio 1966).

which 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; we neglect mass diffusion within the interface. In addition, we limit our discussion to a continuous diffusion potential (chemical potential) and to a coherent interface, we neglect the elasticity of the interface, and we consider only infinitesimal deformations, neglecting inertia. (The generalization to multi-component systems involves neither conceptual nor analytical difficulty; the inclusion of inertia and the extension to finite strains and interfacial elasticity follows as in Gurtin and Struthers 1990; the extension to a discontinuous chemical potential can be carried out using the analysis of Gurtin and Voorhees 1992.)

Our study is related to the thermodynamics of solid-liquid interfaces developed by Caroli, Caroli, and Roulet (1984), which is a nonequilibrium theory based on a treatment of immiscible fluids by Bedeaux, Albano and Mazur (1976), Kovak (1977), and Vodak (1978). Our work differs from that of Caroli, Caroli, and Roulet in many respects, of which we mention two:

(i) Caroli, Caroli, and Roulet consider only one force system, while we follow Gurtin and Struthers (1990) and consider two, each with its own force balance: a deformational system that arises as a response to the motion of material points; an accretional system needed to describe the power expended on the motion of the interface. That additional forces may be required is at least intimated by Gibbs (1878) and Cahn (1980), who note that the area of a solid surface may be changed by creating or destroying surface or by an elastic strain, and that each of these kinematical processes leads to a conjugate thermodynamic surface stress. This observation is strengthened by the variational calculations of Alexander and Johnson (1985, 1986) and Leo and Sekerka (1989) in which an additional scalar balance law arises as an Euler-Lagrange equation corresponding to variations in the position of the interface.

(ii) Caroli, Caroli, and Roulet postulate a Gibbs relation for the interface and bulk phases; in contrast we apply an extension (Gurtin 1988) of a proceedure developed by Coleman and Noll for single-phase systems to develop a thermodynamically consistent constitutive theory; in our work the Gibbs relation - linking the free energy, composition, chemical potential, stress, and strain - is a consequence rather than a postulate.

Using this thermodynamic framework it is possible to derive the field equations that describe mass flow in the bulk phases in a manner consistent with the approximations employed in developing the interface conditions. We show that the field equations can be developed in a simple manner in terms of the chemical potential and its time derivatives, as opposed to the usual formulation in terms of concentration.

Natural consequences of the underlying thermodynamic framework are Lyapunov functions for the resulting evolution problems. In this manner we are led to a heirachy of variational principles that should describe the equilibrium shapes of misfitting particles as well as possible microstructures that might form; these principles are applicable both in the absence and presence of an applied stress.

2. The interface. Notation.

We write $\Phi^{\cdot}$ for the *time derivative* of a function $\Phi(t)$ or of a function $\Phi(x,t)$ holding x fixed; $\partial_z\Phi$ for the partial (and sometimes total derivative) of a function Φ with respect to a scalar, vector, or tensor variable z; and Φ' for the derivative of a function Φ of a single scalar variable.

We consider a body $\Omega \subset \mathbb{R}^3$ consisting of two phases, labelled α and β, separated, at each time t, by an **interface** $\mathcal{S}(t)$, and write $\Omega_\alpha(t)$ and $\Omega_\beta(t)$ for the subregions of the body occupied by phases α and β. We assume that the **phase regions** $\Omega_\alpha(t)$ and $\Omega_\beta(t)$ are closed regions with Ω as their union and $\mathcal{S}(t)$ as their intersection; and that $\mathcal{S}(t)$ is a smoothly propagating surface *that does not intersect* $\partial\Omega$. We orient $\mathcal{S}(t)$ by choosing the unit normal field $\mathbb{m}(x,t)$ such that:

$\mathbb{m}(x,t)$ *coincides with the outward unit normal to* $\partial\Omega_\alpha(t)$.

We write $V(\mathbf{x},t)$ for the **normal velocity** of $\mathcal{S}(t)$ in the direction $\mathbf{n}(\mathbf{x},t)$ and K for (twice) the **mean curvature** (with $K<0$ for Ω_α a ball).

We use the notation and results of Gurtin and Murdoch (1974) and Gurtin (1988) concerning surfaces. In particular, we write Φ° for the *normal time-derivative* of a function Φ (the derivative following the interface), and $\nabla_{\mathcal{S}}$ and $\mathrm{div}_{\mathcal{S}}$ for the *surface gradient* and *surface divergence* on the interface. We then have the identity

$$\mathbf{n}^\circ = -\nabla_{\mathcal{S}} V. \tag{2.1}$$

Let $\mathcal{R}(t)$ denote a smoothly propagating subsurface of $\mathcal{S}(t)$ (see Figure 1), and let $\boldsymbol{\nu}(\mathbf{x},t)$ with $\boldsymbol{\nu}\cdot\mathbf{n} = 0$ denote the outward unit normal to the boundary curve $\partial\mathcal{R}(t)$. The motion of the curve $\partial\mathcal{R}(t)$ may be characterized intrinsically by the velocity field

$$v_{\partial\mathcal{R}} = V\mathbf{n} + v_{(\partial\mathcal{R})\tan}\boldsymbol{\nu}, \tag{2.2}$$

where $v_{(\partial\mathcal{R})\tan}$, the **tangential edge velocity**, is the velocity of $\partial\mathcal{R}$ in the direction $\boldsymbol{\nu}$: given any local parametrization $\mathbf{x} = \mathbf{r}(u,t)$ for $\partial\mathcal{R}(t)$, $v_{(\partial\mathcal{R})\tan}(\mathbf{x},t) = \boldsymbol{\nu}(\mathbf{x},t)\cdot\mathbf{r}_t(u,t)$ $(\mathbf{r}_t = \partial\mathbf{r}/\partial t)$. We will refer to $v_{\partial\mathcal{R}}$ as the **intrinsic velocity of** $\partial\mathcal{R}$.

Our theory is characterized by: (i) **bulk fields**, defined in $\Omega_\alpha(t)$ and $\Omega_\beta(t)$ for all t, that describe the bulk behavior of the individual phases; (ii) **interfacial fields**, defined on $\mathcal{S}(t)$ for all t, that describe the behavior of the interface. We will generally not specify regularity hypotheses other than to note that *bulk fields are allowed to suffer jump discontinuities across the interface.* For Φ a bulk field, we write Φ^- and Φ^+ 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: for $\mathbf{x}\in\mathcal{S}(t)$,

$$\Phi^-(x,t) = \lim_{\substack{y\to x\\ y\in\Omega_\alpha(t)}} \Phi(y,t), \qquad \Phi^+(x,t) = \lim_{\substack{y\to x\\ y\in\Omega_\beta(t)}} \Phi(y,t), \tag{2.3}$$

$$[\Phi] = \Phi^+ - \Phi^-. \tag{2.4}$$

Let $\mathscr{r}(t)$ denote a smoothly propagating subsurface of $\mathscr{s}(t)$, and let $\boldsymbol{\nu}(x,t)$ denote the outward unit normal to the boundary curve $\partial\mathscr{r}(t)$. The following transport identity, valid for any interfacial field φ, will be useful:

$$\Big\{\int_{\mathscr{r}} \varphi\, da\Big\}^{\boldsymbol{\cdot}} = \int_{\mathscr{r}} (\varphi^\circ - \varphi K V)\, da + \int_{\partial\mathscr{r}} \varphi\, v_{(\partial\mathscr{r})\tan}\, ds \tag{2.5}$$

(cf. Petryk and Mroz 1986; Gurtin, Struthers, and Williams 1989; Estrada and Kanwal 1991; Jaric 1991).

