A unified treatment of evolving interfaces accounting for small deformations and atomic transport: grain-boundaries, phase transitions, epitaxy

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1 Introduction

This review presents a unified treatment of several topics at the intersection of continuum mechanics and materials science; the thrust concerns processes involving evolving interfaces, focusing on grain-boundaries, solid-vapor interfaces (with emphasis on epitaxy), and coherent phase-transitions. Central to our discussion is the interaction of deformation, atomic transport, and accretion within a dissipative, dynamical framework, but as our interest is crystalline materials, we restrict our attention to small deformations.[1] To avoid geometrical complications associated with surfaces in $\mathbb{R}^3$, *we work in two space-dimensions when discussing interfaces*, but in $\mathbb{R}^3$ when discussing the theory in bulk.

1.1 Some important interface conditions

The past half-century has seen much activity among materials scientists and mechanicians concerning interface problems, a central outcome being the realization that such problems generally result in an interface equation over and above those that follow from the classical balances for forces, moments, and mass. This extra interface condition takes a variety of forms, the most important examples being:

(i) **Herring's equation** (1951). This is an equation,

$$U = -\left(\psi + \frac{\partial^2\psi}{\partial\vartheta^2}\right)K, \tag{1.1}$$

relating the chemical potential U of a solid-vapor interface to its curvature K. Here $\psi(\vartheta) > 0$ is the free-energy (density) of the interface with $\vartheta = \vartheta(\mathbf{x})$ the *orientation*; that is, the counterclockwise angle to the interface tangent $\mathbf{t}$ (Figure 10, page 69). Invoking an assumption of local equilibrium, Herring defines the chemical potential as the variational derivative of the total free energy with respect to variations in the configuration of the interface. Following Herring, Wu (1996), Norris (1998), and Freund (1998), generalizing earlier work of Asaro and Tiller (1972) and Rice and Chuang (1981), compute the chemical potential of a solid-vapor interface in the

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[1] Most applications in which deformation, atomic transport, and accretion are present involve small deformations. An abbreviated account of the formal analysis involved in the approximation of small deformations within a finite-deformational framework is provided in Appendix C.

presence of deformation, allowing for interfacial stress. Their result, which allows for finite deformations, is, when set within a framework of small deformations, given by

$$U = \Psi - \mathbf{Tn} \cdot (\nabla \mathbf{u})\mathbf{n} - \gamma \mathbf{n} \cdot \mathbf{Tt} - (\psi - \bar{\sigma}\varepsilon)K - \frac{\partial \tau}{\partial s}. \tag{1.2}$$

Here Ψ is the bulk free-energy (density); $\mathbf{T}$ is the bulk stress; $\mathbf{u}$ is the displacement; $\mathbf{n}$ and $\mathbf{t}$ are the interface normal and tangent; s denotes arc length;

$$\varepsilon = \mathbf{t} \cdot (\nabla \mathbf{u})\mathbf{t} \qquad \text{and} \qquad \gamma = \mathbf{n} \cdot (\nabla \mathbf{u})\mathbf{t}$$

are the tensile and shear strains within the interface. The result (1.2) is derived variationally; consequently, it is based on a constitutive equation

$$\psi = \hat{\psi}(\varepsilon, \vartheta)$$

for the interfacial free-energy, with $\bar{\sigma}$ and τ defined by

$$\bar{\sigma} = \frac{\partial \hat{\psi}(\varepsilon, \vartheta)}{\partial \varepsilon}, \qquad \tau = \frac{\partial \hat{\psi}(\varepsilon, \vartheta)}{\partial \vartheta}.$$

The presence of the shear strain γ in (1.2) is a consequence of our assumption of small deformations. Specifically, it follows from the fact that the interfacial stress $\mathbf{s} = \bar{\sigma}\mathbf{t}$ is tangent to the interface, but the interfacial strain $(\nabla \mathbf{u})\mathbf{t}$ is not (cf. Footnote 68, page 91).

(ii) **Mullins's equations** (1956, 1957). These are geometric equations,

$$bV = \psi K \qquad \text{and} \qquad V = -\left(\frac{L\psi}{\rho^2}\right)\frac{\partial^2 K}{\partial s^2}, \tag{1.3}$$

for the respective motions of an isotropic grain-boundary and an isotropic grain-vapor interface, neglecting evaporation-condensation. Here V is the (scalar) normal velocity of the grain-boundary (or interface) $\mathcal{S}$, while ψ, b, ρ, and L are strictly positive constants, with ψ the interfacial free-energy (density), b a kinetic modulus (or, reciprocal mobility), ρ the atomic density of the solid, and L the mobility for Fickean diffusion within $\mathcal{S}$. Mullins's argument in support of $(1.3)_1$ is physical in nature and based on work of Smoluchowski (1951), Turnbull (1951), and Beck (1952). To derive $(1.3)_2$, Mullins appeals to balance of mass supplemented by Fick's law and Herring's equation (1.1) for the chemical potential.

(iii) **Kinetic Maxwell equation**. This is a condition

$$\left[\!\left[\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha - \mathbf{Tn} \cdot (\nabla \mathbf{u})\mathbf{n} \right]\!\right] = bV. \tag{1.4}$$

for a propagating coherent phase interface between two phases composed of atomic species $\alpha = 1, 2, \ldots, N$. Here, μ^α and ρ^α are the chemical potentials and atomic densities in bulk, $[\![f]\!]$ represents the jump in a field f across the interface, and, as in $(1.3)_1$, b is a constitutively determined kinetic modulus. The kinetic Maxwell condition was first obtained by Heidug and Lehner (1985), Truskinovsky (1987), and Abeyaratne and Knowles (1990), who ignored atomic diffusion but allowed for both inertia and finite deformations.[2] Their derivations are based on determining the energy dissipation, per unit interfacial area, associated with the propagation of the interface and then appealing to the second law. When the kinetic modulus $b = 0$, (1.4) reduces to the classical Maxwell equation

$$\left[\!\left[\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha - \mathbf{Tn} \cdot (\nabla \mathbf{u})\mathbf{n} \right]\!\right] = 0,$$

which was first derived variationally by Larché and Cahn (1978).[3]

(iv) **Leo–Sekerka relation** (1989). This is a condition for an interface in *equilibrium.* Relying on a variational framework set forth by Larché and Cahn (1978) (cf., also, Alexander and Johnson, 1985; Johnson and Alexander, 1986), Leo and Sekerka consider coherent and incoherent solid-solid interfaces as well as solid-fluid interfaces, and allow for finite deformations. For an interface between a vapor and an alloy composed of atomic species $\alpha = 1, 2, \dots, N$, neglecting vapor pressure and thermal influences and assuming small deformations, the Leo–Sekerka relation takes the form

$$\sum_{\alpha=1}^{N} (\rho^\alpha - \delta^\alpha K)\mu^\alpha = \Psi - \mathbf{Tn} \cdot (\nabla \mathbf{u})\mathbf{n} - \gamma \mathbf{n} \cdot \mathbf{Tt} - (\psi - \bar{\sigma}\varepsilon)K - \frac{\partial \tau}{\partial s}. \tag{1.5}$$

The relation (1.5) is based on a constitutive equation

$$\psi = \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,), \qquad \vec{\delta} = (\delta^1, \delta^2, \dots, \delta^N),$$

for the interfacial free-energy, supplemented by the definitions

$$\bar{\sigma} = \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \varepsilon}, \qquad \tau = \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \vartheta}, \qquad \mu^\alpha = \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \delta^\alpha}.$$

Here δ^α are the interfacial atomic-densities of species α.

1.2 The need for a configurational force balance

One cannot deny the applicability of the interface conditions (1.1)–(1.5); nor can one deny the great physical insight underlying their derivation. But in studying these derivations one is left trying to ascertain the status of the resulting equations (1.1)–(1.5): are they balances, or constitutive equations, or neither?[4] This and the disparity between the physical bases underlying their derivation would seem to at least indicate *the absence of a basic unifying principle.*

That additional configurational forces[5] may be needed to describe phenomena associated with the material itself is clear from the seminal work of Eshelby (1951, 1956, 1970, 1975), Peach and Koehler (1950), and Herring (1951) on lattice defects. But these

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[2] Under these circumstances, the kinetic Maxwell condition is (1.4) with $\mu^\alpha = 0$, $\alpha = 1, 2, \dots, N$, and with $\mathbf{T}$ the first Piola–Kirchhoff stress. Although the first derivations ignored atomic diffusion, its inclusion is straightforward.

[3] Cf. also Eshelby (1970), Robin (1974), Grinfeld (1981), James (1981), and Gurtin (1983), who neglect compositional effects.

[4] Successful theories of continuum mechanics are typically based on a clear separation of balance laws and constitutive equations; the former describing large classes of materials, the latter describing particular materials.

[5] We use the term *configurational* to differentiate these forces from classical Newtonian forces, which we refer to as *standard.*

studies are based on variational arguments, arguments that, by their very nature, cannot characterize dissipation. Moreover, the introduction of configurational forces through such formalisms is, in each case, based an underlying constitutive framework and hence restricted to a particular class of materials.[6]

A completely different point of view is taken by Gurtin and Struthers (1990),[7] who — using an argument based on invariance under observer changes — conclude that a configurational force balance should join the standard (Newtonian) force balance as a *basic* law of continuum physics. Here the operative word is "basic". Basic laws are by their very nature independent of constitutive assumptions; when placed within a thermodynamic framework such laws allow one to use the now standard procedures of continuum thermodynamics to develop suitable constitutive theories.

1.3 A format for the study of evolving interfaces in the presence of deformation and atomic transport

We here develop a complete theory of evolving interfaces in the presence of deformation and atomic transport using a format based on:

(a) Standard (Newtonian) balance laws for forces and moments that account for standard stresses in bulk and within the interface.

(b) An *independent balance law for configurational forces* that accounts for configurational stresses in bulk and within the interface.[8]

(c) Atomic balances, one for each atomic species. These balances account for bulk and surface diffusion.

(d) A mechanical (isothermal) version of the second law in the form of a *free-energy imbalance*. This imbalance, which accounts for temporal changes in free-energy, energy flows due to atomic transport, and *power expended by both standard and configurational forces*, may be derived as a consequence of more typical forms of the first two laws under isothermal conditions.

(e) Thermodynamically consistent constitutive relations for the interface and for the interaction between the interface and its environment.

We show that each of the interface conditions in (i)–(iv) may be derived within this framework without assumptions of local equilibrium. One of the more interesting outcomes of the format we use is an explicit relation for the configurational surface tension σ in terms of other interfacial fields; viz.,

$$\sigma = \psi - \sum_{\alpha=1}^{N} \delta^{\alpha}\mu^{\alpha} - \bar{\sigma}\varepsilon. \tag{1.6}$$

This relation, a direct consequence of the free-energy imbalance applied to the interface, is a basic relation valid for all isothermal interfaces, independent of constitutive assumptions and hence of material; it places in perspective the basic difference between the

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[6] A vehicle for the discussion of configurational forces within a dynamical, dissipative framework derives configurational force balances by manipulating the standard momentum balance, supplemented by hypereslastic constitutive relations (e.g., Maugin, 1993). But such derived balances, while interesting, are satisfied automatically whenever the momentum balance is satisfied and are hence superfluous.

[7] This work is rather obtuse; better references for the underlying ideas are Gurtin (1995, 2000).

[8] As extended by Davì and Gurtin (1990), Gurtin (1991), Gurtin and Voorhees (1995), and Fried and Gurtin (1999, 2003) to account for atomic transport.

configurational surface tension σ and standard surface stress $\bar{\sigma}$ (cf. Footnote 72). There is much confusion in the literature concerning surface tension σ and its relation to surface free-energy ψ. By (1.6), we see that these two notions coincide if and only if standard interfacial stress as well as interfacial atomic densities are negligible.

1.4 The normal configurational force balance for a solid-vapor interface

To illustrate the format described above, we consider the special case of a solid-vapor interface discussed in Part E. In this case, neglecting the vapor pressure (and hence configurational forces exerted by the vapor on the interface), the configurational force balance for the interface takes the simple form

$$\frac{\partial \mathbf{c}}{\partial s} + \mathbf{g} = \mathbf{C}\mathbf{n}.$$

Here $\mathbf{c}$ is the configurational surface stress, $\mathbf{g}$ is an internal force associated with the attachment kinetics of vapor atoms at the solid surface, and $\mathbf{C}$ is the limit, at the interface, of the configurational stress in the solid. The tangential and normal components of $\mathbf{c}$,

$$\sigma = \mathbf{c} \cdot \mathbf{t}, \qquad \tau = \mathbf{c} \cdot \mathbf{n},$$

are the configurational *surface tension* and the configurational shear;[9] the theory in bulk shows $\mathbf{C}$ to be the Eshelby tensor

$$\mathbf{C} = \left(\Psi - \sum_{\alpha=1}^{N} \rho^{\alpha} \mu^{\alpha} \right) \mathbf{1} - (\nabla \mathbf{u})^{\top} \mathbf{T} \tag{1.7}$$

(cf. (12.15)). Of most importance is the component

$$\sigma K + \frac{\partial \tau}{\partial s} + g = \mathbf{n} \cdot \mathbf{C}\mathbf{n}, \qquad g = \mathbf{g} \cdot \mathbf{n},$$

of the configurational force balance normal to the interface, as this is the component relevant to the motion of the interface.

For a solid-vapor interface in the presence of deformation and atomic transport, the normal configurational force balance, when combined with (1.6), (1.7), and the standard force, moment, and atomic balances, yields the interface condition (Fried and Gurtin, 2003)

$$\sum_{\alpha=1}^{N} (\rho^{\alpha} - \delta^{\alpha} K) \mu^{\alpha} = \Psi - \mathbf{T}\mathbf{n} \cdot (\nabla \mathbf{u}) \mathbf{n} - \gamma \mathbf{n} \cdot \mathbf{T}\mathbf{t} - (\psi - \bar{\sigma} \epsilon) K - \frac{\partial \tau}{\partial s} - g, \tag{1.8}$$

with $\bar{\sigma}$ the standard surface-tension. This balance is basic, as its derivation utilizes only basic laws; as such it is independent of material. A consequence of the theory is that, thermodynamically, the force g is conjugate to the normal velocity V of the interface, and *dissipative*. Within a constitutive framework, thermodynamics renders this force often, but not always, of the form $g = -bV$, with $b \geq 0$ a *kinetic modulus*. The force g represents the sole dissipative force associated with the exchange of atoms between the solid and the vapor at the interface, the corresponding energy dissipated, per unit interfacial area, being $-gV$.

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[9] Thus, in contrast to more classical discussions, the surface tension actually represents a *force* tangent to the interface, with no *a priori* relationship to surface energy.

If we take $g \equiv 0$, then the normal configurational force balance (1.8) reduces to the Leo–Sekerka relation (1.5). The Leo–Sekerka relation follows rigorously as an Euler–Lagrange equation associated with the variational problem of minimizing the total free energy of a solid particle surrounded by a vapor. Thus, for solid-vapor interfaces in equilibrium, the format adopted here is completely consistent with results derived variationally.

The Leo–Sekerka relation (or similar relations for other types of phase interfaces) is typically applied, as is, to dynamical problems, often with an accompanying appeal to an hypothesis of "local equilibrium", although the precise meaning of this assumption is never spelled out. Within the more general framework leading to the normal configurational force balance (1.8), the question as to when the Leo–Sekerka relation is applicable is equivalent to the question as to when the internal force g is negligible. Our more general framework provides an answer to this question: *for sufficiently small length scales the internal force g cannot be neglected*, because the term emanating from g in the evolution equations for the interface is of the same order of magnitude as the other kinetic term in these equations, which results from accretion (cf. §26.3). On the other hand, for sufficiently large length scales the force g is negligible. Quantification of the terms "small" and "large" would require a knowledge of the kinetic modulus b.

If we restrict attention to a single atomic species, neglect the adatom density, and take $g = 0$, then the normal configurational force balance reduces to the Wu–Norris–Freund relation (1.2) with $U = \rho\mu$. The chemical potential U of Wu, Norris, and Freund is, by its very definition, a potential associated with the addition of material at the solid-vapor interface, without regard to the specific composition of that material. As such, U cannot be used to discuss alloys.

1.5 Scope

We begin with a discussion of the theory in bulk, as this allows for a simple presentation of basic ideas. Our discussion of *substitutional alloys* follows Larché and Cahn (1985),[10] who introduce a scalar constant, ρ^{sites}, that represents the density of substitutional sites, per unit volume, available for occupation by atoms. The atomic densities ρ^α for a substitutional alloy are then required to satisfy the lattice constraint

$$\sum_{\alpha=1}^{N} \rho^\alpha = \rho^{\text{sites}},$$

a constraint that Larché and Cahn show to have important consequences, the most important being the result that Fickean diffusion in bulk is driven not by the individual chemical potentials μ^α, but instead by the *relative chemical potentials* $\mu^{\alpha\beta} = \mu^\alpha - \mu^\beta$. Larché and Cahn arrive at this result using a variational argument. Here following the framework set forth in §1.3, we show that this result of Larché and Cahn is independent of constitutive equations, as it follows directly from the bulk free-energy imbalance and the requirement that the bulk atomic-fluxes $\boldsymbol{\jmath}^\alpha$ satisify the substitutional flux constraint

$$\sum_{\alpha=1}^{N} \boldsymbol{\jmath}^\alpha = \mathbf{0}$$

(Ågren (1982), Cahn and Larché (1983)).

To arrive at thermodynamically consistent equations, we follow Coleman and Noll (1963), who use the laws of continuum thermodynamics to suitably restrict constitutive

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[10] Mechanicians seem unaware of this work.

equations. This process involves differentiating the constitutive relation for the bulk free-energy with respect to atomic densities. For substitutional alloys any such differentiation must respect the lattice constraint. We overcome this obstacle with the aid of the Larché–Cahn derivative (Larché and Cahn, 1985), a procedure that results in constitutive relations for the *relative* chemical potentials. To our knowledge, ours is the first work to combine the approach of Coleman and Noll with that of Larché and Cahn.

We consider also *unconstrained materials*, which are materials whose atomic densities are unencumbered by a lattice constraint. A material whose mobile atoms are interstitial would be unconstrained, as the high density of interstitial vacancies renders a lattice constraint unimportant. More generally, some workers (cf. Mullins and Sekerka 1985) circumvent the discussion of a lattice constraint by assuming the existence of a defect mechanism that accomodates an excess or deficiency of substitutional atoms; materials treated under such an assumption are, by fiat, unconstrained.

Our discussion of interfaces is based on the format presented in §1.3. We begin with a discussion of grain boundaries (Part D). Anisotropy often renders the underlying evolution equations backward-parabolic and hence unstable, leading to the formation of facets and wrinklings (§17.6); we show that the use of a curvature-dependent energy (along with concomitant configurational moments) may be used to regularize the resulting evolution equations (§18). We also discuss grain-vapor interactions with atomic diffusion and evaporation-condensation, but within a more or less classical setting (§19). With this as background, we turn to more general grain-vapor interactions, focusing on the derivation of equations of sufficient complexity to characterize phenomena such as molecular-beam epitaxy (Part E). We close with a discussion of coherent solid-state phase-transitions (Part F).