R will *always* denote a control volume (subregion of Ω) with $\mathbf{n}_R$ the outward unit normal on ∂R (see Figure 2). Let R contain the interface, and let $\mathscr{r}$ be the portion of the interface that lies in R:

$$\mathscr{r}(t) = R \cap \mathscr{s}(t). \tag{2.6}$$

Another important transport identity, valid for Φ a bulk field, is

$$\Big\{\int_R \Phi\, dv\Big\}^{\boldsymbol{\cdot}} = \int_R \Phi^{\boldsymbol{\cdot}}\, dv - \int_{\mathscr{r}} [\Phi] V\, da; \tag{2.7}$$

this yields the limiting relation

$$\Big\{\int_R \Phi\, dv\Big\}^{\boldsymbol{\cdot}} \longrightarrow -\int_{\mathscr{r}} [\Phi] V\, da \tag{2.8}$$

as R shrinks to the interface. Further, $\mathbf{n}_R$ has limit $-\mathbf{m}$ or $\mathbf{m}$ as ∂R approaches the interface from phase α or phase β, respectively.

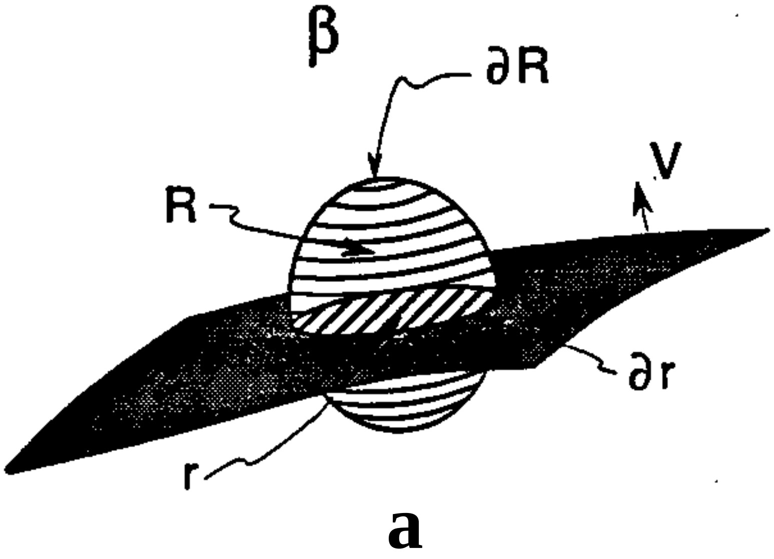

Figure 2. A control volume R.

Thus, for f a bulk vector field,

$$\int_{\partial R} f\cdot n_R\,da \;\longrightarrow\; \int_{\mathcal{S}} [f]\cdot \mathbf{m}\,da. \qquad (2.9)$$

We will repeatedly use the surface divergence-theorem for vector fields $\mathbf{f}$ tangential to the interface and for superficial tensor fields $\mathbb{C}$:

$$\int_{\partial\mathcal{S}} \mathbf{f}\cdot\boldsymbol{\nu}\,ds = \int_{\mathcal{S}} \mathrm{div}_{\mathcal{S}}\mathbf{f}\,da, \qquad \int_{\partial\mathcal{S}} \mathbb{C}\boldsymbol{\nu}\,ds = \int_{\mathcal{S}} \mathrm{div}_{\mathcal{S}}\mathbb{C}\,da \qquad (2.10)$$

(cf. Gurtin 1988).

The identity (2.7) — with $R=\Omega$, $\Phi(x,t)\equiv 1$ in $\Omega_\alpha(t)$, $\Phi(x,t)\equiv 0$ in $\Omega_\beta(t)$ — yields

$$\mathrm{vol}(\Omega_\alpha)^\cdot = \int_{\mathcal{S}} V\,da, \qquad (2.11)$$

where vol(A) denotes the volume of a set A. More generally, when Φ is *spatially constant* in each of the phase regions,

$$\Big\{\int_{\Omega} \Phi\,dv\Big\}^\cdot = -[\Phi]\,\mathrm{vol}(\Omega_\alpha)^\cdot \qquad (2.12)$$

3. Basic quantities.

We assume that the motion of the phase interface is induced by deformation and by the diffusion of a *single independent chemical component*. We neglect mass flow within the interface, and therefore consider the behavior of the body as characterized by the following fields:

bulk fields

$\psi(x,t)$, energy (volume),
$\rho(x,t)$, density (volume),

$\mu(x,t)$, **diffusion potential**,
$\mathbf{h}(x,t)$, **mass flux** (area),
$\mathbf{T}(x,t)$, **deformational stress** (area),
$\mathbf{u}(x,t)$, **displacement**,

interfacial fields

$f(x,t)$, **energy** (area),
$\mathbb{C}(x,t)$, **accretive stress** (length),
$\mathbb{\pi}(x,t)$, **interaction** (area),

where (volume) is shorthand for "per unit volume", and so forth. For the bulk fields: ψ, ρ, and μ are scalar fields, $\mathbf{h}$ and $\mathbf{u}$ are vector fields, and $\mathbf{T}$ is a *symmetric* tensor field. For the interfacial fields: f is a scalar field, $\mathbb{\pi}$ is a vector field, and $\mathbb{C}$ is a tensor field.

A basic asumption of our theory is that:

> *the diffusion potential* μ *and the displacement* $\mathbf{u}$
> *are continuous across the interface.*

The continuity of $\mathbf{u}$ renders the interface *coherent:* the two phases neither slip nor separate at the interface. A consequence is the jump condition

$$[\mathbf{u}'] = -V[\nabla \mathbf{u}]\mathbb{m}. \tag{3.1}$$

We restrict attention to infinitesimal deformations, and therefore characterize strains using the (infinitesimal) **strain tensor**

$$\mathbf{E} = \tfrac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^{\mathrm{T}}), \tag{3.2}$$

with $\nabla \mathbf{u}^{\mathrm{T}}$ the transpose of $\nabla \mathbf{u}$.

We define the **bulk Gibbs function** ω through

$$\omega = \psi - \mu\rho. \tag{3.3}$$

Our theory is purely mechanical: the only active processes are deformation and mass transport. We use the terms "energy" and "Gibbs function" in a generic sense; the thermodynamic potential actually represented depends on which thermodynamic theory this *purely mechanical theory* is meant to "approximate". For an isothermal thermodynamic system our energy is the Helmholtz free energy, while the Gibbs function is the grand canonical free energy.

The theory generalizes almost without change to N independent species. An example with a single component arises when the mobile atoms are interstitial and of the same species. An example with a single *independent* component is a binary substitutional alloy all of whose atoms lie on lattice points; here the densities and mass fluxes of the individual components satisfy

$$\rho_1 + \rho_2 = \text{constant}, \qquad \mathbf{h}_1 = -\mathbf{h}_2,$$

and our theory is applicable with

$$\rho = \tfrac{1}{2}(\rho_1 - \rho_2), \qquad \mathbf{h} = \mathbf{h}_1, \qquad \mu = \mu_1 - \mu_2;$$

we could also take $\rho = \rho_1$, $\mathbf{h} = \mathbf{h}_1$, $\mu = \mu_1 - \mu_2$, but then the Gibbs function $\omega = \psi - \rho\mu$ depends on the choice of independent component.

4. Balance of forces.

The results of this section are taken from Gurtin (1988) and Gurtin and Struthers (1990). We consider two force systems, an accretive force system, characterized by $\mathbf{C}$ and $\boldsymbol{\pi}$, that acts within the crystal lattice to drive the transformation process, and a deformational force system, characterized by the more classical bulk stress $\mathbf{T}$, that acts in response to deformation; what is most important,

> *we presume that each of these systems*
> *is governed by its own force balance.*

We do not include a deformational stress within the interface, an assumption equivalent to neglecting the dependence of interfacial energy on strain (Cahn and Larche' 1982, Leo and Sekerka 1989, Gurtin and Struthers 1990).

4.1. Accretive force-balance.

Let $\mathcal{R}(t)$ be a subsurface of $\mathcal{S}(t)$, and let $\boldsymbol{\nu}(x,t)$ be the outward unit normal to the boundary curve $\partial\mathcal{R}(t)$. The integrals

$$\int_{\partial\mathcal{R}} \mathbb{C}\boldsymbol{\nu}\, ds, \qquad \int_{\mathcal{R}} \boldsymbol{\pi}\, ds \tag{4.1}$$

represent forces involved with the *creation* of new surface: the first gives the force exerted across $\partial\mathcal{R}$ by the portion of the interface exterior to $\mathcal{R}$; the second represents forces exerted on $\mathcal{R}$ by the bulk material. We assume that these forces are balanced in the sense of the **accretive force-balance**

$$\int_{\partial\mathcal{R}} \mathbb{C}\boldsymbol{\nu}\, ds + \int_{\mathcal{R}} \boldsymbol{\pi}\, da = 0 \tag{4.2}$$

for all subsurfaces $\mathcal{R}(t)$ of $\mathcal{S}(t)$. The surface divergence theorem then yields the local force balance

$$\mathrm{div}_{\mathcal{S}}\,\mathbb{C} + \boldsymbol{\pi} = 0. \tag{4.3}$$

Let $\boldsymbol{\nu}$ be an arbitrary vector tangent to the interface at $\mathbf{x}$ and t. The force $\mathbb{C}(x,t)\boldsymbol{\nu}$ will generally have a component *normal* to the interface, a component characterized by the *tangent* vector

$$\mathbf{c}(x,t) = \mathbb{C}(x,t)^{T}\mathbf{m}(x,t),$$

which we call the **surface shear**. Using $\mathbf{c}(x,t)$ we can write $\mathbb{C}(x,t)$ as a tensor $\mathbb{C}_{\tan}(x,t)$ that maps tangent vectors into tangent vectors plus the tensor **n(x,t)®c(x,t).** which maps tangent vectors into normal vectors:

$$C(x,t)F - C_{tan}(x,t)v + [c(x,t)\cdot v]m(x,t).$$

We assume that the tangential stress $C_{ten}(x,t)$ is a scalar **surface tension** cr(x,t) in the sense that $C_{tan}(x,t)v$«cr(x,t)v for all tangent vectors V. Then

$$C(x.t)v \text{ « tfCx.Ov • } [c(x,t)v]mi(x,t). \qquad (4.4)$$

(Granted the results (6.5) and (7.15), the vector *an* + **e** is the |-vector of Cahn and Hoffman (1974).) An argument of Gurtin and Struthers (1990) may be used to *prove* that C_{tan} is necessarily a surface tension *a.*

The interaction W represents the force exerted by the bulk material on the interface, and the velocity conjugate to this force is the velocity of the interface. The intrinsic motion of the interface is normal to itself: tangential motion is irrelevant. The essential component of W is therefore the **normal Interaction**

$$\text{IT} = v\text{-}n, \qquad (4.5)$$

which acts conjugate to the normal velocity V. The tangential component of « is needed to balance forces, but other than that it is irrelevant; we will regard this tangential component as indeterminate, its value being determined by the tangential component of (4.3). On the other hand, the normal component of (4.3), the **normal force balance**

$$\sigma\text{K} + \text{div\^{}C} + \text{IT} \text{ « } 0, \qquad (4.6)$$

plays a central role in the theory. .

4.2. Deformational force-balance.

Consider an arbitrary fixed control volume R. Since we neglect inertia as well as deformational stresses in the interface, balance of deformational forces has the simple form

$$\int_{\partial R} T n_R \, da = 0, \qquad (4.7)$$

which yields the classical relation

$$\operatorname{div} T = 0 \qquad (4.8)$$

in bulk in conjunction with the interfacial balance

$$[T]\mathbb{m} = 0. \qquad (4.9)$$

4.3. Expended power.

Let R be a control volume, let $\mathscr{r}$ be the portion (2.6) of the interface that lies in R, and let $\boldsymbol{\nu}$ denote the outward unit normal to $\partial\mathscr{r}$. The integral $(4.1)_1$ characterizes the force exerted on R *by the portion of the interface* exterior to $\mathscr{r}$. This portion of the interface also expends power on R, and a basic assumption of our theory is that this power expenditure be reckoned using the intrinsic velocity $v_{\partial\mathscr{r}}$ of the boundary curve $\partial\mathscr{r}$:

$$\int_{\partial\mathscr{r}} \mathbb{C}\boldsymbol{\nu}\cdot v_{\partial\mathscr{r}} \, ds. \qquad (4.10)$$

Accretive power balance. *The accretive power expenditure may be written in the form:*

$$\int_{\partial\mathscr{r}} \mathbb{C}\boldsymbol{\nu}\cdot v_{\partial\mathscr{r}} \, ds = -\int_{\mathscr{r}} (\sigma K V + \mathbf{c}\cdot\mathbb{m}^{\circ} + V\pi) \, da + \int_{\partial\mathscr{r}} \sigma v_{(\partial\mathscr{r})\tan} \, ds. \qquad (4.11)$$

The term $-\sigma K V$ represents power expended in creating new surface; $-\mathbb{c}\cdot\mathbb{n}^\circ$ represents power expended in changing the orientation of the interface; $-\pi V$ represents power expended in the exchange of matter between phases; $\sigma v_{(\partial \mathscr{r})\tan}$ represents power expended through the tangential motion of $\partial \mathscr{r}$.

To derive (4.11), note that, by (2.2) and (4.4),

$$\mathbb{c}\boldsymbol{\nu}\cdot v_{\partial \mathscr{r}} = \sigma v_{(\partial \mathscr{r})\tan} + V\mathbb{c}\cdot\boldsymbol{\nu}.$$

Further, by (2.1), $\mathrm{div}_{\mathscr{s}}(V\mathbb{c}) = V\mathrm{div}_{\mathscr{s}}\mathbb{c} - \mathbb{c}\cdot\mathbb{n}^\circ$; the surface divergence theorem and (4.6) therefore yield (4.11).

The power expended on R by the deformational stress is given by

$$\int_{\partial R} T\mathbf{n}_R\cdot\mathbf{u}'\,da. \tag{4.12}$$

If R does not contain the interface, then, by (4.8) and the symmetry of T,

$$\int_{\partial R} T\mathbf{n}_R\cdot\mathbf{u}'\,da = \int_R T\cdot E'\,dv; \tag{4.13}$$

if R contains the interface, with $\mathscr{r}$ the portion of the interface in R, then (2.9), (4.7), and (4.9) yield the conclusion that, as R shrinks to the interface,

$$\int_{\partial R} T\mathbf{n}_R\cdot\mathbf{u}'\,da \longrightarrow \int_{\mathscr{r}} T\mathbb{n}\cdot[\mathbf{u}']\,ds = -\int_{\mathscr{r}} VT\mathbb{n}\cdot[\nabla\mathbf{u}]\mathbb{n}\,ds. \tag{4.14}$$

Further, since the interface is coherent $[\nabla\mathbf{u}]\mathbb{t} = 0$ for every vector $\mathbb{t}$ tangent to the interface; thus, since T is symmetric,

$$T\mathbb{n}\cdot[\nabla\mathbf{u}]\mathbb{n} = T^{\pm}\cdot[E] = [T\cdot E]. \tag{4.15}$$

5. Balance of mass.

Balance of mass is the requirement that

$$\Big\{\int_R \rho\, dv\Big\}^{\cdot} = -\int_{\partial R} \mathbf{h}\cdot\mathbf{n}_R\, da. \qquad (5.1)$$

for all control volumes R. Applying (5.1) to control volumes that exclude the interface leads to the the standard bulk relation

$$\rho^{\cdot} = -\operatorname{div} h \qquad (5.2)$$

(to be satisfied in each of the bulk regions for all time). On the other hand, shrinking a control volume R (with $\mathcal{r} \neq \emptyset$) to the interface in (5.1) using (2.8) and (2.9) yields the **interfacial mass balance**

$$[\rho]V = [h]\cdot\mathbb{m} \qquad (5.3)$$

(to be satisfied on the interface for all time).