Although worthy of discussion, other phenomena, such as incoherent phase transitions, are not included due to limitations of space.

A Deformation and atomic transport in bulk

2 Mechanics

We consider a homogeneous *crystalline body* $\mathcal{B}$ that occupies a region of three-dimensional space. We work within the framework of "small deformations" as described by a *displacement* field $\mathbf{u}(\mathbf{x},t)$ and infinitesimal *strain* $\mathbf{E}(\mathbf{x},t)$ related through the *strain-displacement relation*

$$\mathbf{E} = \tfrac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\top}). \tag{2.1}$$

When we wish to emphasize its time-dependent nature, we will refer to $\mathbf{u}$ as a *motion*; the time-rate $\dot{\mathbf{u}}$ of $\mathbf{u}$, which represents the velocity of material points, will be referred to as the *motion velocity.*

For convenience, *we neglect inertia* as it is generally unimportant in solid-state problems involving the interaction of composition and stress.

We associate with each motion of $\mathcal{B}$ a system of forces represented by a stress (tensor) $\mathbf{T}(\mathbf{x},t)$. Given any *part* $\mathcal{P}$ of $\mathcal{B}$ and letting $\boldsymbol{\nu}$ denote the outward unit normal to $\partial\mathcal{P}$, $\mathbf{T}\boldsymbol{\nu}$ represents the surface traction (force per unit area) exerted on $\mathcal{P}$ across $\partial\mathcal{P}$; to simplify the presentation, we neglect external body forces. The balance laws for forces and torques then take the form

$$\int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\, da = \mathbf{0}, \qquad \int\limits_{\partial\mathcal{P}} (\mathbf{x}-\mathbf{0}) \times \mathbf{T}\boldsymbol{\nu}\, da = \mathbf{0}, \tag{2.2}$$

for every part $\mathcal{P}$. These yield the local force and moment balances

$$\operatorname{div}\mathbf{T} = \mathbf{0}, \qquad \mathbf{T} = \mathbf{T}^{\top}. \tag{2.3}$$

Given any part $\mathcal{P}$,

$$\mathcal{W}(\mathcal{P}) = \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\, da \tag{2.4}$$

represents the power expended by the tractions on $\mathcal{P}$. Using the moment balance $(2.3)_2$, which implies that $\mathbf{T}\cdot\nabla\dot{\mathbf{u}} = \mathbf{T}\cdot\dot{\mathbf{E}}$, and the force balance $(2.3)_1$, we find that

$$\mathcal{W}(\mathcal{P}) = \int\limits_{\mathcal{P}} \mathbf{T}\cdot\dot{\mathbf{E}}\, dv. \tag{2.5}$$

3 Balance law for atoms

Our treatment of solids is, in some respects, more complicated than descriptions usually encountered in continuum mechanics as the theory, although macroscopic, allows for microstructure by associating with each $\mathbf{x}\in\mathcal{B}$ a *lattice* (or network) through which atoms diffuse.

We consider N species of atoms, labelled $\alpha = 1, 2, \ldots, N$, and let $\rho^{\alpha}(\mathbf{x}, t)$ denote the *atomic density* of species α, which is the density measured in atoms per unit volume. If $\mathcal{P}$ is a part of $\mathcal{B}$, then $\int_{\mathcal{P}} \rho^{\alpha}\, dv$ represents the number of atoms of α in $\mathcal{P}$. Changes in the number of α-atoms in $\mathcal{P}$ are generally brought about by the diffusion of species α across the boundary $\partial\mathcal{P}$. This diffusion is characterized by an *atomic flux* (vector) $\boldsymbol{\jmath}^{\alpha}(\mathbf{x}, t)$, measured in atoms per unit area, per unit time, so that $-\int_{\partial\mathcal{P}} \boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\, da$ represents the number of α-atoms entering $\mathcal{P}$ across $\partial\mathcal{P}$, per unit time. The *balance law for atoms* therefore takes the form

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^{\alpha}\, dv = -\int\limits_{\partial\mathcal{P}} \boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\, da, \tag{3.1}$$

for all species α and every part $\mathcal{P}$.[11]

Bringing the time derivative in (3.1) inside the integral and using the divergence theorem on the integral over $\partial\mathcal{P}$, we find that

$$\int\limits_{\mathcal{P}} (\dot{\rho}^{\alpha} + \operatorname{div}\boldsymbol{\jmath}^{\alpha})\, dv = 0;$$

since $\mathcal{P}$ is arbitrary, this leads to a (local) *balance law for atoms*: for any species α,

$$\dot{\rho}^{\alpha} = -\operatorname{div}\boldsymbol{\jmath}^{\alpha}. \tag{3.2}$$

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[11] If we multiply (3.1) by the mass of an α-atom, the resulting equation then represents a mass balance for α-atoms.

4 Thermodynamics. The free-energy imbalance

We base the theory on a free-energy imbalance that represents the first two laws of thermodynamics under isothermal conditions. In this subsection we derive this free-energy imbalance from versions of the first two laws appropriate for continuum mechanics.

4.1 Chemical potentials. Balance of energy. Entropy imbalance

We write $\epsilon(\mathbf{x},t)$ for the *internal energy*, per unit volume, so that $\int_{\mathcal{P}} \epsilon\,dv$ represents the internal energy of a part $\mathcal{P}$.[12] Changes in the internal energy of $\mathcal{P}$ are balanced by energy carried into $\mathcal{P}$ by atomic transport, heat transferred to $\mathcal{P}$, and power expended on $\mathcal{P}$. We view chemical potentials as *primitive quantities* that enter the theory through the manner in which they appear in the basic law expressing balance of energy. This contrasts sharply with what is done in the materials science literature, where chemical potentials are defined as derivatives of free energy with respect to composition, or introduced variationally — via an assumption of equilibrium — as Lagrange multipliers corresponding to a mass constraint; in either case the chemical potentials require a constitutive structure. To the contrary, the framework we use considers balance of energy as basic, and in a continuum theory that involves a flow of atoms through the material it is necessary to account for energy carried with the flowing atoms.[13] To characterize the energy carried into parts $\mathcal{P}$ by atomic transport, we introduce the *chemical potentials* $\mu^\alpha(\mathbf{x},t)$ of the individual species α; specifically, the flow of atoms of species α, as represented by $\boldsymbol{\jmath}^\alpha$, is presumed to carry with it a flux of energy described by $\mu^\alpha\boldsymbol{\jmath}^\alpha$; thus

$$-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}} \mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da \tag{4.1}$$

represents the net rate at which energy is carried into $\mathcal{P}$ by the flow of atoms across $\partial\mathcal{P}$.

The heat transferred to $\mathcal{P}$ is characterized by a *heat flux* (vector) $\mathbf{q}(\mathbf{x},t)$, measured per unit area, that represents heat conduction across $\partial\mathcal{P}$; precisely, $-\int_{\partial\mathcal{P}} \mathbf{q}\cdot\boldsymbol{\nu}\,da$ represents the net heat transfered to $\mathcal{P}$. Thus since the expended power is given by (2.4), balance of energy has the form

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \epsilon\,dv = \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da - \int\limits_{\partial\mathcal{P}} \mathbf{q}\cdot\boldsymbol{\nu}\,da - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}} \mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da \tag{4.2}$$

for all parts $\mathcal{P}$ of $\mathcal{B}$.

The second law of thermodynamics is the requirement that the entropy of a part $\mathcal{P}$ change at a rate not less than the entropy flow into $\mathcal{P}$. Parallel to our treatment of internal energy, we write the entropy of an arbitrary part $\mathcal{P}$ as an integral $\int_{\mathcal{P}} \eta\,dv$ with $\eta(\mathbf{x},t)$ the *entropy*, per unit volume. We let

$$\theta(\mathbf{x},t) > 0$$

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[12] We use ϵ for internal energy and ε for interfacial tensile strain. While it is difficult to differentiate between these symbols, it should be clear from the context which is meant. Moreover, our discussion of internal energy is limited to §4, where there is no mention of interfacial strain.

[13] Eckart (1940), in his discussion of fluid mixtures, notes that chemical potentials should enter balance of energy through terms of the form (4.1). (Jaumann (1911) and Lohr (1917) seem also to have this view, but we are unable to fully comprehend their work.) While Eckart employs constitutive equations, their use is unnecessary. Related works are Meixner and Reik (1959), Müller (1968), Gurtin and Vargas (1971), Davì and Gurtin (1990), and Gurtin (1991).

denote the *absolute temperature* and assume that, given any $\mathcal{P}$, the conduction of heat induces a net transfer of entropy to $\mathcal{P}$ of amount

$$-\int_{\partial\mathcal{P}} \frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\,da.$$

The second law is therefore represented by the *entropy imbalance*[14]

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \eta\,dv \geq -\int\limits_{\partial\mathcal{P}} \frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\,da, \tag{4.3}$$

to be satisfied for all parts $\mathcal{P}$.

4.2 Isothermal conditions. The free-energy imbalance

Assume now that *isothermal* conditions prevail, so that

$$\theta \equiv \text{constant},$$

and consider the (Helmholtz) *free-energy* (*density*) defined by

$$\Psi = \varepsilon - \theta\eta. \tag{4.4}$$

Multiplying the entropy imbalance (4.3) by θ and subtracting the result from the energy balance (4.2) then yields the *free-energy imbalance*

$$\frac{d}{dt}\int\limits_{\mathcal{P}} \Psi\,dv \leq \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}} \mu^{\alpha}\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\,da. \tag{4.5}$$

We henceforth restrict attention to isothermal processes and for that reason base the theory on the free-energy imbalance (4.5).

If, in the free-energy imbalance, we bring the time derivative inside the integral and use the divergence theorem on the integral over $\partial\mathcal{P}$ together with the expression (2.5) for the expended power, we find that

$$\int\limits_{\mathcal{P}} \Big(\dot{\Psi} - \mathbf{T}\cdot\dot{\mathbf{E}} + \sum_{\alpha=1}^{N} \operatorname{div}(\mu^{\alpha}\boldsymbol{\jmath}^{\alpha})\Big)\,dv \leq 0,$$

so that, since $\mathcal{P}$ is arbitrary,

$$\dot{\Psi} - \mathbf{T}\cdot\dot{\mathbf{E}} + \sum_{\alpha=1}^{N} \operatorname{div}(\mu^{\alpha}\boldsymbol{\jmath}^{\alpha}) \leq 0.$$

Thus expanding the divergence and appealing to the atomic balance (3.1), we are led to the inequality

$$\dot{\Psi} - \mathbf{T}\cdot\dot{\mathbf{E}} - \sum_{\alpha=1}^{N}(\mu^{\alpha}\dot{\rho}^{\alpha} - \boldsymbol{\jmath}^{\alpha}\cdot\nabla\mu^{\alpha}) \leq 0. \tag{4.6}$$

The quantity

$$\delta \overset{\text{def}}{=} -\sum_{\alpha=1}^{N}(\boldsymbol{\jmath}^{\alpha}\cdot\nabla\mu^{\alpha} - \mu^{\alpha}\dot{\rho}^{\alpha}) + \mathbf{T}\cdot\dot{\mathbf{E}} - \dot{\Psi} \geq 0 \tag{4.7}$$

represents the *dissipation* per unit volume, since its integral over any part $\mathcal{P}$ gives the right side of (4.5) minus the left. For that reason, we refer to local forms of the free-energy imbalance as *dissipation inequalities*.

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[14] Usually referred to as the Clausius–Duhem inequality (cf. Truesdell and Toupin, 1960).

5 Substitutional alloys

Our discussion to this point does not distinguish between substitutional and interstitial species. Here, following Larché and Cahn (1985, §2), we use the terms "substitutional" and "interstitial" in the following sense: "[Lattice] sites that are mostly filled are occupied by what are called substitutional atoms, while sites that are mostly vacant are occupied by interstitial atoms." The high density of interstitial vacancies renders a corresponding lattice constraint unimportant.[15] This section is concerned solely with substitutional alloys, neglecting the presence of interstitials.

5.1 Lattice constraint. Vacancies

We introduce a scalar constant ρ^{sites} that represents the density of *substitutional sites*, per unit volume, available for occupation by atoms. We restrict attention to *substitutional alloys*, so that the atoms are constrained to lie on lattice sites.[16] A minor abuse of terminology allows for *vacancies* (unoccupied substitutional sites) within the same framework as the theory without vacancies: when vacancies are to be considered, we reserve the label v of one substitutional species for vacancies,[17] so that $\rho^{\text{v}}(\mathbf{x},t)$ represents the *vacancy density*, $\boldsymbol{\jmath}^{\text{v}}(\mathbf{x},t)$ the *vacancy flux*, and $\mu^{\text{v}}(\mathbf{x},t)$ the *chemical potential for vacancies*. Then, whether or not vacancies are being considered, the substitutional densities must be consistent with the *lattice constraint*

$$\sum_{\alpha=1}^{N} \rho^{\alpha} = \rho^{\text{sites}}. \tag{5.1}$$

A consequence of the lattice constraint is *conservation of substitutional atoms*,

$$\sum_{\alpha=1}^{N} \dot{\rho}^{\alpha} = 0, \tag{5.2}$$

a condition that, by virtue of the local atomic balance (3.2), is equivalent to the diffusional constraint

$$\sum_{\alpha=1}^{N} \operatorname{div} \boldsymbol{\jmath}^{\alpha} = 0. \tag{5.3}$$

---

[15] We do not allow for interstitial defects, which are substitutional atoms forced into interstitial positions, and which are hence incompatible with the lattice constraint. According to DeHoff (1993, p. 411): "At the same temperature it can be expected that the concentration of interstitial defects is very much smaller (usually by several orders of magnitude) than that of vacancies at equilibrium." Allowance for interstitial defects may be important when considering neutron irradiation (DeHoff 1993, p. 411) or deformation (Shewman 1969, p. 47). Finally, DeHoff (1993, p. 406) notes that: "Even in the extreme, near the melting point, defect sites occur at only about one site in 10,000 … Nonetheless, this small fraction of defect sites plays a crucial role in materials science." Some workers (cf. Mullins and Sekerka 1985) circumvent the discussion of a lattice constraint by assuming the existence of a defect mechanism that accomodates an excess or deficiency of substitutional atoms.

[16] Our discussion of the lattice constraint follows Larché and Cahn (1985, §2).

[17] Thus "all atoms" means "all atoms and vacancies," and so forth.

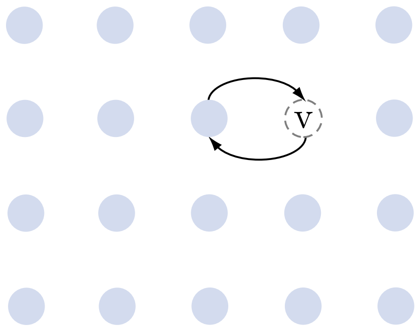

Figure 1: Schematic of an atom-vacancy exchange.

5.2 Substitutional flux constraint. Relative chemical potentials

(a) Importance of relative chemical potentials

A restriction stronger than the diffusional constraint (5.3) is the *substitutional flux constraint*

$$\sum_{\alpha=1}^{N} \boldsymbol{\jmath}^{\alpha} = \mathbf{0} \tag{5.4}$$

discussed by Ågren (1982) and Cahn and Larché (1983), who argue that (5.4) is a consequence of the requirement that diffusion, as represented by atomic fluxes, arises, microscopically, from exchanges of atoms or exchanges of atoms with vacancies (Figure 1).

> FLUX HYPOTHESIS FOR SUBSTITUTIONAL ALLOYS *We assume henceforth that the substitutional flux constraint is satisfied.*

Essential to the treatment of substitutional alloys are the *relative chemical potentials* defined by

$$\mu^{\alpha\zeta} = \mu^{\alpha} - \mu^{\zeta}. \tag{5.5}$$

Direct consequences of this definition are the identities

$$\mu^{\alpha\alpha} = 0, \qquad \mu^{\alpha\beta} = -\mu^{\beta\alpha}, \qquad \mu^{\alpha\beta} = \mu^{\alpha\zeta} - \mu^{\beta\zeta}. \tag{5.6}$$

The next result is fundamental to the discussion of substitutional alloys.

> THEOREM ON RELATIVE CHEMICAL POTENTIALS Given any choice of reference species ζ, we may, without loss in generality, replace the free-energy imbalance (4.5) with that obtained by replacing each chemical potential μ^{α} by the corresponding relative chemical potential $\mu^{\alpha\zeta}$:
>
> $$\frac{d}{dt}\int\limits_{\mathcal{P}} \Psi\, dv \le \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\, da - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}} \mu^{\alpha\zeta}\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\, da. \tag{5.7}$$

To establish this result, we first show that the free-energy imbalance (4.5) is invariant under all transformations of the form

$$\mu^{\alpha}(\mathbf{x},t) \to \mu^{\alpha}(\mathbf{x},t) + \lambda(\mathbf{x},t) \qquad \text{for all species } \alpha, \tag{5.8}$$

with $\lambda(\mathbf{x},t)$ independent of α. In view of the substitutional flux constraint, given any such field $\lambda(\mathbf{x},t)$,

$$\sum_{\alpha=1}^{N}(\mu^{\alpha}+\lambda)\boldsymbol{\jmath}^{\alpha}=\sum_{\alpha=1}^{N}\mu^{\alpha}\boldsymbol{\jmath}^{\alpha}+\lambda\sum_{\alpha=1}^{N}\boldsymbol{\jmath}^{\alpha}=\sum_{\alpha=1}^{N}\mu^{\alpha}\boldsymbol{\jmath}^{\alpha}, \tag{5.9}$$

and hence

$$\frac{d}{dt}\int_{\mathcal{P}}\Psi\,dv\le\int_{\partial\mathcal{P}}\mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da-\sum_{\alpha=1}^{N}\int_{\partial\mathcal{P}}(\mu^{\alpha}+\lambda)\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\,da. \tag{5.10}$$

Thus the free-energy imbalance is invariant under the transformation (5.8). The specific choice $\lambda=-\mu^{\zeta}$ in (5.10) yields the desired result (5.7). This completes the proof of the theorem.

The free-energy imbalance (5.7), when localized, yields the *dissipation inequality*[18]

$$\dot{\Psi}-\mathbf{T}\cdot\dot{\mathbf{E}}-\sum_{\alpha=1}^{N}(\mu^{\alpha\zeta}\,\dot{\rho}^{\alpha}-\boldsymbol{\jmath}^{\alpha}\cdot\nabla\mu^{\alpha\zeta})\le 0, \tag{5.11}$$

which is to hold for any given choice of ζ. This inequality will be useful in developing a suitable constititutive theory for substitutional alloys.

(b) Remarks

1. Of the basic laws, it is only the free-energy imbalance that involves chemical potentials. We may therefore conclude from the theorem on relative chemical potentials that *the individual chemical potentials are irrelevant to the theory in bulk.* At external or internal boundaries, however, it is often the individual chemical potentials that are needed, a specific example being a solid-vapor interface (cf. §24.2 as well as Larché and Cahn (1985)).

2. The free-energy imbalance (5.7) and the dissipation inequality (5.11) may be written with the chemical potentials expressed *relative* to that of any arbitrarily chosen species ζ, in which case both (5.7) and (5.11) are independent of ρ^{ζ} and $\boldsymbol{\jmath}^{\zeta}$.

3. Larché and Cahn (1973, 1985) were apparently the first to emphasize the importance of the relative chemical potentials when discussing substitutional alloys. Specifically, Larché and Cahn (1973) consider a variational problem that, within our framework, consists in minimizing a body's free energy under a mass constraint for each atomic species. Larché and Cahn define the chemical potentials μ^{α}, $\alpha=1,2,\dots,N$, to be the Lagrange multipliers associated with the mass constraints; they show that *only the relative chemical potentials $\mu^{\alpha}-\mu^{\beta}$ enter the corresponding equilibrium conditions.*

4. Like the pressure in an incompressible body, the individual chemical potentials are indeterminate in bulk.

5. One might refer to invariance of the free-energy imbalance under all transformations of the form

$$\mu^{\alpha}(\mathbf{x},t)\to\mu^{\alpha}(\mathbf{x},t)+\lambda(\mathbf{x},t)\qquad\text{for all species }\alpha$$

---

[18] When dealing with relative chemical potentials, we will often encounter expressions such as (5.11), in which ζ appears as a free-index.

as *invariance of the lattice chemistry.* As is clear from the proof of the theorem on relative chemical potentials, invariance of the lattice chemistry is equivalent to the conclusions of that theorem. Moreover, as we shall show, *invariance of the lattice chemistry is equivalent to the substitutional flux constraint*, so that we could equally well have taken — as our starting hypothesis — invariance of the lattice chemistry rather than the flux hypothesis for substitutional alloys.

In view of (5.8)–(5.10), to prove our assertion of equivalence we have only to show that invariance of the lattice chemistry implies the substitutional flux constraint. Indeed, if (5.10) holds for all fields λ and all parts $\mathcal{P}$. Then

$$\sum_{\alpha=1}^{N} \int\limits_{\partial\mathcal{P}} \lambda\, \boldsymbol{\jmath}^{\alpha} \cdot \boldsymbol{\nu}\, da = 0, \tag{5.12}$$

for otherwise we could choose λ to violate (5.10). Thus

$$\int\limits_{\partial\mathcal{P}} \lambda\, \mathbf{z} \cdot \boldsymbol{\nu}\, da = 0, \qquad \mathbf{z} = \sum_{\alpha=1}^{N} \boldsymbol{\jmath}^{\alpha} \tag{5.13}$$

for all *fields* λ and all parts $\mathcal{P}$. A standard argument in the calculus of variations then implies that $\mathbf{z} \equiv \mathbf{0}$.

6. Invariance of the lattice chemistry has the following physical interpretation. Roughly speaking, the chemical potential of a given species at a point $\mathbf{x}$ represents the energy the body would gain, per unit time, were we to add one atom, per unit time, of that species at $\mathbf{x}$. Because of the lattice constraint, adding an atom A of a given species involves removing an atom B of that or another species. Thus, *increasing the chemical potential of each species by the same amount should not affect the free-energy imbalance*, because the marginal increase in energy associated with the addition of A would be balanced by the marginal decrease associated with the removal of B.

5.3 Elimination of the lattice constraint

Because of the lattice constraint (5.1), we may omit the atomic balance for the substitutional species ζ, say, and simply define

$$\rho^{\zeta} = \rho^{\mathrm{sites}} - \sum_{\substack{\alpha=1 \\ \alpha\neq\zeta}}^{N} \rho^{\alpha}. \tag{5.14}$$

Thus and by the substitutional flux constraint (5.4),

$$\dot{\rho}^{\zeta} = -\sum_{\substack{\alpha=1 \\ \alpha\neq\zeta}}^{N} \dot{\rho}^{\alpha}, \qquad \boldsymbol{\jmath}^{\zeta} = -\sum_{\substack{\alpha=1 \\ \alpha\neq\zeta}}^{N} \boldsymbol{\jmath}^{\alpha},$$

so that *the atomic balance for species ζ is satisfied automatically* provided the atomic balances for each remaining species $\alpha \neq \zeta$ are satisfied.

In view of this discussion, we may, without loss in generality, use the following *normalization* in which a given species ζ is used as *reference*:

- We consider the atomic density ρ^{ζ} and the atomic flux $\boldsymbol{\jmath}^{\zeta}$ defined by the lattice constraint and the substitutional flux constraint, respectively.

- We omit the atomic balance law for the species ζ.
- We use as chemical potentials for the species α the relative chemical potentials $\mu^{\alpha\zeta}$.
- We use the free-energy imbalance and dissipation inequality (5.11) with ζ as reference (since these are independent of ρ^ζ and $\jmath^\zeta$).

As we shall see, for solid-vapor interfaces with interfacial atomic transport, the absence of a lattice constraint at the interface renders this normalization of little use (cf. §24.2).

6 Global theorems

Granted appropriate boundary conditions, the atomic balance

$$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, dv = -\int\limits_{\partial\mathcal{B}} \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} \, da \tag{6.1}$$

(cf. (2.4)) and the free-energy imbalance

$$\frac{d}{dt}\int\limits_{\mathcal{B}} \Psi \, dv \le \int\limits_{\partial\mathcal{B}} \Bigl(\mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}} - \sum_{\alpha=1}^{N} \mu^\alpha \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu}\Bigr) da \tag{6.2}$$

(cf. (4.5), (3.1)) applied to the body itself yield important global conservation and decay relations. Such relations are important for two reasons: they suggest variational principles appropriate to a discussion of equilibrium; and they are useful for establishing a priori estimates and, hence, results concerning the existence and qualitative properties of solutions to initial-boundary-value problems.

With a view toward establishing such global relations, we introduce the following definitions. Let $\mathcal{A}$ be a subsurface of $\partial\mathcal{B}$. We say that:

(i) $\mathcal{A}$ is *fixed* if

$$\dot{\mathbf{u}} = \mathbf{0} \quad \text{on } \mathcal{A};$$

(ii) $\mathcal{A}$ is subject to *dead loads* if there is a constant symmetric (stress) tensor $\mathbf{T}_*$ such that

$$\mathbf{T}\boldsymbol{\nu} = \mathbf{T}_*\boldsymbol{\nu} \quad \text{on } \mathcal{A};$$

(iii) $\mathcal{A}$ is *impermeable* if, for each atomic species α,

$$\boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} = 0 \quad \text{on } \mathcal{A};$$

(iv) (for unconstrained materials) $\mathcal{A}$ is in *chemical equilibrium* if, for each atomic species α, there is a constant chemical potential μ^α_* such that

$$\mu^\alpha = \mu^\alpha_* \quad \text{on } \mathcal{A};$$

(iv′) (for substitutional alloys) $\mathcal{A}$ is in *chemical equilibrium* if, for some fixed choice of species ζ and any other species α, there is a constant relative chemical potential $\mu^{\alpha\zeta}_*$ such that

$$\mu^{\alpha\zeta} = \mu^{\alpha\zeta}_* \quad \text{on } \mathcal{A}.$$

(When $\mathcal{A}$ separates the solid from a vapor, the boundary values $\mu^{\alpha\zeta}_*$ would be given by the corresponding difference in vapor potentials: $\mu^{\alpha\zeta}_* = \mu^\alpha_v - \mu^\zeta_v$.)

A direct consequence of (i) and (iii) with $\mathcal{A} = \partial\mathcal{B}$, (6.1), and (6.2) is the

> Theorem for an Isolated Body If the body is isolated, that is if $\partial\mathcal{B}$ is fixed and impermeable, then the total number of atoms of each species remains fixed, while the total free-energy is nonincreasing:
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, dv = 0, \quad \alpha = 1, 2, \dots, N,$$
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} \Psi \, dv \le 0.$$

For a nonisolated body under sufficiently simple boundry conditions one can still prove a global decay relation for a physically meaningful integral.

> Global Decay Theorem Assume that a portion $\mathcal{A}$ of $\partial\mathcal{B}$ is fixed and the remainder, $\partial\mathcal{B} \setminus \mathcal{A}$, subject to dead loads.
>
> (a) If $\partial\mathcal{B}$ is impermeable, then
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, dv = 0, \quad \alpha = 1, 2, \dots, N,$$
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} (\Psi - \mathbf{T}_* \cdot \mathbf{E}) \, dv \le 0.$$
>
> (b) If a portion $\mathcal{E}$ of $\partial\mathcal{B}$ is impermeable and the remainder, $\partial\mathcal{B}\backslash\mathcal{E}$, in chemical equilibrium, then, if the material is unconstrained,
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} \Big(\Psi - \mathbf{T}_* \cdot \mathbf{E} - \sum_{\alpha=1}^{N} \mu_*^\alpha \rho^\alpha\Big) \, dv \le 0,$$
>
> while
>
> $$\frac{d}{dt}\int\limits_{\mathcal{B}} \Big(\Psi - \mathbf{T}_* \cdot \mathbf{E} - \sum_{\alpha=1}^{N} \mu_*^{\alpha\zeta} \rho^\alpha\Big) \, dv \le 0$$
>
> if the material is a substitutional alloy.

To prove this theorem, note first that, by hypothesis,

$$\int\limits_{\partial\mathcal{B}} \mathbf{T}\boldsymbol{\nu} \cdot \dot{\mathbf{u}} \, da = \int\limits_{\partial\mathcal{B}} \mathbf{T}_*\boldsymbol{\nu} \cdot \dot{\mathbf{u}} \, da = \frac{d}{dt}\int\limits_{\partial\mathcal{B}} \mathbf{T}_*\boldsymbol{\nu} \cdot \mathbf{u} \, da = \frac{d}{dt}\int\limits_{\mathcal{B}} \mathbf{T}_* \cdot \nabla\mathbf{u} \, dv = \frac{d}{dt}\int\limits_{\mathcal{B}} \mathbf{T}_* \cdot \mathbf{E} \, dv; \tag{6.3}$$

hence assertion (a) follows from (6.1), (6.2), and the stipulated boundary condition $\boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} = 0$ on $\partial\mathcal{B}$ for all α.

To establish part (b) of the theorem, consider an unconstrained material. Then, by (iv) applied to $\mathcal{A} = \partial\mathcal{B} \setminus \mathcal{E}$ and the atomic balance (6.1),

$$\begin{aligned} -\sum_{\alpha=1}^{N} \int\limits_{\partial\mathcal{B}} \mu^\alpha \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} \, da &= -\sum_{\alpha=1}^{N} \mu_*^\alpha \int\limits_{\partial\mathcal{B}} \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} \, da \\ &= \sum_{\alpha=1}^{N} \mu_*^\alpha \Big\{\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, dv\Big\} = \frac{d}{dt}\Big\{\sum_{\alpha=1}^{N} \int\limits_{\mathcal{B}} \mu_*^\alpha \rho^\alpha \, dv\Big\}. \end{aligned} \tag{6.4}$$

Similarly, for a substitutional alloy we may use the substitutional flux constraint (5.4) and (iv′) to conclude that

$$-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{B}}\mu^\alpha \boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da = -\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{B}}\mu^{\alpha\zeta}\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da = \sum_{\alpha=1}^{N}\left\{\frac{d}{dt}\int\limits_{\mathcal{B}}\mu_*^{\alpha\zeta}\rho^\alpha\,dv\right\}. \tag{6.5}$$

Assertion (b) follows from (6.2) and (6.3)–(6.5).

7 Constitutive theory for multiple atomic species in the absence of a lattice constraint

The force and moment balances, the balance law for atoms, and the free-energy imbalance are basic laws, common to large classes of materials; we keep such laws distinct from specific constitutive equations, which differentiate between particular materials. We view the dissipation inequality as a guide in the development of suitable constitutive theories. In this regard we do not seek general constitutive equations consistent with the dissipation inequality, but instead we begin with constitutive equations close to those upon which more classical theories are based.

7.1 Basic constitutive theory for an elastic material with Fickean diffusion

Guided by the dissipation inequality (4.6) and by standard theories of elasticity and diffusion, we assume that the free energy, stress, and chemical potential are prescribed functions of the strain and the list

$$\vec{\rho} \stackrel{\text{def}}{=} (\rho^1, \rho^2, \dots, \rho^N)$$

of atomic densities,

$$\left.\begin{aligned} \Psi &= \hat{\Psi}(\mathbf{E}, \vec{\rho}),\\ \mathbf{T} &= \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}),\\ \mu^\alpha &= \hat{\mu}^\alpha(\mathbf{E}, \vec{\rho}), \end{aligned}\right\} \tag{7.1}$$

and that the atomic flux is given by *Fick's law*

$$\boldsymbol{\jmath}^\alpha = -\sum_{\beta=1}^{N}\mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})\nabla\mu^\beta, \tag{7.2}$$

with $\mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})$ the *mobility tensor* for species α with respect to species β. Such a "mixed" description with μ^α as independent variables in (7.1) and $\nabla\mu^\alpha$ as dependent variables in (7.2) is widely used by materials scientists (Larché and Cahn, 1985, §8.1).[19]

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[19] We, therefore, do not adhere to the principle of equipresence, as discussed by Truesdell and Toupin (1960) and Truesdell and Noll (1964), which asserts that "a quantity present as an independent variable in one constitutive equation should be so present in all, unless … its presence contradicts some law of physics or rule of invariance." According to Truesdell and Noll (1965, §96), "This principle forbids us to eliminate any of the 'causes' present from interacting with any other as regards a particular 'effect.' It reflects on the scale of gross phenomena the fact that all observed effects result from a common structure such as the motions of molecules.". A general treatment consistent with equipresence is provided by

The functions $\hat{\Psi}$, $\hat{\mathbf{T}}$, $\hat{\mu}^\alpha$, and $\mathbf{M}^{\alpha\beta}$ represent *constitutive response functions* for the material.

The constitutive equation (7.2) is simple in form but complicated in nature, as each of the mobilities $\mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})$ is a second-order tensor reflecting the underlying symmetry of the material. The mobilities can be arranged in a matrix array

$$\begin{bmatrix} \mathbf{M}^{11} & \mathbf{M}^{12} & \dots & \mathbf{M}^{1N} \\ \mathbf{M}^{21} & \mathbf{M}^{22} & \dots & \mathbf{M}^{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{M}^{N1} & \mathbf{M}^{N2} & \dots & \mathbf{M}^{NN} \end{bmatrix} \tag{7.3}$$

with tensor entries, but it should be kept in mind that, since each mobility tensor has 9 components, (7.3) represents $9N^2$ scalar constitutive moduli. We refer to (7.3) as the *mobility matrix*.

Following the procedure of Coleman and Noll (1963), we require that the dissipation inequality (5.11) hold in all "processes" related through the constitutive equations (7.1) and (7.2); equivalently,

$$\left\{\frac{\partial\hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial\mathbf{E}} - \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho})\right\} \cdot \dot{\mathbf{E}} + \sum_{\alpha=1}^{N}\left\{\frac{\partial\hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial\rho^\alpha} - \hat{\mu}^\alpha(\mathbf{E}, \vec{\rho})\right\}\dot{\rho}^\alpha \\ - \sum_{\alpha,\beta=1}^{N} \nabla\mu^\alpha \cdot \mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})\nabla\mu^\beta \le 0, \tag{7.4}$$

with $(\partial\hat{\Psi}/\partial\mathbf{E})_{ij} = \partial\hat{\Psi}/\partial E_{ij}$. We can always find fields $\mathbf{u}$ and $\vec{\rho}$ such that $\mathbf{E}$, $\dot{\mathbf{E}}$, ρ^α, $\dot{\rho}^\alpha$, and $\nabla\mu^\alpha$ (for each α) have arbitrarily prescribed values at some $(\mathbf{x}, t)$. Thus, since $\dot{\rho}^\alpha$ and $\dot{\mathbf{E}}$ appear linearly in (7.4), their "coefficients" must vanish, for otherwise $\dot{\rho}^\alpha$ and $\dot{\mathbf{E}}$ may be chosen to violate (7.4). This leaves the inequality $\sum_{\alpha,\beta=1}^{N} \nabla\mu^\alpha \cdot \mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})\nabla\mu^\beta \ge 0$. Therefore, as *thermodynamic restrictions*, the free energy must determine the stress and the chemical potentials through the "state relations"

$$\left.\begin{aligned} \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}) &= \frac{\partial\hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial\mathbf{E}}, \\ \hat{\mu}^\alpha(\mathbf{E}, \vec{\rho}) &= \frac{\partial\hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial\rho^\alpha}, \end{aligned}\right\} \tag{7.5}$$

and the mobility matrix (7.3) must be positive semi-definite:[20]

$$\sum_{\alpha,\beta=1}^{N} \mathbf{a}^\alpha \cdot \mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})\mathbf{a}^\beta \ge 0, \tag{7.6}$$

for all vector-lists $\vec{\mathbf{a}} = (\mathbf{a}^1, \mathbf{a}^2, \dots, \mathbf{a}^N)$. Reversing this argument we see that the restrictions (7.5) and (7.6) are sufficient that all process related through the constitutive

---

Fried and Gurtin (1999). Our results concur with theirs and, hence, equipresence provided the relation between the chemical potentials and atomic densities is invertible, a condition satisfied when $\hat{\Psi}$ is a strictly convex function of the densities. This assumption is often imposed when discussing single-phase materials. Phase transitions are more complicated, as there are two standard models: (i) the material is described by two or more strictly convex free energies, one for each phase, with the phases separated by a sharp interface; (ii) the material is described by a single "multi-well" free energy and the interface is diffuse. We here consider only case (i), in which case our treatment would be applicable for each phase.

[20] At least when the set of $(\mathbf{E}, \vec{\rho})$ at which the matrix with entries $\partial\hat{\mu}^\alpha(\mathbf{E}, \vec{\rho})/\partial\rho^\beta$ is invertible is dense in the space of all $(\mathbf{E}, \vec{\rho})$.

equations (7.1) and (7.2) obey the dissipation inequality (5.11) (irrespective of whether or not the condition specified in Footnote 20 is satisfied).