6. Global dissipation.

Within a mechanical theory of the type considered here, the second law is the assertion that the rate of energy increase cannot be greater than the power expended plus the energy inflow due to diffusion. Given an arbitrary control volume R,

$$\int_R \psi\, dv + \int_{\mathcal{r}} f\, da$$

is the total energy of R, (4.10) gives the power expended on R by the interface, (4.12) gives the power expended on R by the bulk stresses,

$$-\int_{\partial R} \mu \mathbf{h}\cdot\mathbf{n}_R \, da$$

is the energy carried into R by diffusion. The second law thus has the form of the **global dissipation inequality**

$$\Big\{\int_R \psi \, dv + \int_{\mathscr{r}} f \, da\Big\}' \le \int_{\partial \mathscr{r}} \mathbb{C}\boldsymbol{v}\cdot\mathbf{v}_{\partial \mathscr{r}} \, ds + \int_{\partial R} \mathbf{T}\mathbf{n}_R\cdot\mathbf{u}' \, da - \int_{\partial R} \mu \mathbf{h}\cdot\mathbf{n}_R \, da \qquad (6.1)$$

to be satisfied for all time and for all control volumes R. This version of the second law can be derived as a consequence of balance of energy and growth of entropy under the assumption of constant temperature (Gurtin 1991).

If we apply (6.1) to control volumes that exclude the interface, we conclude, with the aid of (4.13), that

$$\psi' \le \mathbf{T}\cdot\mathbf{E}' - \mathrm{div}(\mu \mathbf{h}), \qquad (6.2)$$

which may be combined with (3.3) and (5.2) to give the **bulk dissipation inequality**

$$\omega' + \rho\mu' - \mathbf{T}\cdot\mathbf{E}' + \mathbf{h}\cdot\nabla\mu \le 0. \qquad (6.3)$$

The global dissipation inequality yields important results regarding the interface. If we apply (6.1) to a control volume R (with $\mathscr{r} \ne \emptyset$), and then shrink R to the interface, we conclude, with the aid of (2.5), (2.8), and (4.11), that

$$\int_{\mathscr{r}} \Big\{(-[\psi] + \pi + [\mathbf{T}\cdot\mathbf{E}])V + f^\circ + \mathbf{c}\cdot\mathbb{m}^\circ + (\sigma - f)KV + \mu[\mathbf{h}]\cdot\mathbb{m}\Big\} da \le$$

$$\int_{\partial \mathscr{r}} (\sigma - f) v_{(\partial \mathscr{r})\tan} \, ds. \qquad (6.4)$$

This inequality must hold for all smoothly propagating subsurfaces t(t) of the interface. Given any such *(t) and any time t_0, we can find another smoothly propagating subsurface that coincides with *v(t) at $t«t_0$, but has $v_{(K)tan}$ an arbitrary scalar field at $t»t_0$. The coefficients of $v_{(d>t)tari}$ In (6.4) must therefore vanish, and this yields

$$cr - f. \qquad (6.5)$$

In analyzing this equality of surface energy f and surface tension cr it must be remembered that cr involves only accretive forces: or performs work only when new surface is created or destroyed.

Returning to (6.4), we may use (3.3), (5.3), and (6.5) to deduce the **Interfacial dissipation Inequality**

$$f^{\circ} + cmi^{e} + QV\ i\ O, \qquad (6.6)$$

with to the bulk Gibbs function (3.3) and

$$Q = IT - [u] + [TE]. \qquad (6.7)$$

The energy dissipated in an arbitrary control volume R is the right side of (6.1) minus the left, and is given by

$$£)(R) = |_{R} rdv + |_{n,} rda \geq 0, \qquad (6.8)$$

with the **Interfaciai and bulk energy dissipation,** 7 and I", defined by

$$-7 - f \bullet c.n- \bullet QV \leq 0. \qquad (6\,g)$$

$$-r - u'' \bullet pp.* - TE' \bullet hVu, \leq 0.$$

7. Constitutive equations.

7.1. Bulk constitutive equations.

We consider bulk constitutive equations of the form

$$\omega = \omega_\alpha(\mu,\mathbf{p},\mathbf{E}), \qquad \rho = \rho_\alpha(\mu,\mathbf{p},\mathbf{E}),$$
$$\mathbf{T} = \mathbf{T}_\alpha(\mu,\mathbf{p},\mathbf{E}), \qquad \mathbf{h} = \mathbf{h}_\alpha(\mu,\mathbf{p},\mathbf{E}), \tag{7.1}$$

in phase α and

$$\omega = \omega_\beta(\mu,\mathbf{p},\mathbf{E}), \qquad \rho = \rho_\beta(\mu,\mathbf{p},\mathbf{E}),$$
$$\mathbf{T} = \mathbf{T}_\beta(\mu,\mathbf{p},\mathbf{E}), \qquad \mathbf{h} = \mathbf{h}_\beta(\mu,\mathbf{p},\mathbf{E}), \tag{7.2}$$

in phase β, with $\mathbf{p} = \nabla\mu$ the potential gradient and $\mathbf{E}$ the infinitesimal strain (3.2).

We assume that the bulk constitutive equations are *compatible with the second law* in the sense that

> *the bulk dissipation inequality* (6.3) *is satisfied for all choices of the fields representing the displacement and the diffusion potential.*

To determine the consequences of this assumption, we restrict attention to one of the phases and, for convenience, omit the corresponding subscript α or β. Then, writing $\mathbf{Z} = (\mu,\mathbf{p},\mathbf{E})$, we see that, granted (7.1), (6.3) is equivalent to the inequality

$$\partial_{\mathbf{p}}\omega(\mathbf{Z})\cdot\mathbf{p}^{\bullet} + \{\partial_\mu\omega(\mathbf{Z}) + \rho(\mathbf{Z})\}\mu^{\bullet} + \{\partial_{\mathbf{E}}\omega(\mathbf{Z}) - \mathbf{T}(\mathbf{Z})\}\cdot\mathbf{E}^{\bullet} + \mathbf{h}(\mathbf{Z})\cdot\mathbf{p} \le 0,$$

and since we can always find fields μ and $\mathbf{u}$ such that μ, $\mathbf{p}$, $\mathbf{E}$, $\mu^{\bullet}$, $\mathbf{p}^{\bullet}$, and $\mathbf{E}^{\bullet}$ have *arbitrarily prescribed values* at some chosen point and time, we are led to the following *constitutive restrictions*, which we write with the subscript α or β omitted:

(i) *The Gibbs function, the density, and the stress are independent of the potential gradient* $\mathbf{p}$ *and related through*

$$\rho(\mu,\mathbf{E}) = -\partial_\mu\omega(\mu,\mathbf{E}), \qquad \mathbf{T}(\mu,\mathbf{E}) = \partial_{\mathbf{E}}\omega(\mu,\mathbf{E}); \tag{7.3}$$

(ii) *the mass flux satisfies the inequality*

$$h(\mu,p,E)\cdot p \leq 0. \tag{7.4}$$

The nonequilibrium restrictions (7.3) are similar to standard results derived using equilibrium considerations.

The next lemma will simplify the study of inequalities such as (7.4).