Thus, for a single species, $\boldsymbol{\jmath}\cdot\nabla\mu\le 0$, asserting that *atoms flow down a gradient in chemical-potential.* More generally, note that the dissipation (4.7), which is the negative of the left side of (7.4), is given by

$$\delta=\sum_{\alpha,\beta=1}^{N}\nabla\mu^{\alpha}\cdot\mathbf{M}^{\alpha\beta}(\mathbf{E},\vec{\rho}\,)\nabla\mu^{\beta}\ge 0.$$

7.2 Consequences of the thermodynamic restrictions

Immediate consequences of (7.5) are the *Maxwell relations*

$$\frac{\partial\hat{\mathbf{T}}}{\partial\rho^{\alpha}}=\frac{\partial\hat{\mu}^{\alpha}}{\partial\mathbf{E}} \tag{7.7}$$

and the *Gibbs relation*[21]

$$\dot{\Psi}=\mathbf{T}\cdot\dot{\mathbf{E}}+\mu^{\alpha}\dot{\rho}^{\alpha}. \tag{7.8}$$

It is convenient to define scalar and tensor moduli

$$\left.\begin{aligned}\mathbb{C}(\mathbf{E},\vec{\rho}\,)&=\frac{\partial\hat{\mathbf{T}}(\mathbf{E},\vec{\rho}\,)}{\partial\mathbf{E}}=\frac{\partial^{2}\hat{\Psi}(\mathbf{E},\vec{\rho}\,)}{\partial\mathbf{E}^{2}},\\ \mathbf{A}^{\alpha}(\mathbf{E},\vec{\rho}\,)&=\frac{\partial\hat{\mathbf{T}}(\mathbf{E},\vec{\rho}\,)}{\partial\rho^{\alpha}}=\frac{\partial\hat{\mu}^{\alpha}(\mathbf{E},\vec{\rho}\,)}{\partial\mathbf{E}}=\frac{\partial^{2}\hat{\Psi}(\mathbf{E},\vec{\rho}\,)}{\partial\mathbf{E}\,\partial\rho^{\alpha}}.\end{aligned}\right\} \tag{7.9}$$

We refer to $\mathbb{C}$ as the *elasticity tensor* and to $\mathbf{A}^{\alpha}$ as *stress-composition* (or chemistry-strain) *tensors* for α. The elasticity tensor $\mathbb{C}$ is a symmetric linear transformation of symmetric tensors into symmetric tensors; that is, $\mathbb{C}$ associates with each symmetric tensor $\mathbf{U}$ a symmetric tensor $\mathbf{H}=\mathbb{C}[\mathbf{U}]$ (or, more precisely, $\mathbf{H}=\mathbb{C}(\mathbf{E},\vec{\rho}\,)[\mathbf{U}]$). For each atomic species α, $\mathbf{A}^{\alpha}$ is a symmetric tensor that represents the marginal increase in stress due to an incremental increase in the atomic density ρ^{α}, holding the other densities and the strain fixed, or equivalently, the marginal increase in μ^{α} due to an incremental increase in the strain holding the densities fixed. The elasticity tensor has components

$$C_{ijkl}=\frac{\partial^{2}\hat{\Psi}}{\partial E_{ij}\,\partial E_{kl}}$$

and for symmetric tensors $\mathbf{H}$ and $\mathbf{U}$, $\mathbf{H}=\mathbb{C}[\mathbf{U}]$ has the component form $H_{ij}=C_{ijkl}U_{kl}$, with components that satisfy

$$C_{ijkl}=C_{klij}=C_{ijlk}. \tag{7.10}$$

Because of these symmetries, there are at most 21 independent elastic moduli.

For $\mathbf{E}=\mathbf{E}(\mathbf{x},t)$, $\vec{\rho}=\vec{\rho}\,(\mathbf{x},t)$, and $\mathbf{T}=\hat{\mathbf{T}}(\mathbf{E}(\mathbf{x},t),\vec{\rho}\,(\mathbf{x},t))$, the definitions (7.9) of the elasticity and stress-composition tensors are consistent with the chain-rule calculation

$$\dot{\mathbf{T}}=\mathbb{C}(\mathbf{E},\vec{\rho}\,)[\dot{\mathbf{E}}]+\sum_{\alpha=1}^{N}\mathbf{A}^{\alpha}(\mathbf{E},\vec{\rho}\,)\dot{\rho}^{\alpha}. \tag{7.11}$$

---

[21] In the materials literature (cf., e.g., Caroli, Caroli, and Roulet (1984)) the Gibbs relation is generally a postulate rather than a consequence of the underlying thermodynamical development.

Note that, by $(7.9)_2$, Fick's law becomes

$$\jmath^{\alpha} = -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\mathbf{E},\vec{\rho})\Big(\sum_{\gamma=1}^{N} \frac{\partial^2\hat{\Psi}(\mathbf{E},\vec{\rho})}{\partial\rho^{\beta}\,\partial\rho^{\gamma}}\nabla\rho^{\gamma} + \mathbf{A}^{\beta}(\mathbf{E},\vec{\rho})\nabla\mathbf{E}\Big), \tag{7.12}$$

where, using Cartesian components,

$$(\mathbf{A}^{\beta}\nabla\mathbf{E})_j \overset{\text{def}}{=} A^{\beta}_{kl}\,\frac{\partial E_{kl}}{\partial x_j}, \tag{7.13}$$

so that

$$\jmath_i^{\alpha} = -\sum_{\beta=1}^{N} M_{ij}^{\alpha\beta}(\mathbf{E},\vec{\rho})\Big(\sum_{\gamma=1}^{N} \frac{\partial^2\hat{\Psi}(\mathbf{E},\vec{\rho})}{\partial\rho^{\beta}\,\partial\rho^{\gamma}}\,\frac{\partial\rho^{\gamma}}{\partial x_j} + A^{\beta}_{kl}(\mathbf{E},\vec{\rho})\,\frac{\partial E_{kl}}{\partial x_j}\Big). \tag{7.14}$$

Thus both density gradients and strain gradients may drive atomic diffusion.

7.3 Free enthalpy

It is often more convenient to use stress rather than strain as an independent variable. As is reasonable within the context of small elastic deformations, we assume that $\hat{\mathbf{T}}(\mathbf{E},\vec{\rho})$ is a smoothly invertible function of $\mathbf{E}$ with inverse

$$\mathbf{E} = \tilde{\mathbf{E}}(\mathbf{T},\vec{\rho});$$

we may then define new functions for the free energy and the chemical potential through

$$\begin{aligned}\Psi &= \tilde{\Psi}(\mathbf{T},\vec{\rho}) = \hat{\Psi}(\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}),\vec{\rho}),\\ \mu^{\alpha} &= \tilde{\mu}^{\alpha}(\mathbf{T},\vec{\rho}) = \hat{\mu}^{\alpha}(\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}),\vec{\rho}).\end{aligned}$$

With stress as independent variable, it is most convenient to work with the (Gibbs) *free-enthalpy* (density) defined by the Legendre transformation

$$\Phi = \Psi - \mathbf{T}\cdot\mathbf{E} \tag{7.15}$$

and given by the constitutive response function

$$\tilde{\Phi}(\mathbf{T},\vec{\rho}) = \tilde{\Psi}(\mathbf{T},\vec{\rho}) - \mathbf{T}\cdot\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}). \tag{7.16}$$

(We consistently use a "tilde" to denote a function of $(\mathbf{T},\vec{\rho})$, retaining the "hat" for a function of $(\mathbf{E},\vec{\rho})$.) Then, using the chain-rule and the restrictions (7.5), a straightforward calculation shows that

$$\left.\begin{aligned}\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}) &= -\frac{\partial\tilde{\Phi}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}},\\ \tilde{\mu}^{\alpha}(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\Phi}(\mathbf{T},\vec{\rho})}{\partial\rho^{\alpha}},\end{aligned}\right\} \tag{7.17}$$

a direct consequence of which is the *Maxwell relation*

$$\frac{\partial\tilde{\mathbf{E}}}{\partial\rho^{\alpha}} = -\frac{\partial\tilde{\mu}^{\alpha}}{\partial\mathbf{T}}. \tag{7.18}$$

We can also define moduli analogous to those of (7.9):

$$\left.\begin{aligned}\mathbb{K}(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}} = -\frac{\partial^2\tilde{\Psi}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}^2},\\ \mathbf{N}^\alpha(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho})}{\partial\rho^\alpha} = -\frac{\partial\tilde{\mu}^\alpha(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}},\end{aligned}\right\} \tag{7.19}$$

with $\mathbb{K}$ the *compliance tensor* and to $\mathbf{N}^\alpha$ the *strain-composition* (or chemistry-strain) *tensor* for α. The tensor $\mathbf{N}^\alpha$ represents the marginal increase in strain due to an incremental increase in the atomic density ρ^α, holding the other densities and the stress fixed, or equivalently, the marginal increase in μ^α due to an incremental increase in the stress holding the densities fixed.

For $\mathbf{T} = \mathbf{T}(\mathbf{x},t)$, $\vec{\rho} = \vec{\rho}(\mathbf{x},t)$, and $\mathbf{E} = \tilde{\mathbf{E}}(\mathbf{T}(\mathbf{x},t),\vec{\rho}(\mathbf{x},t))$, the definitions (7.19) of the compliance and chemistry-strain tensors are consistent with the chain-rule calculation

$$\dot{\mathbf{E}} = \mathbb{K}(\mathbf{T},\vec{\rho})[\dot{\mathbf{T}}] + \sum_{\alpha=1}^{N}\mathbf{N}^\alpha(\mathbf{T},\vec{\rho})\dot{\rho}^\alpha. \tag{7.20}$$

The compliance tensor $\mathbb{K}$ obeys

$$\mathbb{K}(\mathbf{T},\vec{\rho}) = \mathbb{C}(\mathbf{E},\vec{\rho})^{-1} \quad \text{for} \quad \mathbf{E} = \tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}) \tag{7.21}$$

(i.e., $H_{ij} = C_{ijkl}U_{kl}$ if and only if $U_{ij} = K_{ijkl}H_{kl}$); $\mathbb{K}$ therefore has symmetries analogous to those displayed in (7.10). Differentiating the identity $\hat{\mathbf{T}}\big(\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}),\vec{\rho}\big) = \mathbf{T}$ with respect to ρ^α, we arrive at the important relation

$$\mathbf{N}^\alpha = -\mathbb{K}[\mathbf{A}^\alpha] \tag{7.22}$$

in which, for convenience, we have omitted arguments. Thus:

$$\left.\begin{array}{rl}\mathbb{C},\ \mathbf{A}^\alpha\ (\alpha = 1,2,\dots N) & \text{are independent of strain and composition}\\ & \qquad\text{if and only if}\\ \mathbb{K},\ \mathbf{N}^\alpha\ (\alpha = 1,2,\dots N) & \text{are independent of stress and composition.}\end{array}\right\} \tag{7.23}$$

Finally, we note that the *free energy* and the *chemical potentials at zero stress*,

$$\left.\begin{aligned}\Psi_0(\vec{\rho}) &= \tilde{\Psi}(\mathbf{T},\vec{\rho})\big|_{\mathbf{T}=\mathbf{0}},\\ \mu_0^\alpha(\vec{\rho}) &= \tilde{\mu}^\alpha(\mathbf{T},\vec{\rho})\big|_{\mathbf{T}=\mathbf{0}},\end{aligned}\right\} \tag{7.24}$$

are, by (7.16) and (7.17), related through

$$\mu_0^\alpha(\vec{\rho}) = \frac{\partial\Psi_0(\vec{\rho})}{\partial\rho^\alpha}. \tag{7.25}$$

7.4 Mechanically simple materials

We refer to a material as being *mechanically simple* if:

(i) the elasticity tensor $\mathbb{C}$ and stress-composition tensors $\mathbf{A}^\alpha$ are independent of strain and composition (cf. (7.23));

(ii) the mobilities $\mathbf{M}^{\alpha\beta}$ are independent of strain.

Assumption (i) has strong consequences. Since $\mathbb{C}$ and $\mathbf{A}^\alpha$ are independent of $\mathbf{E}$ and $\vec{\rho}$, we may integrate $\mathbf{A}^\alpha = \partial\hat{\mathbf{T}}/\partial\rho^\alpha$, from an arbitrary reference list $\vec{\rho}_0$ to $\vec{\rho}$ and then use the relation $\mathbb{C} = \partial\hat{\mathbf{T}}/\partial\mathbf{E}$; the result is an equation for the stress of the form

$$\mathbf{T} = \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} \mathbf{A}^\alpha(\rho^\alpha - \rho_0^\alpha). \tag{7.26}$$

Next, to obtain the free energy, we integrate the relation $\partial\hat{\Psi}/\partial\mathbf{E} = \mathbf{T}$ using (7.26); the result is the relation

$$\Psi = \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\cdot\mathbf{E} + F(\vec{\rho}), \tag{7.27}$$

which, when differentiated with respect to the density ρ^α, yields an expression

$$\mu^\alpha = \frac{\partial F(\vec{\rho})}{\partial\rho^\alpha} + \mathbf{A}^\alpha\cdot\mathbf{E} \tag{7.28}$$

for the chemical potential μ^α.

Next, using (7.22), we may explicitly invert (7.26) to obtain a relation

$$\mathbf{E} = \mathbb{K}[\mathbf{T}] + \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{N}^\alpha \tag{7.29}$$

for $\mathbf{E}$ in terms of $\mathbf{T}$ and $\vec{\rho}$. Then, by (7.27), (7.26) and (7.29),

$$\begin{aligned}\Psi - F(\vec{\rho}) &= \tfrac{1}{2}\mathbf{E}\cdot\Big(\mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\Big) + \tfrac{1}{2}\sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\cdot\mathbf{E}\\ &= \tfrac{1}{2}\Big(\mathbb{K}[\mathbf{T}] + \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{N}^\alpha\Big)\cdot\mathbf{T} + \tfrac{1}{2}\sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\cdot\mathbf{E}\\ &= \tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] + \tfrac{1}{2}\sum_{\alpha,\beta=1}^{N}(\rho^\alpha - \rho_0^\alpha)(\rho^\beta - \rho_0^\beta)\mathbf{A}^\alpha\cdot\mathbf{N}^\beta \end{aligned} \tag{7.30}$$

and it follows that

$$\Psi = \tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] + \Psi_0(\vec{\rho}) \tag{7.31}$$

and, hence, that $F(\vec{\rho})$ is related to $\Psi_0(\vec{\rho})$, the free energy at zero stress, through

$$F(\vec{\rho}) = \Psi_0(\vec{\rho}) - \tfrac{1}{2}\sum_{\alpha,\beta=1}^{N}(\rho^\alpha - \rho_0^\alpha)(\rho^\beta - \rho_0^\beta)\mathbf{A}^\alpha\cdot\mathbf{N}^\beta. \tag{7.32}$$

Next, using (7.29) and (7.31) in (7.16), we find that

$$\Phi = -\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{N}^\alpha\cdot\mathbf{T} + \Psi_0(\vec{\rho}); \tag{7.33}$$

thus, by $(7.17)_2$ and (7.25), the chemical potentials may be expressed alternatively as

$$\mu^\alpha = \mu_0^\alpha(\vec{\rho}) - \mathbf{N}^\alpha\cdot\mathbf{T}. \tag{7.34}$$

Turning to Fick's law (7.12), since the mobility is also independent of strain, we see that, by (7.28),

$$\boldsymbol{\jmath}^\alpha = -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho})\Bigg(\sum_{\gamma=1}^{N} \frac{\partial^2 F(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma + \mathbf{A}^\beta\nabla\mathbf{E}\Bigg). \tag{7.35}$$

Alternatively, appealing to (7.2) and (7.34),

$$\boldsymbol{\jmath}^\alpha = -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho})\Bigg(\sum_{\gamma=1}^{N} \frac{\partial^2 \Psi_0(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma - \mathbf{N}^\beta\nabla\mathbf{T}\Bigg). \tag{7.36}$$

Thus, spatial variations of either strain or stress may drive atomic diffusion.

7.5 Cubic symmetry

A special but important class of materials consists of those with *cubic symmetry.* Here, we consider the ramifications of cubic symmetry for mechanically simple materials.

To display the explicit form of the elasticity tensor it is convenient to tabulate the 21 independent elasticities as

$$\begin{array}{cccccc}
C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1131} & C_{1112} \\
 & C_{2222} & C_{2233} & C_{2223} & C_{2231} & C_{2212} \\
 & & C_{3333} & C_{3323} & C_{3331} & C_{3312} \\
 & & & C_{2323} & C_{2331} & C_{2312} \\
 & & & & C_{3131} & C_{3112} \\
 & & & & & C_{1212}
\end{array}$$

The elasticity tensor for a cubic material (with unit cube generated by the basis vectors of the underlying Cartesian coordinates) then has the tabular form

$$\begin{array}{cccccc}
C_{1111} & C_{1122} & C_{1122} & 0 & 0 & 0 \\
 & C_{1111} & C_{1122} & 0 & 0 & 0 \\
 & & C_{1111} & 0 & 0 & 0 \\
 & & & C_{2323} & 0 & 0 \\
 & & & & C_{2323} & 0 \\
 & & & & & C_{2323}
\end{array} \tag{7.37}$$

showing that there are only 3 independent elasticities. The compliance tensor admits a similar representation. Moreover, the tensors $\mathbf{M}^\alpha$, $\mathbf{A}^\alpha$, $\mathbf{N}^\alpha$ are isotropic:

$$\mathbf{M}^\alpha = m^\alpha\mathbf{1}, \qquad \mathbf{A}^\alpha = a^\alpha\mathbf{1}, \qquad \mathbf{N}^\alpha = \eta^\alpha\mathbf{1}. \tag{7.38}$$

Further, because $\mathbb{C}[\mathbf{1}]$ is a (second-order) tensor, it must be isotropic and hence of the form

$$\mathbb{C}[\mathbf{1}] = 3k\mathbf{1}, \tag{7.39}$$

with k the *compressibility.* By (7.22), $\mathbf{A}^\alpha = -\mathbb{C}[\mathbf{N}^\alpha]$; the moduli a^α and η^α are therefore related through the compressibility k via

$$a^\alpha = -3k\eta^\alpha. \tag{7.40}$$

In view of $(7.38)_{2,3}$ and (7.39), the free energy (7.27) and free enthalpy (7.33) specialize to

$$\left.\begin{aligned}\Psi &= \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} a^\alpha(\rho^\alpha-\rho_0^\alpha)\,\mathrm{tr}\,\mathbf{E} + F(\vec{\rho}),\\ \Phi &= -\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \sum_{\alpha=1}^{N}\eta^\alpha(\rho^\alpha-\rho_0^\alpha)\,\mathrm{tr}\,\mathbf{T} + \Psi_0(\vec{\rho}),\end{aligned}\right\} \tag{7.41}$$

where, by (7.32) and (7.40),

$$F(\vec{\rho}) = \Psi_0(\vec{\rho}) + \tfrac{9}{2}\sum_{\alpha,\beta=1}^{N} k\eta^\alpha\eta^\beta(\rho^\alpha-\rho_0^\alpha)(\rho^\beta-\rho_0^\beta). \tag{7.42}$$

We therefore have the equivalent sets of relations:

$$\left.\begin{aligned}\mathbf{T} &= \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} a^\alpha(\rho^\alpha-\rho_0^\alpha)\mathbf{1}, &\qquad \mu^\alpha &= \frac{\partial F(\vec{\rho})}{\partial\rho^\alpha} + a^\alpha\,\mathrm{tr}\,\mathbf{E},\\ \mathbf{E} &= \mathbb{K}[\mathbf{T}] + \sum_{\alpha=1}^{N}\eta^\alpha(\rho^\alpha-\rho_0^\alpha)\mathbf{1}, &\qquad \mu^\alpha &= \mu_0^\alpha(\vec{\rho}) - \eta^\alpha\,\mathrm{tr}\,\mathbf{T},\end{aligned}\right\} \tag{7.43}$$

with μ_0^α given by (7.25).

Note that we may write the stress as

$$\mathbf{T} = \mathbb{C}[\mathbf{E}-\mathbf{E}_{\mathrm{com}}], \qquad \mathbf{E}_{\mathrm{com}} \overset{\mathrm{def}}{=} \sum_{\alpha=1}^{N}\eta^\alpha(\rho^\alpha-\rho_0^\alpha)\mathbf{1}. \tag{7.44}$$

We refer to $\mathbf{E}_{\mathrm{com}}$ as the *compositional strain* and to η^α as the *solute-expansion modulus* for species α. Since we would generally expect the body to expand when atoms are added, we should have

$$\eta^\alpha > 0, \qquad a^\alpha < 0, \tag{7.45}$$

where the second inequality follows from (7.40), assuming that $k > 0$. Granted (7.45), if the body is, instead, constrained to have vanishing strain, then, by $(7.43)_2$, the resulting *compositional stress* would be $a^\alpha(\rho^\alpha-\rho_0^\alpha)\mathbf{1}$ and compressive when atoms are added.

By $(7.38)_1$, the alternative expressions (7.35) and (7.36) of Fick's law become

$$\left.\begin{aligned}\boldsymbol{\jmath}^\alpha &= -\sum_{\beta=1}^{N} m^{\alpha\beta}(\vec{\rho})\Big(\sum_{\gamma=1}^{N}\frac{\partial^2 F(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma + a^\beta\nabla\mathrm{tr}\,\mathbf{E}\Big),\\ \boldsymbol{\jmath}^\alpha &= -\sum_{\beta=1}^{N} m^{\alpha\beta}(\vec{\rho})\Big(\sum_{\gamma=1}^{N}\frac{\partial^2 \Psi_0(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma - \eta^\beta\nabla\mathrm{tr}\,\mathbf{T}\Big).\end{aligned}\right\} \tag{7.46}$$

8 Digression: The Gibbs relation and Gibbs–Duhem equation at zero stress

Consider the free energy $\Psi_0(\vec{\rho})$ and the chemical potentials $\mu_0^\alpha(\vec{\rho})$, at zero stress, as defined in (7.24). Our derivation of the Gibbs–Duhem equation at zero stress utilizes the *atomic density*, *atomic volume*, and *concentrations*:

$$\rho \overset{\text{def}}{=} \sum_{\alpha=1}^{N} \rho^\alpha, \qquad \Omega \overset{\text{def}}{=} \frac{1}{\rho}, \qquad c^\alpha \overset{\text{def}}{=} \Omega\rho^\alpha.$$

The mass density ρ_m is related to the atomic masses m^α of the individual species through $\rho_m = \sum_{\alpha=1}^{N} \rho^\alpha m^\alpha = \rho \sum_{\alpha=1}^{N} c^\alpha m^\alpha$. Thus, for $v_m = 1/\rho_m$ the *specific volume*,

$$v_m = \frac{\Omega}{\sum\limits_{\alpha=1}^{N} c^\alpha m^\alpha}. \tag{8.1}$$

The free energy Ψ_0 is measured per unit volume, so that $v_m\Psi_0$ represents the specific-free energy. We derive the Gibbs relation by noting that for p the thermodynamic pressure, $-p$ is the derivative, with respect to v_m, of the specific free-energy at fixed composition $\vec{c}$. Thus, by (8.1), $-p$ is the derivative, with respect to Ω, of $\Omega\Psi_0$ at fixed composition:

$$\begin{aligned} \frac{\partial}{\partial\Omega}\Big[\Omega\Psi_0\Big(\frac{c^1}{\Omega}, \frac{c^2}{\Omega}, \dots, \frac{c^N}{\Omega}\Big)\Big] &= \Psi_0(\vec{\rho}) - \sum_{\alpha=1}^{N} \frac{\partial\Psi_0(\vec{\rho})}{\partial\rho^\alpha}\frac{c^\alpha}{\Omega} \\ &= \Psi_0(\vec{\rho}) - \sum_{\alpha=1}^{N} \rho^\alpha \mu_0^\alpha(\vec{\rho}). \end{aligned} \tag{8.2}$$

On the other hand, if we identify this pressure with the actual pressure, then, since $\mathbf{T} \equiv \mathbf{0}$, (8.2) must vanish; thus we have the *Gibbs relation* (Gibbs, 1875, eqt. 12):

$$\Psi_0(\vec{\rho}) = \sum_{\alpha=1}^{N} \rho^\alpha \mu_0^\alpha(\vec{\rho}). \tag{8.3}$$

The relation (8.3) is well defined for all $\vec{\rho}$ and provides a method of determining the free energy from a knowledge of the chemical potentials. But the latter cannot be arbitrary, but instead must be consistent with the (classical) *Gibbs–Duhem equation*:[22]

$$\sum_{\alpha=1}^{N} \rho^\alpha \frac{\partial\mu_0^\alpha(\vec{\rho})}{\partial\rho^\beta} = 0 \tag{8.4}$$

for all species β. This set of N relations follows upon differentiating (8.3) with respect to ρ^β and appealing to (7.25). The Gibbs–Duhem equation (8.4) *represents a condition that is both necessary and sufficient that* (8.3) *hold*.

A *simple set of constitutive relations at zero stress* is based on the assumption that the chemical potentials $\mu_0^\alpha(\vec{\rho})$ depend on $\rho^1, \rho^2, \dots, \rho^N$ through the concentrations $c^1, c^2, \dots, c^N$. Granted this, we may use the identity

$$\frac{\partial c^\alpha}{\partial\rho^\beta} = \Omega(\delta^{\alpha\beta} - c^\alpha) \qquad (\delta^{\alpha\beta} = \text{Kronecker delta}), \tag{8.5}$$

to write the Gibbs–Duhem equation (8.4) in the form

$$\sum_{\alpha=1}^{N} c^\alpha \frac{\partial\mu_0^\alpha}{\partial c^\beta} = \sum_{\alpha=1}^{N} c^\alpha \frac{\partial\mu_0^\alpha}{\partial c^\gamma} c^\gamma \overset{\text{def}}{=} \Lambda. \tag{8.6}$$

---

[22] Cf., e.g., Kirkwood and Oppenheim (1961, eqt. (6.61)).

If, in addition, we assume that μ^α is a function of c_0^α (only), then Λ is independent of composition and (8.6) yields

$$c^\alpha \frac{\partial \mu_0^\alpha}{\partial c^\alpha} = \Lambda, \tag{8.7}$$

which has the explicit solution

$$\mu_0^\alpha = U^\alpha + \Lambda \ln c^\alpha, \tag{8.8}$$

so that[23]

$$\Psi_0(\vec{\rho}) = \sum_{\alpha=1}^{N} \rho^\alpha \big(U^\alpha + \Lambda \ln c^\alpha\big). \tag{8.9}$$

9 Constitutive theory for a substitutional alloy

The lattice constraint

$$\sum_{\alpha=1}^{N} \rho^\alpha = \rho^{\text{sites}}$$

renders the constitutive theory for a substitutional alloy more difficult than that for an unconstrained material. In many respects the substitutional theory mirrors that for unconstrained materials; in particular, the theory is based on constitutive equations in which the density-list

$$\vec{\rho} = (\rho^1, \rho^2, \dots, \rho^N)$$

appears as an independent variable. Difficulties arise because each such list $\vec{\rho}$ must be *admissible*; that is, must satisfy the lattice constraint and must have $0 \le \rho^\alpha < \infty$ for all atomic species α. Thus, since varying one of the densities while holding the others fixed violates the lattice constraint, *standard partial differentiation of the constitutive response functions with respect to the atomic densities is not well-defined.* The next subsection comes to grips with this problem.

9.1 Larché–Cahn derivatives

Let $f(\vec{\rho})$ be defined on the set of admissible density lists. As noted above, the standard partial derivatives $\partial f/\partial \rho^\alpha$ are not defined. To free f of the lattice constraint, choose a species ζ as reference, use the lattice constraint to express ρ^ζ as a function

$$\rho^\zeta = \rho^{\text{sites}} - \sum_{\substack{\alpha=1\\ \alpha\neq\zeta}}^{N} \rho^\alpha$$

of the list

$$(\rho^1, \rho^2, \dots, \rho^{\zeta-1}, \rho^{\zeta+1} \dots \rho^N)$$

---

[23] Materials scientists typically choose $\Lambda = R\theta$, with R the gas constant and θ the absolute temperature, and rewrite (8.9) in the form

$$\Psi_0(\vec{\rho}) = \sum_{\alpha=1}^{N} \rho^\alpha \underbrace{\big(U_*^\alpha + R\theta \ln(\gamma^\alpha c^\alpha)\big)}_{\mu_0^\alpha(\vec{c})},$$

where γ^α is an activity coefficient and U_*^α is the chemical potential when $\rho^\alpha = 1/\gamma^\alpha$, and where γ^α and U_*^α generally depend on θ.

of remaining densities, and consider f as a function $f^{(\zeta)}$ of the remaining densities by defining

$$f^{(\zeta)}\underbrace{(\rho^1,\rho^2,\dots,\rho^{\zeta-1},\rho^{\zeta+1}\dots\rho^N)}_{\rho^\zeta\ \text{missing}} \;=\; f(\vec{\rho})\Big|_{\rho^\zeta=\rho^{\text{sites}}-\sum\limits_{\substack{\alpha=1\\ \alpha\neq\zeta}}^{N}\rho^\alpha}. \tag{9.1}$$

The domain of $f^{(\zeta)}$ is then open, since the arguments of $f^{(\zeta)}$ may be varied slightly without violating the lattice constraint; thus the partial derivatives

$$\frac{\partial f^{(\zeta)}}{\partial\rho^\alpha} \qquad \text{and} \qquad \frac{\partial^2 f^{(\zeta)}}{\partial\rho^\alpha\partial\rho^\beta}$$

are well defined. Note that when α, say, is equal to ζ, the left side of (9.1) is independent of ρ^ζ, so that, trivially,

$$\frac{\partial f^{(\zeta)}}{\partial\rho^\zeta}=0. \tag{9.2}$$

We refer to $f^{(\zeta)}$ as the *description of f relative to ζ*.

An alternative treatment of differentiation that respects the lattice constraint may be developed as follows. Choose species α and ζ. If the list $\vec{\rho}=(\rho^1,\rho^2,\dots,\rho^N)$ is consistent with the lattice constraint, then so also is the list

$$(\rho^1,\dots,\rho^\alpha+\epsilon,\dots,\rho^\zeta-\epsilon,\dots,\rho^N)$$

obtained by increasing the atomic density of species α by an amount ϵ and decreasing the density of ζ by an equal amount (while holding the remaining densities fixed). Bearing this in mind, we define the *Larché–Cahn derivative* $\partial^{(\zeta)}/\partial\rho^\alpha$ by

$$\frac{\partial^{(\zeta)}f(\vec{\rho})}{\partial\rho^\alpha}=\frac{d}{d\epsilon}\,f(\rho^1,\dots,\rho^\alpha+\epsilon,\dots,\rho^\zeta-\epsilon,\dots,\rho^N)\Big|_{\epsilon=0}; \tag{9.3}$$

$\partial^{(\zeta)}f(\vec{\rho})/\partial\rho^\alpha$ represents the change in $f(\vec{\rho})$ due to a unit increase in the density of α-atoms and an equal decrease in the density of ζ-atoms.[24] Second Larché–Cahn derivatives are defined similarly:

$$\frac{\partial^{2(\zeta)}f(\vec{\rho})}{\partial\rho^\alpha\,\partial\rho^\beta}=\frac{d^2}{d\epsilon\,d\lambda}\,f(\rho^1,\dots,\rho^\alpha+\epsilon,\dots,\rho^\beta+\lambda,\dots,\rho^\zeta-\epsilon-\lambda,\dots,\rho^N)\Big|_{\epsilon=\lambda=0}. \tag{9.4}$$

For convenience, we define

$$\frac{\partial^{(\zeta)}f}{\partial\rho^\zeta}=0. \tag{9.5}$$

A direct consequence of (9.3) is then the *skew-symmetry relation*

$$\frac{\partial^{(\zeta)}f}{\partial\rho^\alpha}=-\frac{\partial^{(\alpha)}f}{\partial\rho^\zeta}, \tag{9.6}$$

valid for all species α and ζ. Thus, $\sum_{\alpha=1}^N\sum_{\zeta=1}^N\partial^{(\zeta)}f/\partial\rho^\alpha=-\sum_{\alpha=1}^N\sum_{\zeta=1}^N\partial^{(\alpha)}f/\partial\rho^\zeta=-\sum_{\alpha=1}^N\sum_{\zeta=1}^N\partial^{(\zeta)}f/\partial\rho^\alpha$ and we have

$$\sum_{\alpha,\zeta=1}^{N}\frac{\partial^{(\zeta)}f}{\partial\rho^\alpha}=0. \tag{9.7}$$

---

[24] Larché and Cahn (1985, eqt. 3.7) use the notation $\partial/\partial\rho^{\alpha\zeta}$ rather than $\partial^{(\zeta)}/\partial\rho^\alpha$.

Using the description $f^{(\zeta)}$ of f relative to ζ, the Larché–Cahn derivative may be given an alternative representation which is convenient in calculations. Increasing an argument ρ^α by an amount ϵ (while holding the other arguments of $f^{(\zeta)}$ fixed) corresponds, via the definition (9.1), to decreasing the argument ρ^ζ in f by ϵ. Therefore, as a consequence of (9.3), *the Larché–Cahn derivative $\partial f^{(\zeta)}/\partial\rho^\alpha$ is simply the derivative of f with respect to ρ^α taken with the density ρ^ζ eliminated via the lattice constraint*; thus and by (9.2) and (9.5),

$$\frac{\partial^{(\zeta)} f}{\partial\rho^\alpha} = \frac{\partial f^{(\zeta)}}{\partial\rho^\alpha}, \tag{9.8}$$

and similarly for second derivatives,

$$\frac{\partial^{2(\zeta)} f}{\partial\rho^\alpha\partial\rho^\beta} = \frac{\partial^2 f^{(\zeta)}}{\partial\rho^\alpha\partial\rho^\beta}. \tag{9.9}$$

Note that (9.8) and (9.9) are meaningful even though their left sides are functions of the complete list $\vec{\rho} = (\rho^1, \rho^2, \dots, \rho^\zeta, \dots \rho^N)$, while their right sides are functions of the list

$$\underbrace{(\rho^1, \rho^2, \dots, \rho^{\zeta-1}, \rho^{\zeta+1} \dots \rho^N)}_{\rho^\zeta \text{ missing}};$$

indeed, the left sides are defined only for those arguments $\vec{\rho}$ consistent with the lattice constraint, a constraint that renders ρ^ζ known when the other densities are known (cf. (9.1)).

It may happen that $f(\vec{\rho})$ may be extended smoothly to an open region of $\mathbb{R}^N$.[25] In that case the Larché–Cahn derivative may be computed as the difference

$$\frac{\partial^{(\zeta)} f}{\partial\rho^\alpha} = \frac{\partial f}{\partial\rho^\alpha} - \frac{\partial f}{\partial\rho^\zeta}; \tag{9.10}$$

e.g., for the function defined on the set of admissible density lists by $f(\vec{\rho}) = \lambda^\alpha\rho^\alpha$ with each of the λ's constant,

$$\frac{\partial^{(\zeta)} f}{\partial\rho^\alpha} = \lambda^\alpha - \lambda^\zeta. \tag{9.11}$$

Next, choose a species ζ and bear in mind that $\partial f^{(\zeta)}/\partial\rho^\alpha$ is a standard partial derivative. Then, for $\vec{\rho}(t)$ an admissible, time-dependent density list and $\varphi(t) = f(\vec{\rho}(t))$,

$$\dot{\varphi} = \underbrace{\sum_{\alpha=1}^{N} \frac{\partial f^{(\zeta)}(\vec{\rho})}{\partial\rho^\alpha}\,\dot{\rho}^\alpha}_{\text{chain-rule}} = \underbrace{\sum_{\alpha=1}^{N} \frac{\partial^{(\zeta)} f(\vec{\rho})}{\partial\rho^\alpha}\,\dot{\rho}^\alpha}_{\text{by (9.8)}}, \tag{9.12}$$

which is the *chain-rule for Larché–Cahn derivatives.*

9.2 Constitutive equations

(a) General relations

Given a fixed choice of the reference species ζ and guided by the dissipation inequality (5.11), viz.,

$$\dot{\Psi} - \mathbf{T}\cdot\dot{\mathbf{E}} - \sum_{\alpha=1}^{N}(\mu^{\alpha\zeta}\dot{\rho}^\alpha - \boldsymbol{\jmath}^\alpha\cdot\nabla\mu^{\alpha\zeta}) \le 0, \tag{9.13}$$

---

[25] For example, when f is the free energy described in Footnote 23, a free energy used by materials scientists also for substitutional alloys (cf. Larché and Cahn, 1985, §4.2).

and the requirement that the bulk theory for a substitutional alloy depend only on the relative chemical potentials (cf. the theorem containing (5.7)), we base the theory on constitutive equations

$$\Psi = \hat{\Psi}(\mathbf{E}, \vec{\rho}), \qquad \mathbf{T} = \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}), \tag{9.14}$$

for the free energy and stress, constitutive equations

$$\mu^{\alpha\beta} = \hat{\mu}^{\alpha\beta}(\mathbf{E}, \vec{\rho}) \tag{9.15}$$

for the relative chemical potentials, and Fick's law

$$\boldsymbol{\jmath}^{\alpha} = -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho}) \nabla \mu^{\beta\zeta} \tag{9.16}$$

for the atomic fluxes.

(b) Constraints on $\hat{\mu}^{\alpha\beta}$

The constitutive relations (9.15), which are prescribed for *all* relative chemical potentials, are presumed to be consistent with the identities (5.6); more pragmatically, we need only assume that the response functions $\hat{\mu}^{\alpha\zeta}$ are prescribed for all α and some *fixed* choice of reference species ζ, for then the response functions relative to any other species β may be *defined* by

$$\hat{\mu}^{\alpha\beta} = \hat{\mu}^{\alpha\zeta} - \hat{\mu}^{\beta\zeta}, \tag{9.17}$$

and, granted this, the *skew symmetry relation*

$$\hat{\mu}^{\alpha\beta} = -\hat{\mu}^{\beta\alpha} \tag{9.18}$$

is satisfied for each pair of species, so that, in particular, $\hat{\mu}^{\alpha\alpha} = 0$ (no sum).

(c) Mobility constraints

We require that the mobility tensors $\mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho})$:

(a) be consistent with the substitutional flux constraint;

(b) render Fick's law (9.16) independent of the choice of reference species ζ.

To discuss the implications of these constraints, we suppress the arguments $\mathbf{E}$ and $\vec{\rho}$, which are irrelevant to the following discussion. For (b) to hold it is sufficient that

$$\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta} \nabla \mu^{\beta\zeta} = \sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta} \nabla \mu^{\beta\gamma} \tag{9.19}$$

for all choices of ζ and γ and all α. By (9.17), the relative chemical potentials necessarily satisfy

$$\mu^{\beta\zeta} = \mu^{\beta\gamma} - \mu^{\zeta\gamma}$$

for all choices of ζ and γ and all β; therefore, (9.19) will be satisfied provided

$$\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta} \nabla \mu^{\zeta\gamma} = \mathbf{0}$$

for all choices of ζ and γ and for all α, and, hence, provided

$$\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta} = \mathbf{0} \tag{9.20}$$

for all α.