Lemma. *Let* $q(v,z)\in\mathbb{R}^n$ *be a smooth function of* $(v,z)\in\mathbb{R}^p\times\mathbb{R}^n$, *and suppose that*

$$q(v,z)\cdot z \leq 0 \tag{7.5}$$

for all $(v,z)\in\mathbb{R}^n\times\mathbb{R}^p$. *Then for each such* (v,z) *there is an* $n\times n$ *matrix* $K(v,z)$, *with* $K(v,0)$ *positive semi-definite, such that*

$$q(v,z) = -K(v,z)z. \tag{7.6}$$

To prove this lemma, fix v and write $\varphi(z)=q(v,z)\cdot z$. By (7.5), $\varphi(z)$ has a maximum at $z=0$; hence the first derivative of φ vanishes at $z=0$, while its second derivative is negative semi-definite. Thus $q(v,0)=0$, so that $q(v,z)$ has the form (7.6) with $K(v,0)$ positive semi-definite.

The lemma allows us to express the mass flux in the form

$$h(\mu,\nabla\mu,E) = -K(\mu,\nabla\mu,E)\nabla\mu, \tag{7.7}$$

with $K(\mu,0,E)$ positive semi-definite. We write K_α or K_β for K when we wish to make the corresponding phase explicit, and we refer to K_α or K_β as **mobility tensors**. Note that, by (7.3), we can write $(6.9)_2$ in the form

$$\Gamma = -h(\mu,\nabla\mu,E)\cdot\nabla\mu = \nabla\mu\cdot K(\mu,\nabla\mu,E)\nabla\mu. \tag{7.8}$$

7.2. Natural states. Transition potential.

We assume that, for each choice of the potential μ, there are unique strain-values $E_\alpha(\mu)$ and $E_\beta(\mu)$ that minimize the Gibbs functions of the α and β phases. By (7.3), these strains render the bulk phases stress-free,

$$T_\alpha(\mu,E_\alpha(\mu)) = 0, \qquad T_\beta(\mu,E_\beta(\mu)) = 0, \tag{7.9}$$

and represent **natural states** of the individual phases; the difference $E_\beta(\mu)-E_\alpha(\mu)$ represents the "misfit" in strain between the natural states. It is convenient to measure the strain in each phase relative to the natural state of that phase using the **relative strain**

$$\mathcal{E} = \begin{cases} E - E_\alpha(\mu) & \text{in phase } \alpha, \\ E - E_\beta(\mu) & \text{in phase } \beta, \end{cases} \tag{7.10}$$

Let μ_0 satisfy

$$\omega_\alpha(\mu_0,E_\alpha(\mu_0)) = \omega_\beta(\mu_0,E_\beta(\mu_0)) \tag{7.11}$$

so that the Gibbs functions of the two phases - in their natural states - coincide at μ_0. We will refer to potentials μ_0 with this property as **transition potentials**; they (generally) characterize changes in the relative stability of the bulk phases, and mark changes of phase in the absence of stress and interfacial structure. (In addition, we will assume, without loss in generality, that the Gibbs functions (7.11) at μ_0 vanish.)

7.3. Interfacial constitutive equations.

We consider constitutive equations in which the interfacial energy f, the surface shear $\mathbf{c}$, and the normal interaction π depend on the diffusion potential μ, the normal $\mathbf{n}$, the normal velocity V, and the values $\nabla\mu^\pm$ and $\nabla u^\pm$ of the potential gradient and the displacement gradient at the interface:

$$f = f(\mathbf{z}), \qquad \mathbf{C} = \mathbf{C}(\mathbf{z}), \qquad \pi = \pi(\mathbf{z}), \tag{7.12}$$

with

$$\mathbf{z} = (\mathbf{n}, V, \mu, \nabla\mu^-, \nabla\mu^+, \nabla u^-, \nabla u^+).$$

By (6.7) and the bulk constitutive equations, a similar constitutive relation applies to Q:

$$Q = Q(\mathbf{z}). \tag{7.13}$$

We require that (7.12) be *compatible with the second law* in the sense that:

> *the interfacial dissipation inequality* (6.6) *is satisfied in all motions of the interface for all choices of the fields representing the displacement and the diffusion potential.*

This requirement places strong restrictions on the constitutive functions. Let $\mathbf{w}$ denote the list $\mathbf{z}$ with the argument $\mathbf{n}$ removed: $\mathbf{w} = (V, \mu, \nabla\mu^-, \nabla\mu^+, \nabla u^-, \nabla u^+)$. If we substitute the constitutive equations into (6.6), we find that

$$\{\partial_{\mathbf{n}} f(\mathbf{z}) + \mathbf{C}(\mathbf{z})\}\cdot\mathbf{n}^\circ + \partial_{\mathbf{w}} f(\mathbf{z})\cdot\mathbf{w}^\circ + Q(\mathbf{z})V \le 0. \tag{7.14}$$

We can always find a motion of the interface and compatible bulk fields μ and $\mathbf{u}$ such that $\mathbf{z}$, $\mathbf{n}^\circ$, and $\mathbf{w}^\circ$ have *arbitrarily prescribed values* at some chosen point of the interface and time (cf. Gurtin (1988) for the proof of analogous results). We are therefore led to the *constitutive restrictions:*

(i) f *and* $\mathbf{C}$ *depend only on* $\mathbf{n}$ *with*

$$c(n) - -d_n f(n); \qquad (7.15)$$

(1i) *there is a scalar function* b(s) *I* 0 *such that*

$$Q - -b(z)V. \qquad (7.16)$$

Using $(6.9)_2$ and the result (i) and (ii), we can rewrite the Interfacial dissipation in the form

$$\mathbf{T} - b(2)V^2. \qquad (7.17)$$

Remark. We have established the thermodynamic restrictions (7.3), (7.4), (7.15), and (7.16) as necessary conditions for the satisfaction of the dissipation inequalities (6.3) and (6.6), but tracing the argument backward we see that these restrictions are also sufficient for the satisfaction of (6.3) and (6.6). Thus granted the thermodynamic restrictions (7.3), (7.4), (7.15), and (7.16), consistency with all of the relations expressing balance of force and mass ensures satisfaction of the global dissipation inequality (6.1) in all processes.

6. The general free-boundary problem.

6.1. The problem.

Summarizing the results derived thus far, we have the **bulk equations**

$$p^1 \text{ «-divh}, \qquad \text{divT « 0}. \qquad (6.1)$$

with

$$p_{tt}(u.,E) - -a\hat{}u_a(n.E). \quad T_a(u.,E) - d_E u_a(ji,E),$$

$$h = h_a(u.,Vu.,E) \qquad (8.2)$$

in phase oc, and similarly in phase J3;

the **interface condition**

$$[\omega] = [\mathbf{T}\cdot\mathbf{E}] - fK - \mathrm{div}_{\mathcal{S}}\mathbf{c} + b(\mathbf{z})V \tag{8.3}$$

found using (4.6), (6.7), and (7.16); and the **interface conditions**

$$[\rho]V = [\mathbf{h}]\cdot\mathbf{m}, \qquad [\mathbf{T}]\mathbf{m} = 0, \qquad \mathbf{c}(\mathbf{m}) = -\partial_{\mathbf{m}}f(\mathbf{m}). \tag{8.4}$$

The general problem consists of (8.1)-(8.4) supplemented by:

(i) **initial conditions** prescribing the initial diffusion-potential $\mu(\mathbf{x},0)$ for all $\mathbf{x}\in\Omega$ as well as the initial phase-regions $\Omega_\alpha(0)$ and (hence) $\Omega_\beta(0)$;

(ii) **diffusive boundary conditions** giving $\mu(\mathbf{x},t)$ on a portion of $\partial\Omega$ and $\mathbf{h}(\mathbf{x},t)\cdot\mathbf{n}_\Omega(\mathbf{x})$ on the remainder, with $\mathbf{n}_\Omega(\mathbf{x})$ the outward unit normal to $\partial\Omega$;

(iii) **mechanical boundary conditions** giving $\mathbf{u}(\mathbf{x},t)$ on a portion of $\partial\Omega$ and $\mathbf{T}(\mathbf{x},t)\mathbf{n}_\Omega(\mathbf{x})$ on the remainder.

Since we neglect inertia, initial conditions for the displacement are not required.

8.2. Energy identities. Energy-decay relations.

By (6.9), (7.8), and (7.17), we have a simple expression for the total dissipation:

$$\mathfrak{D}(\Omega) = -\int_\Omega \mathbf{h}\cdot\nabla\mu\,dv - \int_{\mathcal{S}} QV\,da \geq 0. \tag{8.5}$$

In view of the remark following (7.17) the global dissipation inequality (6.1) holds whenever all of the constitutive equations and balance laws are satisfied. Thus, taking $R = \Omega$ in (5.1) and (6.1), and using the fact that $\mathcal{S}$ does not intersect $\partial\Omega$, we arrive at the **mass and energy identities**:

$$\Big\{\int_{\Omega}\rho\,dv\Big\}^{\cdot} = -\int_{\partial\Omega}\mathbf{h}\cdot\mathbf{n}_{\Omega}\,da, \tag{6.6}$$

$$\Big\{\int_{\Omega}\psi\,dv + \int_{\mathcal{S}}f\,da\Big\}^{\cdot} - \int_{\partial\Omega}\mathbf{T}\mathbf{n}_{\Omega}\cdot\mathbf{u}'\,da + \int_{\partial\Omega}\mu\mathbf{h}\cdot\mathbf{n}_{\Omega}\,da = -\mathcal{D}(\Omega) \le 0. \tag{6.7}$$

We now consider the general problem with **quiescent boundary conditions** consisting of the *diffusive boundary conditions*

$$\mu = \mu^{*} \text{ (= constant) on a portion } M \text{ of } \partial\Omega \text{ and } \mathbf{h}\cdot\mathbf{n}_{\Omega} = 0 \text{ on the remainder,} \tag{6.8}$$

in conjunction with the *mechanical boundary conditions*

$$\mathbf{u}' = \mathbf{0} \text{ on a portion } D \text{ of } \partial\Omega, \quad \mathbf{T}\mathbf{n}_{\Omega} = \mathbf{T}^{*}\mathbf{n}_{\Omega} \text{ on the remainder,} \tag{6.9}$$

with $\mathbf{T}^{*}$ *symmetric* and *constant*, so that the boundary tractions are **dead loads**. (For $D = \partial\Omega$, simply take $\mathbf{T}^{*} = \mathbf{0}$ in the relations below.) We will consider two special cases of the diffusive boundary conditions (6.8): one has $M = \emptyset$ and corresponds to *zero mass flow across the boundary;* for the other M has nonzero area, so that a *nontrivial portion of the boundary is at the constant potential* μ^{*}.

Energy-decay relations. *Consider the general problem with quiescent boundary conditions. If there is no mass flow across the boundary, then*

$$\Big\{\int_{\Omega}\rho\,dv\Big\}^{\cdot} = 0, \qquad \Big\{\int_{\Omega}(\psi - \mathbf{T}^{*}\cdot\mathbf{E})\,dv + \int_{\mathcal{S}}f\,da\Big\}^{\cdot} = -\mathcal{D}(\Omega) \le 0. \tag{6.10}$$

If a nontrivial portion of the boundary is at the constant potential μ^{*}, *then*

$$\Big\{\int_{\Omega}(\psi - T^{*}\cdot E - \mu^{*}\rho)dv + \int_{\mathcal{S}} f\,da\Big\}^{\cdot} = -\mathfrak{D}(\Omega) \le 0. \tag{8.11}$$

To establish these relations note that the mechanical boundary conditions and the symmetry of T^{*}, yield

$$\int_{\partial\Omega} Tn_{\Omega}\cdot u^{\cdot}da = \Big\{\int_{\partial\Omega} T^{*}n_{\Omega}\cdot u\,da\Big\}^{\cdot} = \Big\{\int_{\Omega} T^{*}\cdot E\,da\Big\}^{\cdot}. \tag{8.12}$$

The verification of (8.10) follows from (8.6), (8.7), and (8.12). On the other hand, when a nontrivial portion of the boundary is at the constant potential μ^{*}, (8.6) implies

$$\int_{\partial\Omega} \mu h\cdot n_{\Omega}\,da = \mu^{*}\int_{\partial\Omega} h\cdot n_{\Omega}\,da = -\Big\{\int_{\Omega}\mu^{*}\rho\,dv\Big\}^{\cdot}, \tag{8.13}$$

and this with (8.7) and (8.12) yields (8.11).

9. Special theories.

In this section we will discuss special theories appropriate to behavior near a given transition potential μ_0. One method of generating such theories is to formally approximate the general equations under the assumption that the *potential difference*

$$U = \mu - \mu_0,$$

is small. A problem with this proceedure is that the resulting approximate equations will generally not lead to conservation laws and Lyapunov functions, chiefly because the underlying thermodynamic structure is lost in the approximation. A procedure that ensures a consistent thermodynamic structure begins with bulk Gibbs functions (of a desired degree of approximation) and uses the thermodynamic relations (3.3) and (7.3) as *defining* relations for the bulk energies, densities, and stresses (cf. Gurtin 1986, Gurtin and Davi 1990). We will discuss two theories: one in which the bulk Gibbs functions are quadratic in E and U, and one in which these Gibbs functions are quadratic in E, but linear in U.

9.1. Gibbs function quadratic in strain and chemical potential.

We seek a theory in which the bulk PDE's are linear. Since this requires constitutive equations for stress and density that are *linear* in E and U, we are led, by virtue of (7.3), to consider Gibbs functions that are *quadratic* in these variables. By hypothesis, for fixed U the stress-free strains minimize the corresponding Gibbs functions. Thus the Gibbs functions necessarily have the form

$$\begin{aligned}\omega_\alpha(\mu,E) &= -\Lambda_\alpha U - \tfrac{1}{2}\lambda_\alpha U^2 + W_\alpha(\mathcal{E}),\\ \omega_\beta(\mu,E) &= -\Lambda_\beta U - \tfrac{1}{2}\lambda_\beta U^2 + W_\beta(\mathcal{E}),\end{aligned} \tag{9.1}$$

where $\Lambda_\alpha, \Lambda_\beta, \lambda_\alpha, \lambda_\beta$ are constant, while

$$W_\alpha(\mathcal{E}) = \tfrac{1}{2}\mathcal{E}\cdot L_\alpha \mathcal{E}, \qquad W_\beta(\mathcal{E}) = \tfrac{1}{2}\mathcal{E}\cdot L_\beta \mathcal{E}, \tag{9.2}$$

with L_α and L_β *positive-definite symmetric linear transformations* from symmetic tensors into symmetric tensors (with the L's independent of μ).

By $(7.3)_2$, (9.1), and (9.2), the stress in each phase is linear in the relative strain $\mathcal{E}$ and given by

$$T = L_\alpha \mathcal{E} \ \text{ in phase } \alpha, \qquad T = L_\beta \mathcal{E} \ \text{ in phase } \beta; \tag{9.3}$$

thus L_α and L_β represent **elasticity tensors**, while $W_\alpha(\mathcal{E})$ and $W_\beta(\mathcal{E})$ are **strain energies**. Further, the stress-free strains $E_\alpha(\mu)$ and $E_\beta(\mu)$ must be affine (for otherwise (9.1) would not be quadratic):

$$E_\alpha(\mu) = E_{0\alpha} + UF_\alpha, \qquad E_\beta(\mu) = E_{0\beta} + UF_\beta, \tag{9.4}$$

with $E_{0\alpha}$, F_α, $E_{0\beta}$, and F_β constant symmetric tensors. The tensors F_a and F_p are analogous to the solute expansion tensor used in other theories.