Next, consider requirement (a). The substitutional flux constraint (5.4) applied to Fick's law is the requirement that

$$\sum_{\alpha=1}^{N} \boldsymbol{\jmath}^{\alpha} = -\sum_{\alpha,\beta=1}^{N} \mathbf{M}^{\alpha\beta}\nabla\mu^{\beta\zeta} = -\sum_{\beta=1}^{N}\Big(\sum_{\alpha=1}^{N}\mathbf{M}^{\alpha\beta}\Big)\nabla\mu^{\beta\zeta} = \mathbf{0},$$

an equation that will be satisfied for each choice of ζ provided the term in parenthesis vanishes. Thus, recalling (9.20), we have the *mobility constraints* of Larché and Cahn (1985, eqts. (8.2), (8.3)):

$$\sum_{\alpha=1}^{N} \mathbf{M}^{\alpha\beta}(\mathbf{E},\vec{\rho}) = \mathbf{0}, \qquad \sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\mathbf{E},\vec{\rho}) = \mathbf{0}. \tag{9.21}$$

9.3 Thermodynamic restrictions

Our next step is to determine restrictions on the constitutive equations that ensure satisfaction of the dissipation inequality (9.13). Because of the lattice constraint, thermodynamic arguments involving arbitrary variations of the atomic densities are delicate. In this regard, the following lemma is useful:

> Lemma Given any admissible density list $\vec{n}$, any scalar a, any two atomic species $\alpha \neq \beta$, and any time τ, there is a time-dependent, admissible density-list $\vec{\rho}(t)$ such that, at τ,
>
> $$\vec{\rho}(\tau) = \vec{n}, \qquad \dot{\rho}^{\alpha}(\tau) = -\dot{\rho}^{\beta}(\tau) = a, \qquad \dot{\rho}^{\gamma}(\tau) = 0 \quad \text{for} \quad \gamma \neq \alpha,\beta. \tag{9.22}$$

To prove this lemma note first that a simple choice $\vec{\rho}(t)$ consistent with the lattice constraint and with (9.22) is given by

$$\rho^{\alpha}(t) = n^{\alpha} + (t-\tau)a, \qquad \rho^{\beta}(t) = n^{\beta} - (t-\tau)a,$$

and

$$\rho^{\gamma}(t) = n^{\gamma} \qquad \text{for} \qquad \gamma \neq \alpha,\beta. \tag{9.23}$$

But this choice does not furnish a solution of our problem, since the densities $\rho^{\alpha}(t)$ and $\rho^{\beta}(t)$ may be negative. This is easily remedied: given any $\epsilon > 0$, we can always find a scalar function $T(t)$ such that $T(\tau) = 0$, $\dot{T}(\tau) = 1$, and $|T(t)| < \epsilon$. The density list $\vec{\rho}(t)$ defined by

$$\rho^{\alpha}(t) = n^{\alpha} + T(t)a \quad \text{and} \quad \rho^{\beta}(t) = n^{\beta} - T(t)a,$$

supplemented by (9.23), satisfies (9.22) and will be admissible for all t provided we choose ϵ small enough. This completes the proof of the lemma.

Recall that, by (9.2), (9.5), and the sentence containing (9.18),

$$\frac{\partial^{(\zeta)}\hat{\Psi}}{\partial\rho^{\zeta}} = \frac{\partial\hat{\Psi}^{(\zeta)}}{\partial\rho^{\zeta}} = \hat{\mu}^{\zeta\zeta} = 0.$$

Fix a species ζ and choose an arbitrary process consistent with the constitutive equations. Then, by (9.12),

$$\dot{\Psi} = \frac{\partial \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \mathbf{E}} \cdot \dot{\mathbf{E}} + \sum_{\alpha=1}^{N} \frac{\partial^{(\zeta)} \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \rho^{\alpha}} \, \dot{\rho}^{\alpha}. \tag{9.24}$$

The requirement that the dissipation inequality (9.13) hold in all such processes leads to the inequality

$$\left\{ \frac{\partial \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \mathbf{E}} - \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}) \right\} \cdot \dot{\mathbf{E}} \ + \sum_{\alpha=1}^{N} \left\{ \frac{\partial \hat{\Psi}^{(\zeta)}(\mathbf{E}, \vec{\rho})}{\partial \rho^{\alpha}} - \hat{\mu}^{\alpha\zeta}(\mathbf{E}, \vec{\rho}) \right\} \dot{\rho}^{\alpha} \\ - \sum_{\alpha,\beta=1}^{N} \nabla \mu^{\alpha\zeta} \cdot \mathbf{M}^{\alpha\beta}(\mathbf{E}, \vec{\rho}) \nabla \mu^{\beta\zeta} \leq 0, \tag{9.25}$$

for each choice of the free-index ζ. If, for the moment, we restrict attention to spatially constant processes, then this inequality reduces to

$$\left\{ \frac{\partial \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \mathbf{E}} - \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}) \right\} \cdot \dot{\mathbf{E}} + \sum_{\alpha=1}^{N} \left\{ \frac{\partial^{(\zeta)} \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \rho^{\alpha}} - \hat{\mu}^{\alpha\zeta}(\mathbf{E}, \vec{\rho}) \right\} \dot{\rho}^{\alpha} \leq 0. \tag{9.26}$$

This inequality must hold for all $\mathbf{E}(t)$ and all admissible density lists $\vec{\rho}(t)$. Assuming that the atomic densities are independent of time leads to the requirement that $\hat{\mathbf{T}} = \partial \hat{\Psi} / \partial \mathbf{E}$ and (9.26) reduces to an ineqality involving only the density-rates. As noted in the density-variation lemma (cf. (9.22)), given any species $\alpha \neq \zeta$, we can always find an admissible density list $\vec{\rho}(t)$ such that, at some time τ, the values $\vec{\rho}(\tau)$ and $\dot{\rho}^{\alpha}(\tau) = -\dot{\rho}^{\zeta}(\tau)$ are arbitrary, *while the remaining rates* $\dot{\rho}^{\alpha}(\tau)$ *vanish.* For this choice of $\vec{\rho}(t)$, (9.26), at time τ, becomes

$$\left\{ \frac{\partial^{(\zeta)} \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \rho^{\alpha}} - \hat{\mu}^{\alpha\zeta}(\mathbf{E}, \vec{\rho}) \right\} \dot{\rho}^{\alpha} \leq 0.$$

Thus, since $\mathbf{E}$, $\vec{\rho}$, and $\dot{\rho}^{\alpha}$ are arbitrary at τ, we must have $\hat{\mu}^{\alpha\zeta} = \partial^{(\zeta)} \hat{\Psi} / \partial \rho^{\alpha}$ for all admissible $\vec{\rho}$, a result that reduces (9.25) to the inequality

$$\sum_{\alpha,\beta=1}^{N} \nabla \mu^{\alpha\zeta} \cdot \mathbf{M}^{\alpha\beta} \nabla \mu^{\beta\zeta} \geq 0,$$

for each choice of the free-index ζ.

Summarizing, the second law in the form of the dissipation inequality requires that

$$\left. \begin{aligned} \hat{\mathbf{T}}(\mathbf{E}, \vec{\rho}) &= \frac{\partial \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \mathbf{E}}, \\ \hat{\mu}^{\alpha\zeta}(\mathbf{E}, \vec{\rho}) &= \frac{\partial^{(\zeta)} \hat{\Psi}(\mathbf{E}, \vec{\rho})}{\partial \rho^{\alpha}}, \end{aligned} \right\} \tag{9.27}$$

for all atomic species α and ζ, and that the matrix

$$\begin{bmatrix} \mathbf{M}^{11} & \mathbf{M}^{12} & \dots & \mathbf{M}^{1N} \\ \mathbf{M}^{21} & \mathbf{M}^{22} & \dots & \mathbf{M}^{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{M}^{N1} & \mathbf{M}^{N2} & \dots & \mathbf{M}^{NN} \end{bmatrix}. \tag{9.28}$$

must be positive semi-definite (cf. Footnote 20).

The dissipation (4.7), which is the negative of the left side of (9.25), is given by

$$\delta = \sum_{\alpha,\beta=1}^{N} \nabla\mu^{\alpha} \cdot \mathbf{M}^{\alpha\beta}(\mathbf{E},\vec{\rho})\nabla\mu^{\beta}.$$

Immediate consequences of $(9.27)_1$ and $(9.27)_2$ are the *Maxwell relations*

$$\frac{\partial^{(\zeta)}\hat{\mathbf{T}}}{\partial\rho^{\alpha}} = \frac{\partial\hat{\mu}^{\alpha\zeta}}{\partial\mathbf{E}} \tag{9.29}$$

and the *Gibbs relation*

$$\dot{\Psi} = \mathbf{T}\cdot\dot{\mathbf{E}} + \mu^{\alpha\zeta}\dot{\rho}^{\alpha}, \tag{9.30}$$

which hold for each choice of the free-index ζ.

9.4 Digression: positive definiteness of the mobility matrix

Thermodynamics (essentially) yields a mobility matrix (9.28) that is *positive semi-definite* in the sense that

$$\sum_{\alpha,\beta=1}^{N} \mathbf{a}^{\alpha}\cdot\mathbf{M}^{\alpha\beta}\mathbf{a}^{\beta} \geq 0, \tag{9.31}$$

for all vector-lists $\vec{\mathbf{a}} = (\mathbf{a}^1, \mathbf{a}^2, \dots, \mathbf{a}^N)$, where for convenience we have suppressed the argument $(\mathbf{E},\vec{\rho})$. The notion of positive definiteness is a bit more delicate, since the mobility constraints render the left side of (9.31) zero whenever all entries of $\vec{\mathbf{a}}$ are the same. With this in mind, we refer to the mobility matrix as *essentially positive definite* if

$$\sum_{\alpha,\beta=1}^{N} \mathbf{a}^{\alpha}\cdot\mathbf{M}^{\alpha\beta}\mathbf{a}^{\beta} > 0 \tag{9.32}$$

whenever at least one entry of $\vec{\mathbf{a}}$ *differs from the others.* If the mobility matrix is essentially positive definite, then for any choice of species ζ,

$$\sum_{\alpha,\beta=1}^{N} \nabla\mu^{\alpha\zeta}\cdot\mathbf{M}^{\alpha\beta}\nabla\mu^{\alpha\zeta} > 0 \tag{9.33}$$

if at least one the relative chemical-potential gradients is nonzero (for then not all such gradients can be the same, since $\mu^{\zeta\zeta} \equiv 0$. For a *binary substitutional alloy* the mobility matrix has the form

$$\begin{bmatrix} \mathbf{M} & -\mathbf{M} \\ -\mathbf{M} & \mathbf{M} \end{bmatrix} \tag{9.34}$$

and is essentially positive definite if and only if the tensor $\mathbf{M}$ is positive definite. Indeed, when the mobility matrix has the form (9.34), the inequality (9.33) becomes

$$(\mathbf{a}^1 - \mathbf{a}^2)\cdot\mathbf{M}(\mathbf{a}^1 - \mathbf{a}^2) > 0.$$

If $\mathbf{M}$ is positive definite, then this inequality holds whenever $\mathbf{a}^1 \neq \mathbf{a}^2$, and conversely.

9.5 Free enthalpy. Moduli

Further, assuming an invertible stress-strain relation as discussed in §7.3, the *free enthalpy* defined by

$$\tilde{\Phi}(\mathbf{T},\vec{\rho}) = \tilde{\Psi}(\mathbf{T},\vec{\rho}) - \mathbf{T}\cdot\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}) \tag{9.35}$$

yields the relations

$$\left.\begin{aligned} \tilde{\mathbf{E}}(\mathbf{T},\vec{\rho}) &= -\frac{\partial\tilde{\Phi}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}}, \\ \tilde{\mu}^{\alpha\zeta}(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\Phi}^{(\zeta)}(\mathbf{T},\vec{\rho})}{\partial\rho^{\alpha}}, \end{aligned}\right\} \tag{9.36}$$

and these in turn yield the Maxwell relations

$$\frac{\partial^{(\zeta)}\tilde{\mathbf{E}}}{\partial\rho^{\alpha}} = \frac{\partial\tilde{\mu}^{\alpha\zeta}}{\partial\mathbf{T}} \tag{9.37}$$

as well as direct counterparts of the other results of §7.3.

As before, we define tensor moduli

$$\left.\begin{aligned} \mathbb{C}(\mathbf{E},\vec{\rho}) &= \frac{\partial\hat{\mathbf{T}}(\mathbf{E},\vec{\rho})}{\partial\mathbf{E}} = \frac{\partial^2\hat{\Psi}(\mathbf{E},\vec{\rho})}{\partial\mathbf{E}^2}, \\ \mathbf{A}^{\alpha\beta}(\mathbf{E},\vec{\rho}) &= \frac{\partial\hat{\mathbf{T}}^{(\beta)}(\mathbf{E},\vec{\rho})}{\partial\rho^{\alpha}} = \frac{\partial\hat{\mu}^{\alpha\beta}(\mathbf{E},\vec{\rho})}{\partial\mathbf{E}}, \\ \mathbb{K}(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\mathbf{E}}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}} = -\frac{\partial^2\tilde{\Psi}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}^2}, \\ \mathbf{N}^{\alpha\beta}(\mathbf{T},\vec{\rho}) &= \frac{\partial\tilde{\mathbf{E}}^{(\beta)}(\mathbf{T},\vec{\rho})}{\partial\rho^{\alpha}} = -\frac{\partial\tilde{\mu}^{\alpha\beta}(\mathbf{T},\vec{\rho})}{\partial\mathbf{T}}. \end{aligned}\right\} \tag{9.38}$$

$\mathbf{A}^{\alpha\beta}$ and $\mathbf{N}^{\alpha\beta}$, respectively, are the *stress- and strain-composition tensors* for α relative to β. $\mathbf{A}^{\alpha\beta}$ represents the marginal increase in stress due to both an incremental increase in ρ^{α} and an incremental decrease of the same amount in ρ^{β}, holding the other densities and the strain fixed. An analogous meaning applies to $\mathbf{N}^{\alpha\beta}$. In view of the skew-symmetry relations (9.6) and (9.18), the tensors $\mathbf{A}^{\alpha\beta}$ and $\mathbf{N}^{\alpha\beta}$ also satisfy skew-symmetry relations:

$$\mathbf{A}^{\alpha\beta} = -\mathbf{A}^{\beta\alpha}, \qquad \mathbf{N}^{\alpha\beta} = -\mathbf{N}^{\beta\alpha}, \tag{9.39}$$

consequences of which are the identities

$$\sum_{\alpha,\beta=1}^{N}\mathbf{A}^{\alpha\beta} = \mathbf{0}, \qquad \sum_{\alpha,\beta=1}^{N}\mathbf{N}^{\alpha\beta} = \mathbf{0}. \tag{9.40}$$

It is also useful to note that, as in the unconstrained theory,

$$\mathbb{K} = \mathbb{C}^{-1}, \qquad \mathbf{N}^{\alpha\beta} = -\mathbb{K}[\mathbf{A}^{\alpha\beta}], \tag{9.41}$$

and

$$\left.\begin{array}{ll} \mathbb{C},\ \mathbf{A}^{\alpha\beta}\ (\alpha,\beta=1,2,\dots,N) & \text{are independent of strain and composition} \\ & \text{if and only if} \\ \mathbb{K},\ \mathbf{N}^{\alpha\beta}\ (\alpha,\beta=1,2,\dots,N) & \text{are independent of stress and composition.} \end{array}\right\} \tag{9.42}$$

Also, as in the unconstrained theory, we note that the *free energy* and the *relative chemical potentials at zero stress*,

$$\left.\begin{aligned}\Psi_0(\vec{\rho}) &= \tilde{\Psi}(\mathbf{T},\vec{\rho})\big|_{\mathbf{T}=\mathbf{0}},\\ \mu_0^{\alpha\beta}(\vec{\rho}) &= \tilde{\mu}^{\alpha\beta}(\mathbf{T},\vec{\rho})\big|_{\mathbf{T}=\mathbf{0}},\end{aligned}\right\} \tag{9.43}$$

are, by (9.35) and (9.36), related through

$$\mu_0^{\alpha\beta}(\vec{\rho}) = \frac{\partial^{(\beta)}\Psi_0(\vec{\rho})}{\partial\rho^\alpha}. \tag{9.44}$$

9.6 Mechanically simple substitutional alloys

Consistent with our discussion of the unconstrained theory in §7.4, we refer to a substitional alloy as being *mechanically simple* if:

(i) the elasticity tensor $\mathbb{C}$ and stress-composition tensors $\mathbf{A}^{\alpha\beta}$ are independent of strain and composition (cf. (9.42));

(ii) the mobilities $\mathbf{M}^{\alpha\beta}$ are independent of strain.

In addition, for a substitutional alloy *without vacancies*, we stipulate that

(iii) there exist functions $\mu_0^\alpha(\vec{\rho})$ such that:

$$\left.\begin{aligned}\Psi_0(\vec{\rho}) &= \rho^\alpha\mu_0^\alpha(\vec{\rho}),\\ \mu_0^{\alpha\beta}(\vec{\rho}) &= \mu_0^\alpha(\vec{\rho}) - \mu_0^\beta(\vec{\rho}).\end{aligned}\right\} \tag{9.45}$$

We refer to (9.45) as the *free-energy conditions at zero stress*, to $\mu_0^\alpha(\vec{\rho})$ as the *species-α chemical potential at zero stress.*[26]

We now show that, interestingly, the free energy and stress of a mechanically simple material within this constrained theory have a form identical to that of a mechanically simple material in the theory without a lattice constraint (cf. (7.27), $(7.28)_1$); only the expression for the chemical potential is different. We now verify this result, which is based on the constancy of the tensors $\mathbb{C}$ and $\mathbf{A}^{\alpha\beta}$.

Fix the species β and consider the relations

$$\frac{\partial\hat{\mathbf{T}}^{(\beta)}}{\partial\rho^\alpha} = \mathbf{A}^{\alpha\beta}, \qquad \alpha = \underbrace{1,2,\dots,\beta-1,\beta+1,\dots,N}_{\beta\text{ missing}}. \tag{9.46}$$

The derivative on the left may be viewed as the *ordinary partial derivative* of $\hat{\mathbf{T}}$ with respect to ρ^α taken with the density ρ^β *eliminated via the lattice constraint* (cf. the discussion following (9.8)). We may therefore integrate (9.46) from an arbitrary reference list $\vec{\rho}_0$ to $\vec{\rho}$; the result is an equation for the stress of the form

$$\mathbf{T} = \sum_{\alpha=1}^{N}\mathbf{A}^{\alpha\beta}(\rho^\alpha - \rho_0^\alpha) + \mathbf{S}(\mathbf{E}), \tag{9.47}$$

---

[26] An argument in support of the free-energy conditions at zero stress is given in Appendix A. These conditions are often used by materials scientists (cf., e.g., Spencer, Voorhees, and Tersoff (2001)). The condition $(9.45)_1$ is used only in our discussion of an interface between a vapor and a substitutional alloy without vacancies (§§26.1,26.2).

with $\mathbf{S}(\mathbf{E})$ an arbitrary function of strain. Even though $\mathbf{A}^{\beta\beta} = \mathbf{0}$ (no sum), we may view (9.47) as a constitutive equation giving the stress as a function of the strain and *all densities*, with the *interpretation* that ρ^β, which does not appear on the right side, has been eliminated via the lattice constraint. The species β was fixed in the foregoing argument, but we are at liberty to view (9.47) as N equations, each of which delivers the stress $\mathbf{T}$. If we sum (9.47) over all β and divide the result by N, we find that

$$\mathbf{T} = \frac{1}{N} \sum_{\alpha,\beta=1}^{N} \mathbf{A}^{\alpha\beta}(\rho^\alpha - \rho_0^\alpha) + \mathbf{S}(\mathbf{E}), \tag{9.48}$$

and, therefore, for

$$\mathbf{A}^\alpha \stackrel{\text{def}}{=} \frac{1}{N} \sum_{\beta=1}^{N} \mathbf{A}^{\alpha\beta}, \tag{9.49}$$

(9.48) becomes

$$\mathbf{T} = \sum_{\alpha=1}^{N} \mathbf{A}^\alpha(\rho^\alpha - \rho_0^\alpha) + \mathbf{S}(\mathbf{E}). \tag{9.50}$$

Note that, by (9.40) and (9.49),

$$\sum_{\alpha=1}^{N} \mathbf{A}^\alpha = \mathbf{0}, \tag{9.51}$$

which would seem natural in lieu of the lattice constraint.