The relation $(7.3)_1$ yields constitutive relations for the densities:

p » A_a + X_aU + G_a·£ in phase a,

p « A_p + XpU + Gp£ in phase p, (9.5)

with

G_a«L_aF_a, G_p-LpF_p; (9.6)

and the relations (3.3) allow us to write the energies in the form

\jj • JXfcU^2 + W_a(6) + UG_a£ + u_op in phase oc,

(9.7)

\jj - JXpU^2 + W_p(6) + UG_rC +)i_op in phase p.

Finally, we consider, as constitutive equations for the mass flux,

h «-K_aVU in phase a, h --K_PVU in phase p, (9.8)

with constant, positive semi-definite mobility tensors K_a and Kp.

Regarding the interface, we assume that the restrictions embodied in (7.15) are satisfied, and that the kinetic coefficient b in (7.16) is constant, so that

Q « -bv\ (9.9)

with *blO.*

The PDE's to be satisfied in bulk are then the diffusion equations

X_aU* + GocX^1 - div(K_aVU) In phase a,

(9.10)

XpIT + GpX" - div(KpVU) in phase j3,

and the mechanical balance

$$\mathrm{div}\,T = 0 \tag{9.11}$$

supplemented by the stress-strain relations (9.3).

To determine the form of the interface conditions, we write, for any quantity with value, say, φ_α in phase α and φ_β in phase β,

$$\varphi(x,t) = \begin{cases} \varphi_\alpha & \text{for } x \in \Omega_\alpha(t), \\ \varphi_\beta & \text{for } x \in \Omega_\beta(t), \end{cases}$$

so that $[\varphi] = \varphi_\beta - \varphi_\alpha$. In the same spirit, we write $W(\mathcal{E}(x,t))$ for the function defined by

$$W(\mathcal{E}(x,t)) = \begin{cases} W_\alpha(\mathcal{E}(x,t)) & \text{for } x \in \Omega_\alpha(t), \\ W_\beta(\mathcal{E}(x,t)) & \text{for } x \in \Omega_\beta(t). \end{cases} \tag{9.12}$$

Then

$$[\rho] = [\Lambda] + [\lambda]U + [G\cdot\mathcal{E}], \qquad [\omega] = -[\Lambda]U - \tfrac{1}{2}[\lambda]U^2 + [W(\mathcal{E})],$$

and the interface conditions (8.3) and (8.4) take the form

$$\begin{gathered} [\Lambda]U + \tfrac{1}{2}[\lambda]U^2 = \\ [W(\mathcal{E})] - [T\cdot E] + fK + \mathrm{div}_{\mathscr{S}}\mathbf{c} - bV, \\ \{[\Lambda] + [\lambda]U + [G\cdot\mathcal{E}]\}V = [h]\cdot\mathbb{m}, \qquad [T]\mathbb{m} = 0. \end{gathered} \tag{9.13}$$

Summarizing, the underlying problem for a Gibbs function quadratic in strain and chemical potential consists of (7.15), (9.2), (9.3), (9.10), (9.11), and (9.13) supplemented by the initial and boundary conditions stated following (8.4) (but phrased in terms of U).

The energy-decay relations (8.10) and (8.11) have interesting consequences for this special theory. These are most easily expressed using the auxiliary constants

$$C_\alpha = \tfrac{1}{2}\lambda_\alpha - W_\alpha(F), \qquad C_\beta = \tfrac{1}{2}\lambda_\beta - W_\beta(F), \tag{9.14}$$

the constants

$$P^* = [\Lambda]U^* + \tfrac{1}{2}[\lambda]U^{*2}, \qquad U^* = \mu^* - \mu_0,$$

and the stress-free strains

$$E^*_\alpha = E_\alpha(\mu^*), \qquad E^*_\beta = E_\beta(\mu^*)$$

at the boundary potential μ^*. In addition, as in (9.12), we write $W(E(x,t)-E_0)$ and $W(E(x,t)-E^*)$ for the functions defined by

$$W(E(x,t)-E_0) = \begin{cases} W_\alpha(E(x,t)-E_{0\alpha}) & \text{for } x\in\Omega_\alpha(t), \\ W_\beta(E(x,t)-E_{0\beta}) & \text{for } x\in\Omega_\beta(t). \end{cases}$$

$$W(E(x,t)-E^*) = \begin{cases} W_\alpha(E(x,t)-E^*_\alpha) & \text{for } x\in\Omega_\alpha(t), \\ W_\beta(E(x,t)-E^*_\beta) & \text{for } x\in\Omega_\beta(t). \end{cases}$$

In addition, it is convenient to introduce the "energy"

$$\mathcal{E}_0(u,\mathcal{S}) = \int_\Omega \{W(E-E_0) - T^*\cdot E\}\,dv + \int_{\mathcal{S}} f(\mathbf{m})\,da, \tag{9.15}$$

which includes the strain energy at the chemical potential μ_0, the energy of the dead loads, and the interfacial energy. (A knowledge of the interface $\mathcal{S}$ implies a knowledge of the phase regions Ω_α and Ω_β.) Similarly, we write

$$\mathcal{E}^*(u,\mathcal{S}) = \int_\Omega \{W(E-E^*) - T^*\cdot E\}\,dv + \int_{\mathcal{S}} f(\mathbf{m})\,da \tag{9.16}$$

for the analogous "energy" at the chemical potential μ^*.

Energy-decay relations. *Consider a solution of* (7.15), (9.2), (9.3), (9.10), (9.11), *and* (9.13) *corresponding to quiescent boundary conditions. If there is no mass flow across the boundary, then*

$$\Big\{-[\Lambda]\mathrm{vol}(\Omega_\alpha) + \int_\Omega \{2CU + \mathbf{G}\cdot(E-E_0)\}\,dv\Big\}^{\boldsymbol{\cdot}} = 0, \tag{9.17}$$

$$\Big\{\mathcal{E}_0(u,\mathcal{S}) + \int_\Omega CU^2\,dv\Big\}^{\boldsymbol{\cdot}} = -\mathcal{D}(\Omega) \le 0. \tag{9.18}$$

If a nontrivial portion of the boundary is at the constant potential μ^*, *then*

$$\Big\{\mathcal{E}^*(u,\mathcal{S}) + P^*\mathrm{vol}(\Omega_\alpha) + \int_\Omega C(U-U^*)^2\,dv\Big\}^{\boldsymbol{\cdot}} = -\mathcal{D}(\Omega) \le 0. \tag{9.19}$$

The relation (9.17) follows from (2.12), (7.10), (8.10), (9.4), (9.5), and (9.14).

To verify (9.18), we first note that

$$\begin{aligned} \psi &= C_\alpha U^2 + W_\alpha(E-E_{0\alpha}) + \mu_0\rho \qquad \text{in phase } \alpha,\\ \psi &= C_\beta U^2 + W_\beta(E-E_{0\beta}) + \mu_0\rho \qquad \text{in phase } \beta. \end{aligned} \tag{9.20}$$

These relations are an immediate consequence of (9.7) and the following identity, which we write supressing the phase label:

$$W(\mathcal{E}) + UG\cdot\mathcal{E} = W(E-E_0) - U^2W(F). \qquad (9.21)$$

The decay relation (9.18) follows from (8.10) and (9.20).