Next, by $(9.38)_1$,

$$\frac{\partial \mathbf{S}(\mathbf{E})}{\partial \mathbf{E}} = \mathbb{C};$$

therefore $\mathbf{S}[\mathbf{E}] = \mathbb{C}(\mathbf{E}) + \mathbf{S}_0$, with $\mathbf{S}_0$ a constant tensor. Thus (9.50) becomes

$$\mathbf{T} = \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} \mathbf{A}^\alpha(\rho^\alpha - \rho_0^\alpha) + \mathbf{S}_0,$$

and if we assume that the reference list $\vec{\rho}_0$ is chosen so that $\mathbf{T} = \mathbf{0}$ when $\mathbf{E} = \mathbf{0}$ and $\vec{\rho} = \vec{\rho}_0$, then $\mathbf{S}_0 = \mathbf{0}$ and we arrive at a constitutive relation for the stress:

$$\mathbf{T} = \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} \mathbf{A}^\alpha(\rho^\alpha - \rho_0^\alpha); \tag{9.52}$$

(9.52) is identical to (9.46) of the unconstrained theory. Finally, to obtain the free energy we integrate the relation $\partial\hat{\Psi}/\partial\mathbf{E} = \mathbf{T}$ using (9.52); the result is the relation (7.27) for the free energy of the unconstrained theory. In (7.27) the function $\sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\cdot\mathbf{E}$ is well defined for all density lists $\vec{\rho}$, irrespective of whether the list is consistent with the lattice constraint. Thus, by (9.10), its Larché–Cahn derivative $\partial^{(\beta)}/\partial\rho^\alpha$ applied to this function gives

$$(\mathbf{A}^\alpha - \mathbf{A}^\beta)\cdot\mathbf{E}.$$

Thus, in view of the state relation $\hat{\mu}^{\alpha\beta} = \partial^{(\beta)}\hat{\Psi}/\partial\rho^\alpha$, we arrive at the following expression for the relative chemical potentials:

$$\mu^{\alpha\beta} = \frac{\partial^{(\beta)} F(\vec{\rho})}{\partial\rho^\alpha} + (\mathbf{A}^\alpha - \mathbf{A}^\beta)\cdot\mathbf{E}. \tag{9.53}$$

Summarizing, the constitutive equations for the free energy, the stress, and the chemical potentials of a mechanically simple, subsitutional alloy must have the specific form

$$\left.\begin{aligned}\Psi &= \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{A}^\alpha\cdot\mathbf{E} + F(\vec{\rho}),\\ \mathbf{T} &= \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N}\mathbf{A}^\alpha(\rho^\alpha - \rho_0^\alpha),\\ \mu^{\alpha\beta} &= \frac{\partial^{(\beta)}F(\vec{\rho})}{\partial\rho^\alpha} + (\mathbf{A}^\alpha - \mathbf{A}^\beta)\cdot\mathbf{E}.\end{aligned}\right\} \tag{9.54}$$

By $(9.38)_2$, the derivative of the right side of $(9.54)_3$ with respect to $\mathbf{E}$ should be $\mathbf{A}^{\alpha\beta}$; thus

$$\mathbf{A}^{\alpha\beta} = \mathbf{A}^\alpha - \mathbf{A}^\beta.$$

The remainder of the proof closely follows the argument for the unconstrained theory ensuing from (7.29). Solving $(9.54)_2$ for $\mathbf{E}$ yields

$$\mathbf{E} = \mathbb{K}[\mathbf{T}] - \sum_{\alpha=1}^{N}\mathbb{K}[\mathbf{A}^\alpha](\rho^\alpha - \rho_0^\alpha) \tag{9.55}$$

and, by (9.38), the Larché–Cahn derivative of the right side of this equation should be $\mathbf{N}^{\alpha\beta}$:

$$\mathbf{N}^{\alpha\beta} = -\mathbb{K}[\mathbf{A}^\alpha - \mathbf{A}^\beta]. \tag{9.56}$$

If we define $\mathbf{N}^\alpha$ through the obvious analog of (9.49), we find, upon summing (9.56) over β, that

$$\mathbf{N}^\alpha = -\mathbb{K}[\mathbf{A}^\alpha], \tag{9.57}$$

and hence that

$$\mathbf{N}^{\alpha\beta} = \mathbf{N}^\alpha - \mathbf{N}^\beta. \tag{9.58}$$

Equation (9.57) is identical to its counterpart in the unconstrained theory. Because of this, the calculation (7.30) remains valid, so that

$$\Psi = \tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] + \Psi_0(\vec{\rho}) \tag{9.59}$$

and $F(\vec{\rho})$ is related to $\Psi_0(\vec{\rho})$, the free energy at zero stress, through

$$F(\vec{\rho}) = \Psi_0(\vec{\rho}) - \tfrac{1}{2}\sum_{\alpha,\beta=1}^{N}(\rho^\alpha - \rho_0^\alpha)(\rho^\beta - \rho_0^\beta)\mathbf{A}^\alpha\cdot\mathbf{N}^\beta. \tag{9.60}$$

Further, by (9.40),

$$\sum_{\alpha=1}^{N}\mathbf{N}^\alpha = \mathbf{0}. \tag{9.61}$$

Finally, using (9.55) and (9.59) in (9.35), we find that

$$\Phi = -\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \sum_{\alpha=1}^{N}(\rho^\alpha - \rho_0^\alpha)\mathbf{N}^\alpha\cdot\mathbf{T} + \Psi_0(\vec{\rho}), \tag{9.62}$$

and therefore, by $(9.36)_2$,

$$\mu^{\alpha\beta} = \mu_0^{\alpha\beta}(\vec{\rho}) - (\mathbf{N}^\alpha - \mathbf{N}^\beta) \cdot \mathbf{T}. \tag{9.63}$$

At any given point, the term

$$-(\mathbf{N}^\alpha - \mathbf{N}^\beta) \cdot \mathbf{T} = -\mathbf{N}^{\alpha\beta} \cdot \mathbf{T} \tag{9.64}$$

represents energy the body would gain, per unit time, were we to replace a β-atom by an α-atom in the presence of the stress $\mathbf{T}$. An analogous interpretation applies to the term $(\mathbf{A}^\alpha - \mathbf{A}^\beta) \cdot \mathbf{E}$.

The results concerning stress as independent variable are summarized as follows:

$$\left.\begin{aligned} \Psi &= \tfrac{1}{2}\mathbf{T} \cdot \mathbb{K}[\mathbf{T}] + \Psi_0(\vec{\rho}), \\ \mathbf{E} &= \mathbb{K}[\mathbf{T}] + \sum_{\alpha=1}^{N} (\rho^\alpha - \rho_0^\alpha)\mathbf{N}^\alpha, \\ \mu^{\alpha\beta} &= \mu_0^{\alpha\beta}(\vec{\rho}) - (\mathbf{N}^\alpha - \mathbf{N}^\beta) \cdot \mathbf{T}. \end{aligned}\right\} \tag{9.65}$$

Next, since the mobilities are independent of the strain, it follows that, for any ζ,

$$\begin{aligned} \boldsymbol{\jmath}^\alpha &= -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho}) \nabla \mu^{\beta\zeta} \\ &= -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho}) \nabla \left(\frac{\partial^{(\zeta)} F(\vec{\rho})}{\partial \rho^\beta} + (\mathbf{A}^\beta - \mathbf{A}^\zeta) \cdot \mathbf{E} \right) \\ &= -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho}) \left(\sum_{\gamma=1}^{N} \frac{\partial^{2(\zeta)} F(\vec{\rho})}{\partial \rho^\beta \, \partial \rho^\gamma} \nabla \rho^\gamma + (\mathbf{A}^\beta - \mathbf{A}^\zeta) \nabla \mathbf{E} \right). \end{aligned} \tag{9.66}$$

Similarly, we have the alternative expression

$$\boldsymbol{\jmath}^\alpha = -\sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}(\vec{\rho}) \left(\sum_{\gamma=1}^{N} \frac{\partial^{2(\zeta)} \Psi_0(\vec{\rho})}{\partial \rho^\beta \partial \rho^\gamma} \nabla \rho^\gamma - (\mathbf{N}^\beta - \mathbf{N}^\zeta) \nabla \mathbf{T} \right). \tag{9.67}$$

In view of the mobility constraint (9.21), we may replace $\mathbf{A}^\beta - \mathbf{A}^\zeta$ in (9.66) by $\mathbf{A}^\beta$ and $\mathbf{N}^\beta - \mathbf{N}^\zeta$ in (9.67) by $\mathbf{N}^\beta$.

9.7 Cubic symmetry

The cubic specializations of the foregoing are straightforward and give results analogous to those presented in the unconstrained case. Because of their importance, we present these here. First, the tensors $\mathbf{M}^{\alpha\beta}$, $\mathbf{A}^{\alpha\beta}$, $\mathbf{N}^{\alpha\beta}$, $\mathbf{A}^\alpha$, and $\mathbf{N}^\alpha$ are isotropic, so that

$$\mathbf{M}^{\alpha\beta} = m^{\alpha\beta}\mathbf{1}, \quad \mathbf{A}^{\alpha\beta} = a^{\alpha\beta}\mathbf{1}, \quad \mathbf{N}^{\alpha\beta} = \eta^{\alpha\beta}\mathbf{1}, \quad \mathbf{A}^\alpha = a^\alpha\mathbf{1}, \quad \mathbf{N}^\alpha = \eta^\alpha\mathbf{1}, \tag{9.68}$$

with $a^{\alpha\beta} = a^\alpha - a^\beta$ and $\eta^{\alpha\beta} = \eta^\alpha - \eta^\beta$. Further, the moduli a^α and η^α are related through the compressibility k via

$$a^\alpha = -3k\eta^\alpha. \tag{9.69}$$

and, by (9.51) and (9.61), satisfy

$$\sum_{\alpha=1}^{N} a^{\alpha} = 0, \qquad \sum_{\alpha=1}^{N} \eta^{\alpha} = 0.$$

In addition, the relations $(9.54)_1$ and (9.62) determining the free energy and free enthalpy specialize to

$$\left.\begin{aligned} \Psi &= \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} a^{\alpha}(\rho^{\alpha}-\rho_0^{\alpha})\,\mathrm{tr}\,\mathbf{E} + F(\vec{\rho}),\\ \Phi &= -\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \sum_{\alpha=1}^{N} \eta^{\alpha}(\rho^{\alpha}-\rho_0^{\alpha})\,\mathrm{tr}\,\mathbf{T} + \Psi_0(\vec{\rho}), \end{aligned}\right\} \tag{9.70}$$

with $\Psi_0(\vec{\rho})$ given by (7.42). Further, as consequences of $(9.54)_{2,3}$, $(9.65)_{2,3}$, and $(9.68)_{4,5}$ we have the equivalent sets of relations:

$$\left.\begin{aligned} \mathbf{T} &= \mathbb{C}[\mathbf{E}] + \sum_{\alpha=1}^{N} a^{\alpha}(\rho^{\alpha}-\rho_0^{\alpha})\mathbf{1}, \qquad & \mu^{\alpha\beta} &= \frac{\partial^{(\beta)}F(\vec{\rho})}{\partial\rho^{\alpha}} + (a^{\alpha}-a^{\beta})\mathrm{tr}\,\mathbf{E},\\ \mathbf{E} &= \mathbb{K}[\mathbf{T}] + \sum_{\alpha=1}^{N} \eta^{\alpha}(\rho^{\alpha}-\rho_0^{\alpha})\mathbf{1}, \qquad & \mu^{\alpha\beta} &= \mu_0^{\alpha\beta}(\vec{\rho}) - (\eta^{\alpha}-\eta^{\beta})\mathrm{tr}\,\mathbf{T}, \end{aligned}\right\} \tag{9.71}$$

with $\mu_0^{\alpha\beta}$ given by (7.25). Finally, we have alternative expressions of Fick's law:

$$\left.\begin{aligned} \boldsymbol{\jmath}^{\alpha} &= -\sum_{\beta=1}^{N} m^{\alpha\beta}(\vec{\rho})\Big(\sum_{\gamma=1}^{N}\frac{\partial^{2(\zeta)}F(\vec{\rho})}{\partial\rho^{\beta}\,\partial\rho^{\gamma}}\nabla\rho^{\gamma} + a^{\beta}\,\nabla\mathrm{tr}\,\mathbf{E}\Big),\\ \boldsymbol{\jmath}^{\alpha} &= -\sum_{\beta=1}^{N} m^{\alpha\beta}(\vec{\rho})\Big(\sum_{\gamma=1}^{N}\frac{\partial^{2(\zeta)}\Psi_0(\vec{\rho})}{\partial\rho^{\beta}\partial\rho^{\gamma}}\nabla\rho^{\gamma} - \eta^{\beta}\nabla\mathrm{tr}\,\mathbf{T}\Big), \end{aligned}\right\} \tag{9.72}$$

in which the choice of species ζ is arbitrary.

10 Governing equations

The local balance laws for forces and atomic densities,

$$\mathrm{div}\,\mathbf{T} = \mathbf{0}, \qquad \dot{\rho}^{\alpha} = -\mathrm{div}\,\boldsymbol{\jmath}^{\alpha}, \tag{10.1}$$

supplemented by the constitutive equations form the governing equations of the theory, which are coupled partial differential equations for the displacement and the atomic densities. For the general theory the resulting equations, while not difficult to write, are complicated and afford little insight. For that reason, we display only the governing equations applicable to mechanically simple unconstrained materials and mechanically simple substitutional alloys without vacancies.

Note that, because of the strain displacement relation $\mathbf{E} = \frac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\top})$ and the symmetry $C_{ijkl} = C_{ijlk}$, we may write the components of $\mathbb{C}[\mathbf{E}]$ in the form

$$\big(\mathbb{C}[\mathbf{E}]\big)_{ij} = C_{ijkl}\,\frac{\partial u_k}{\partial x_l}.$$

For an *unconstrained material* the basic equations take the form

$$\left.\begin{aligned} &C_{ijkl}\frac{\partial^2 u_k}{\partial x_l \partial x_j} + \sum_{\alpha=1}^{N} A^{\alpha}_{ij}\,\frac{\partial \rho^\alpha}{\partial x_j} = 0, \\ &\dot{\rho}^\alpha = \operatorname{div}\left\{ \sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}\left(\sum_{\gamma=1}^{N} \frac{\partial^2 F(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma + \mathbf{A}^\beta\nabla\mathbf{E}\right)\right\}, \end{aligned}\right\} \tag{10.2}$$

where, for $\mathbf{L}$ and $\mathbf{P}$ tensor fields, the vector field $\mathbf{L}\nabla\mathbf{P}$ has the component form

$$(\mathbf{L}\nabla\mathbf{P})_k = L_{ij}\,\frac{\partial P_{ij}}{\partial x_k}.$$

The atomic balance $(10.2)_2$ may also be written in terms of stress and, by (7.36), has the form

$$\dot{\rho}^\alpha = \operatorname{div}\left\{ \sum_{\beta=1}^{N} \mathbf{M}^{\alpha\beta}\left(\sum_{\gamma=1}^{N} \frac{\partial^2 \Psi_0(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}\nabla\rho^\gamma - \mathbf{N}^\beta\nabla\mathbf{T}\right)\right\}. \tag{10.3}$$

In writing these equations we have supressed the dependencies of $\mathbf{M}^{\alpha\beta}$, F, and Ψ_0 on $\vec{\rho}$.

For a *substitutional alloy*, the only change in the basic equations is that

$$\frac{\partial^{2(\zeta)} F(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma} \qquad \text{should replace} \qquad \frac{\partial^2 F(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}$$

and

$$\frac{\partial^{2(\zeta)} \Psi_0(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma} \qquad \text{should replace} \qquad \frac{\partial^2 \Psi_0(\vec{\rho})}{\partial\rho^\beta\,\partial\rho^\gamma}$$

In using the atomic balances for substitutional materials, one should bear in mind that, for their validity, the mobility tensors $\mathbf{M}^{\alpha\beta}$ *must be consistent with the mobility constraints* (9.21).

B CONFIGURATIONAL FORCES IN BULK

In *dynamical* problems, defect structures, such as phase interfaces and dislocation lines, may move relative to the material. In variational treatments of related *equilibrium* problems, independent kinematical quantities may be independently varied, and each such variation yields a corresponding Euler–Lagrange balance. In dynamics with general forms of dissipation there is no encompassing variational principle, but experience has demonstrated the need for an additional balance associated with the kinematics of the defect. An additional balance of this sort is the relation that ensues when one formally sets the variationally derived expression for the driving force on a defect equal to a linear function of the velocity of that defect.[27] Here, guided by variational treatments in which such a balance is a consequence of the assumption of equilibrium, we follow Gurtin and Struthers (1990) and Gurtin (1995, 2000) and introduce, as primitive objects, configurational forces together with an independent *configurational force balance*. Roughly speaking, configurational forces are related to the integrity of the body's material structure and expend power in the transfer of material and in the evolution of defects.

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[27] Classical examples of driving forces are those on: dislocations (Peach and Koehler 1950); triple junctions (Herring 1951); vacancies, interstitial atoms, and inclusions (Eshelby 1951); interfaces (Eshelby 1956, 1970); crack tips (Eshelby 1956, Atkinson and Eshelby 1968, Rice 1968). Other examples of additional balances are discussed in §1.1.

In this part we discuss configurational forces within a context that *neglects defect structures*. Within that context such forces are extraneous to the solution of actual boundary-value problems. But in general situations knowledge of the structure of configurational forces in bulk away from defects is central to the understanding of their localized behavior at defects.