The verification of (9.19) follows along the same lines using, in place of (9.20), the relation

$$\psi = -\Lambda U^* - \tfrac{1}{2}\lambda U^{*2} + C(U-U^*)^2 + W(E-E^*) + \mu^*\rho$$

(with the phase label supressed), which is established using the identity

$$W(\mathcal{E}) + (U-U^*)G\cdot\mathcal{E} = W(E-E^*) - (U-U^*)^2W(F).$$

Remark. If $C>0$ then the phases are "stable" in their natural states, since (9.20) then expresses $\psi-\mu_0\rho$ in each phase as a positive definite function of the strain and potential relative to the natural state at μ_0. The condition $C>0$ resembles a condition found by Cahn (1968) in his work on spinodal decomposition in the presence of compositionally generated elastic stresses. Indeed, by (9.14), C is a sum of two terms: one related to a second derivative of an energy with respect to composition, and one involving an elastic energy.

9.2. Gibbs function quadratic in strain and linear in chemical potential.

In many situations of interest the interface moves slowly compared to the time scale for diffusion. An approximation consistent with this type of behavior is developed by neglecting the terms involving U' and $\mathcal{E}'$ in (9.10). Such an approximation is generated as an *exact theory* within our framework by restricting the Gibbs functions (9.1) of the quasi-linear theory to be affine in U, with no terms involving products of U and E. This is equivalent to taking

$$\lambda_\alpha = \lambda_\beta = 0, \qquad F_\alpha = F_\beta = 0 \qquad (9.22)$$

and leads to constant densities, to constant stress-free strains

E_a-E_{oot} and E_p»E_{op}, and to G_a-B_p«0, C_a-C_p-O.

The PDE's to be satisfied in bulk are then the equations

$$\mathrm{div}(K_a VU) - 0, \qquad \mathrm{div}(KpVU) \ll 0 \qquad (9.23)$$

for the chemical potential in conjunction with the mechanical balance law

$$\mathrm{div}T - 0 \qquad (9.24)$$

supplemented by the stress-strain relations

$$T - L_a[E-E_{0ot}] \text{ in phase a,}$$
$$T-L_p[E-E_{op}] \text{ in phase P;} \qquad (9\text{-}25)$$

while the interface conditions have the form

$$\ell U \bullet [W(E-E_0)] - [\mathbf{TE}] + fK + \mathrm{div}\hat{}C - bV, \qquad (g.26)$$
$$\ell V = [h]\cdot n), \qquad [Tin - 0,$$

with

$$i \ll Ap - A_a.$$

The underlying problem then consists of (7.15), (9.2), (9.23)-(9.26), and the initial and boundary conditions stated following (8.4) (with the initial condition for U omitted). For this problem (9.17)-(9.20) yield the

Energy-decay relations. *Consider d solution of* (7.15), (9.2), *dnd* (9.23)-(9.26) *corresponding to quiescent boundary conditions. If there is no mass flow across the boundary, then*

$$\mathrm{vol}(\Omega_\alpha)' = 0, \qquad \mathcal{E}_0(u,\mathcal{A})' = -\mathfrak{D}(\Omega) \le 0. \tag{9.27}$$

If a nontrivial portion of the boundary is at the constant potential μ^*, *then*

$$\{U^*\ell\,\mathrm{vol}(\Omega_\alpha) + \mathcal{E}^*(u,\mathcal{A})\}' = -\mathfrak{D}(\Omega) \le 0. \tag{9.28}$$

10. Variational problems.

In this section we continue to consider the special theories for which the Gibbs function is quadratic in strain and either quadratic or linear in chemical potential. For these theories the energy-decay relations (9.17)-(9.19) and (9.27)-(9.28) at least formally yield variational principles for the characterization of equilibria and, in particular, for the equilibrium shapes of particles. The right side of each of these decay relations is the negative of the dissipation $\mathfrak{D}(\Omega)$; thus and by (7.8) and (8.5), if the mobility tensors K_α and K_β are positive definite, then one would expect equilibria, if they exist, to have constant chemical potential μ, and for that reason we assume throughout this section that

$$U \equiv \text{constant}. \tag{10.1}$$

The statical version of the boundary condition for u in (8.9) is

$$u = g \quad \text{on} \quad D, \tag{10.2}$$

with $g(x)$ a prescribed function; we use the term **admissible displacement field** for a field u that is consistent with (10.2).

For a Gibbs function that is quadratic in μ and E the energy decay relations (9.17) and (9.18) of the *quasi-linear theory* suggest the following variational problem for the shape of a misfitting particle: given $m_0 > 0$ (the total mass of the chemical component),

$$\textit{minimize} \quad \mathcal{E}_0(u,\mathcal{S}) + U^2\int_\Omega C\,dv \tag{10.3}$$

$$\textit{subject to} \quad -[\Lambda]\mathrm{vol}(\Omega_\alpha) + \int_\Omega \{2CU + G\cdot(E - E_0)\}\,dv = m_0$$

over all interfaces $\mathcal{S} = \partial\Omega_\alpha$, all admissible displacement fields u that are continuous across $\mathcal{S}$, and all scalars U. This variational principle corresponds to no mass flow across the boundary. If a nontrivial portion of the boundary is at the constant chemical potential μ^*, then (10.1) yields $U \equiv U^*$, and (9.19) suggests the variational problem

$$\textit{minimize} \quad \mathcal{E}^*(u,\mathcal{S}) + P^*\mathrm{vol}(\Omega_\alpha) \tag{10.4}$$

over all $\mathcal{S} = \partial\Omega_\alpha$ and all admissible u continuous across $\mathcal{S}$. The functionals to be minimized, (10.3) and (10.4), do not involve the simple sums $\mathcal{E}_0(u,\mathcal{S})$ and $\mathcal{E}^*(u,\mathcal{S})$ of elastic and interfacial energies: even though the chemical potential is constant, there are additional terms due to the coupling between stress and chemistry.

For a Gibbs function that is linear in μ and quadratic in E the energy decay relations (9.27) - appropriate to a boundary across which mass does not flow - suggest the variational problem: given $v_0 > 0$,

$$\textit{minimize} \quad \mathcal{E}_0(u,\mathcal{S}) \quad \textit{subject to} \quad \mathrm{vol}(\Omega_\alpha) = v_0 \tag{10.5}$$

over all $\mathcal{S} = \partial\Omega_\alpha$ and all admissible u continuous across $\mathcal{S}$. Similarly, the appropriate problem for a nontrivial portion of the boundary at constant potential μ^* is

$$\textit{minimize} \quad \mathcal{E}^*(u,\mathcal{S}) + U^*\ell\,\mathrm{vol}(\Omega_\alpha) \tag{10.6}$$

over all such $\mathcal{S} = \partial\Omega_\alpha$ and u.

In contrast to the variational principles described above, one has - in the absence of stress - the classical *Wulff problem,* which is to

$$\textit{minimize} \quad \int_{\mathcal{S}} f(\mathbf{n})da \quad \textit{subject to} \quad \mathrm{vol}(\Omega_\alpha) = v_0 \qquad (10.7)$$

over all $\mathcal{S} = \partial\Omega_\alpha$.

The variational problem (10.5) represents the simplest generalization of the Wulff problem to include bulk elasticity. In the absence of an applied stress ($T^* = 0$) this principle has been used by Johnson and Cahn (1984) and Johnson and Voorhees (1992), without formal justification, to determine equilibrium particle shapes. An interesting aspect of (10.5) is the absence of chemical potential in the variational problem, an absence that follows from the constitutive independence of stress and chemical potential for a Gibbs function linear in μ. This is clearly not the case for a Gibbs function quadratic in μ, for there stress and chemistry are coupled whenever $F \neq 0$.

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