11 Configurational forces. Power

11.1 Configurational force balance

The configurational force system we envisage has two ingredients: a *stress* $\mathbf{C}(\mathbf{x},t)$ and a *body force* $\mathbf{f}(\mathbf{x},t)$, both distributed continuously over the body. This system is required to satisfy the *configurational force balance*

$$\int\limits_{\partial\mathcal{P}} \mathbf{C}\boldsymbol{\nu}\,da + \int\limits_{\mathcal{P}} \mathbf{f}\,dv = \mathbf{0} \tag{11.1}$$

for all parts $\mathcal{P}$, a requirement equivalent to the local force balance[28]

$$\operatorname{div}\mathbf{C} + \mathbf{f} = \mathbf{0}. \tag{11.2}$$

11.2 Migrating control volumes. Accretion

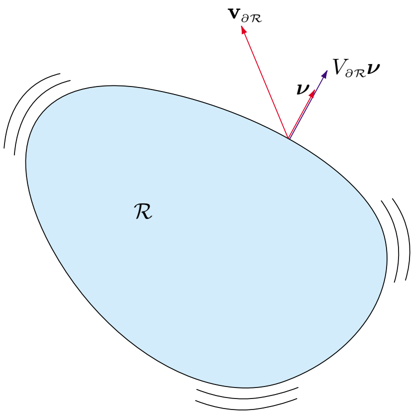

Figure 2: The migrating control volume $\mathcal{R} = \mathcal{R}(t)$; $\mathbf{v}_{\partial\mathcal{R}}$ represents the velocity with which an external agency adds material to $\partial\mathcal{R}$; the normal component $V_{\partial\mathcal{R}}$ of $\mathbf{v}_{\partial\mathcal{R}}$ must coincide with the normal velocity of $\partial\mathcal{R}$.

To characterize the manner in which configurational forces perform work, a means of capturing the kinematics associated with the transfer of material is needed. Following Gurtin (1995, 2000), we accomplish this with the aid of *control volumes* $\mathcal{R}(t)$ that *migrate through* $\mathcal{B}$ and thereby result in the transfer of material to — and the removal of material from — $\mathcal{R}(t)$ at $\partial\mathcal{R}(t)$, a process we refer to as *accretion.* Here it is essential that parts not be confused with migrating control volumes:

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[28] Configurational force balances may be derived as consequences of invariance of the power under Galilean changes of *referential observer* (Gurtin 2000, Podio-Guidugli 2002).

- a part $\mathcal{P}$ is a *fixed* subregion of $\mathcal{B}$;
- a migrating control volume $\mathcal{R}(t)$ *migrates* through $\mathcal{B}$.

Let $\mathcal{R} = \mathcal{R}(t)$ be a *migrating control volume* with $V_{\partial\mathcal{R}}(\mathbf{x},t)$ the (scalar) *normal velocity* of $\partial\mathcal{R}(t)$ in the direction of the outward unit normal $\boldsymbol{\nu}$. To describe power expenditures associated with the migration of $\mathcal{R}(t)$, we introduce a field $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$ defined over $\partial\mathcal{R}(t)$ for all t, which we view as the velocity with which an external agency adds material at $\partial\mathcal{R}(t)$. Compatibility then requires that $\mathbf{v}_{\partial\mathcal{R}}$ have $V_{\partial\mathcal{R}}$ as its normal component,

$$\mathbf{v}_{\partial\mathcal{R}} \cdot \boldsymbol{\nu} = V_{\partial\mathcal{R}}, \tag{11.3}$$

but $\mathbf{v}_{\partial\mathcal{R}}$ is otherwise arbitrary.[29] We refer to any such field $\mathbf{v}_{\partial\mathcal{R}}$ as a *velocity field for* $\partial\mathcal{R}$.

Non-normal velocity fields, while not intrinsic, are important. For example, given an arbitrary time-dependent parametrization $\mathbf{x} = \mathbf{r}(p_1, p_2, t)$ of $\partial\mathcal{R}$, the field defined by $\mathbf{v}_{\partial\mathcal{R}} = \partial\mathbf{r}/\partial t$ (holding (p_1, p_2) fixed) generally represents a non-normal velocity field for $\partial\mathcal{R}$. But while it is important that we allow for the use of non-normal velocity fields, *it is essential that the theory itself not depend on the particular velocity field used to describe a given migrating control volume.* As we shall see (§12.2), this observation has important consequences.

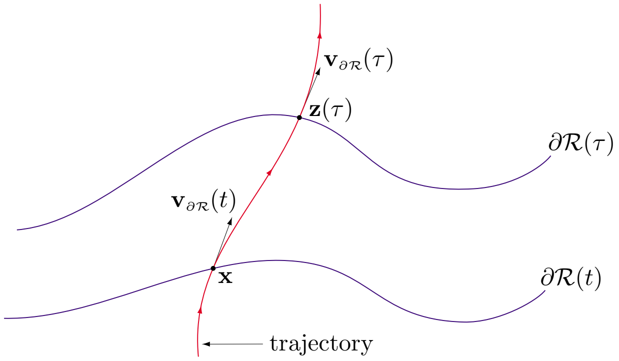

Figure 3: The trajectory $\mathbf{z}(\tau)$ of a particle that passes through $\mathbf{x}$ on $\partial\mathcal{R}(t)$ at time t.

Let $\mathcal{R} = \mathcal{R}(t)$ be a migrating control volume and $\mathbf{v}_{\partial\mathcal{R}}$ a velocity field for $\partial\mathcal{R}$. One might picture $\mathbf{v}_{\partial\mathcal{R}}$ as a velocity field for particles (not material points) evolving on the migrating surface $\partial\mathcal{R}$, in which case the trajectory $\mathbf{z}(\tau)$ of the particle that passes through position $\mathbf{x}$ on $\partial\mathcal{R}(t)$ at time t would be the unique solution of

$$\frac{d\mathbf{z}(\tau)}{d\tau} = \mathbf{v}_{\partial\mathcal{R}}(\mathbf{z}(\tau),\tau), \qquad \mathbf{z}(t) = \mathbf{x}. \tag{11.4}$$

Given a field $f(\mathbf{x},t)$, its rate of change following $\partial\mathcal{R}$, as described by $\mathbf{v}_{\partial\mathcal{R}}$, is the derivative with respect to time along such trajectories:

$$\overset{\circ}{f}(\mathbf{x},t) = \frac{d}{d\tau} f(\mathbf{z}(\tau),\tau)\Big|_{\tau=t}. \tag{11.5}$$

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[29] Non-normal velocity fields, while not intrinsic, are important. For example, given an arbitrary time-dependent parametrization $\mathbf{x} = \mathbf{r}(p_1, p_2, t)$ of $\partial\mathcal{R}$, the field defined by $\mathbf{v}_{\partial\mathcal{R}} = \partial\mathbf{r}/\partial t$ (holding (p_1, p_2) fixed) generally represents a non-normal velocity field for $\partial\mathcal{R}$.

In particular, using the chain-rule, we find, for the displacement field $\mathbf{u}$,

$$\overset{\circ}{\mathbf{u}}(\mathbf{x},t) = \frac{d}{d\tau}\mathbf{u}(\mathbf{z}(\tau),\tau)\Big|_{\tau=t} = \dot{\mathbf{u}}(\mathbf{x},t) + \nabla\mathbf{u}(\mathbf{x},t)\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t). \tag{11.6}$$

We refer to $\overset{\circ}{\mathbf{u}} = \dot{\mathbf{u}} + (\nabla\mathbf{u})\mathbf{v}_{\partial\mathcal{R}}$ as the *motion velocity following* $\partial\mathcal{R}$ *as described by* $\mathbf{v}_{\partial\mathcal{R}}$.

11.3 Power expended on a migrating control volume $\mathcal{R}(t)$

The notion of power is basic to all of mechanics. In its essence, this notion involves the pairing, via an inner product, of velocities with associated forces. In such a pairing the velocity is said to be *power conjugate* to its associated force. In our development of the free-energy imbalance in §4, the power expended on an arbitrary part $\mathcal{P}$ by tractions acting on $\partial\mathcal{P}$ was expressed by (2.4), viz.

$$\mathcal{W}(\mathcal{P}) = \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da. \tag{11.7}$$

Here the integrand $\mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}$ represents the power expended by the traction $\mathbf{T}\boldsymbol{\nu}$ over the motion velocity $\dot{\mathbf{u}}$ of material points on $\partial\mathcal{P}$; so that $\dot{\mathbf{u}}$ is the *power conjugate* velocity for $\mathbf{T}\boldsymbol{\nu}$.

Consider now a migrating control volume $\mathcal{R}(t)$. The migration of $\mathcal{R}(t)$ is accompanied by a transfer of material across $\partial\mathcal{R}(t)$, and one would expect that this transfer of material be accompanied by an expenditure of power over and above the standard expenditure represented by (11.7). A central tenet of our treatment of configurational forces is the presumption that:[30]

Configurational forces expend power in consort with transfers of material.

In particular, for the migrating control volume $\mathcal{R}(t)$, *we view the traction* $\mathbf{C}\boldsymbol{\nu}$ *as a force associated with the transfer of material across* $\partial\mathcal{R}(t)$; since any given velocity field $\mathbf{v}_{\partial\mathcal{R}}$ for $\partial\mathcal{R}(t)$ represents a velocity field with which material is transferred across $\partial\mathcal{R}(t)$, we take $\mathbf{v}_{\partial\mathcal{R}}$ to be an appropriate *power conjugate* velocity for $\mathbf{C}\boldsymbol{\nu}$. We therefore assume that the migration of $\partial\mathcal{R}$ is accompanied by an expenditure of power equal to

$$\int\limits_{\partial\mathcal{R}(t)} \mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}}\,da.$$

Classically, the standard traction $\mathbf{T}\boldsymbol{\nu}$ on $\partial\mathcal{R}$ would be power-conjugate to the motion velocity $\dot{\mathbf{u}}$, as in (11.7), but $\partial\mathcal{R}$ when migrating has no intrinsic material description, as material is continually being added and removed, and it would seem appropriate to use as power-conjugate velocity for $\mathbf{T}\boldsymbol{\nu}$ the motion velocity $\overset{\circ}{\mathbf{u}}$ following (the migration of) $\partial\mathcal{R}$ as described by $\mathbf{v}_{\partial\mathcal{R}}$; granted this,

$$\int\limits_{\partial\mathcal{R}(t)} \mathbf{T}\boldsymbol{\nu}\cdot\overset{\circ}{\mathbf{u}}\,da \tag{11.8}$$

represents the associated expenditure of power.

Material is added to $\mathcal{R}$ only along its boundary $\partial\mathcal{R}$; there is no transfer of material to the interior of $\mathcal{P}$, nor is there any change in the material structure. For that reason the

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[30] Cf. Gurtin (1995, 2000)

configurational body force $\mathbf{f}$ performs no work. We therefore write the power expenditure of the standard and configurational force systems in the form

$$\mathcal{W}(\mathcal{R}(t)) = \int\limits_{\partial\mathcal{R}(t)} (\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\overset{\circ}{\mathbf{u}})\,da. \tag{11.9}$$

Writing the expended power in the form (11.9) might, at first sight, appear artificial, since the tangential component of the velocity $\mathbf{v}_{\partial\mathcal{R}}$ is not uniquely determined by the migration of $\partial\mathcal{R}$; this issue is addressed in §12.2, where we determine conditions both necessary and sufficient for $\mathcal{W}(\mathcal{R}(t))$ to be independent of the specific choice of $\mathbf{v}_{\partial\mathcal{R}}$.

If $\mathbf{v}_{\partial\mathcal{R}} \equiv \mathbf{0}$, then $\mathcal{R}(t)$ is independent of t, so that $\mathcal{R}(t) \equiv \mathcal{P}$, with $\mathcal{P}$ a part. In this case, by (11.6), $\overset{\circ}{\mathbf{u}}$ reduces to $\dot{\mathbf{u}}$ and the expended power assumes its classical form (11.7).

12 Thermodynamical laws for migrating control volumes. The Eshelby relation

We now present extensions of the atomic balance, balance of energy, and the entropy imbalance appropriate to a treatment of configurational forces.[31] Our extensions are based on the use of migrating control volumes to characterize the manner in which configurational forces expend power.

12.1 Migrational balance laws

We begin by rewriting the atomic balance (3.1), balance of energy (4.2), and the entropy imbalance (4.3) for an arbitrary part $\mathcal{P}$ of $\mathcal{B}$:

$$\left.\begin{aligned}
&\frac{d}{dt}\int\limits_{\mathcal{P}} \rho^\alpha\,dv = -\int\limits_{\partial\mathcal{P}} \boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da,\\
&\frac{d}{dt}\int\limits_{\mathcal{P}} \epsilon\,dv = \int\limits_{\partial\mathcal{P}} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da - \int\limits_{\partial\mathcal{P}} \mathbf{q}\cdot\boldsymbol{\nu}\,da - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}} \mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da,\\
&\frac{d}{dt}\int\limits_{\mathcal{P}} \eta\,dv \geq -\int\limits_{\partial\mathcal{P}} \frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\,da.
\end{aligned}\right\} \tag{12.1}$$

Generalizations, to migrating control volumes $\mathcal{R}(t)$, of $(12.1)_{1,3}$, the atomic balance and the entropy inequality, are straightforward, but the generalization of the energy balance $(12.1)_2$ is not at all obvious. Indeed, the standard generalization of this balance, namely

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)} \epsilon\,dv - \int\limits_{\partial\mathcal{R}(t)} \epsilon V_{\partial\mathcal{R}}\,da = \int\limits_{\partial\mathcal{R}(t)} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da - \int\limits_{\partial\mathcal{R}(t)} \mathbf{q}\cdot\boldsymbol{\nu}\,da - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)} \mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da, \tag{12.2}$$

is inapplicable because *it does not account explicitly for the rate at which work is performed by the configurational-force system.*

Here, following Gurtin (1995, 2000, §6c), we consider a more general development based on:

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[31] Due to their absence of temporal derivatives, the standard force and moment balances (2.3) and the configurational force balance (11.1) remain valid as is for migrating control volumes.

- an *atomic balance* for each species α in the (more or less standard) form

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\rho^\alpha\,dv = -\int\limits_{\partial\mathcal{R}(t)}\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da \;+\underbrace{\int\limits_{\partial\mathcal{R}(t)}\rho^\alpha V_{\partial\mathcal{R}}\,da}_{\substack{\text{accretive flow}\\ \text{of atoms}}}; \tag{12.3}$$

- *balance of energy* in the form

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\epsilon\,dv = \overbrace{\int\limits_{\partial\mathcal{R}(t)}(\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\overset{\circ}{\mathbf{u}})\,da}^{\mathcal{W}(\mathcal{R}(t))} - \int\limits_{\partial\mathcal{R}(t)}\mathbf{q}\cdot\boldsymbol{\nu}\,da$$

$$-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da + \underbrace{\int\limits_{\partial\mathcal{R}(t)}QV_{\partial\mathcal{R}}\,da}_{\text{accretive heating}} + \underbrace{\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha\rho^\alpha V_{\partial\mathcal{R}}\,da}_{\substack{\text{accretive flow of}\\ \text{chemical energy}}}, \tag{12.4}$$

  with Q a field defined over the body for all time;

- an *entropy imbalance* in the form

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\eta\,dv \geq -\int\limits_{\partial\mathcal{R}(t)}\frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\,da + \underbrace{\int\limits_{\partial\mathcal{R}(t)}\frac{Q\,V_{\partial\mathcal{R}}}{\theta}\,da}_{\substack{\text{accretive flow}\\ \text{of entropy}}}. \tag{12.5}$$

12.2 The Eshelby relation as a consequence of invariance

We require that the *migrational laws* (12.3)–(12.5) be satisfied for any choice of the migrating control volume $\mathcal{R}(t)$ and — in view of our discussion in the paragraph following (11.3) — that *these laws be independent of the choice of velocity field* $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$ *used to describe the migration of* $\partial\mathcal{R}(t)$. Among the migrational laws it is only the energy balance (12.4) that is influenced by changes in $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$, an influence felt through the expended power $\mathcal{W}(\mathcal{R}(t))$ as described by (11.9). Thus we are led to the

> INTRINSICALITY HYPOTHESIS Given any migrating control volume $\mathcal{R}(t)$, *the expended power* (11.9) *is independent of the choice of velocity field* $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$ *used to describe the migration of* $\partial\mathcal{R}(t)$.

This hypothesis has strong consequences. Choose a migrating control volume $\mathcal{R}(t)$ and an arbitrary *tangential* vector field on $\partial\mathcal{R}$. Then, by (11.3),

$$\mathbf{v}_{\partial\mathcal{R}} = V_{\partial\mathcal{R}}\boldsymbol{\nu} + \mathbf{a} \tag{12.6}$$

is a velocity field for $\partial\mathcal{R}(t)$, and the requirement that the expended power be invariant under changes in $\mathbf{v}_{\partial\mathcal{R}}$ is equivalant to the requirement that this power be independent of the choice of tangential field $\mathbf{a}$. By (11.6) and (12.6),

$$\overset{\circ}{\mathbf{u}} = \dot{\mathbf{u}} + V_{\partial\mathcal{R}}(\nabla\mathbf{u})\boldsymbol{\nu} + (\nabla\mathbf{u})\mathbf{a};$$

thus

$$\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\overset{\circ}{\mathbf{u}} = \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}} + V_{\partial\mathcal{R}}\boldsymbol{\nu}\cdot(\mathbf{C} + (\nabla\mathbf{u})^{\top}\mathbf{T})\boldsymbol{\nu} + \mathbf{a}\cdot(\mathbf{C} + (\nabla\mathbf{u})^{\top}\mathbf{T})\boldsymbol{\nu}$$

and, letting $\mathbf{G} = \mathbf{C} + (\nabla\mathbf{u})^{\top}\mathbf{T}$, the expended power (11.9) becomes

$$\mathcal{W}(\mathcal{R}(t)) = \int\limits_{\partial\mathcal{R}(t)} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da + \int\limits_{\partial\mathcal{R}(t)} V_{\partial\mathcal{R}}\boldsymbol{\nu}\cdot\mathbf{G}\boldsymbol{\nu}\,da + \int\limits_{\partial\mathcal{R}(t)} \mathbf{a}\cdot\mathbf{G}\boldsymbol{\nu}\,da. \tag{12.7}$$

Since $\mathbf{a}$ appears linearly in (12.7), and not elsewhere in (11.9), the invariance of (11.9) under changes in $\mathbf{a}$ is equivalent to the requirement that

$$\int\limits_{\partial\mathcal{R}(t)} \mathbf{a}\cdot\mathbf{G}\boldsymbol{\nu}\,da = 0$$

for all $\mathcal{R}(t)$ and all fields $\mathbf{a}(\mathbf{x},t)$ tangential to $\partial\mathcal{R}(t)$. Since both $\mathcal{R}$ and $\mathbf{a}$ are arbitrary, $\mathbf{G}\boldsymbol{\nu}\cdot\mathbf{a} = 0$ for all orthogonal vectors $\boldsymbol{\nu}$ and $\mathbf{a}$; thus $\mathbf{G}\boldsymbol{\nu}$ must be parallel to $\boldsymbol{\nu}$ for all $\boldsymbol{\nu}$ and every vector must be an eigenvector of $\mathbf{G}$. Thus there is a scalar field π such that $\mathbf{G} = \pi\mathbf{1}$; hence (Gurtin, 2000, p. 37)

$$\mathbf{C} = \pi\mathbf{1} - (\nabla\mathbf{u})^{\top}\mathbf{T} \tag{12.8}$$

and the expended power has the intrinsic form

$$\mathcal{W}(\mathcal{R}(t)) = \int\limits_{\partial\mathcal{R}(t)} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da + \int\limits_{\partial\mathcal{R}(t)} \pi V_{\partial\mathcal{R}}\,da. \tag{12.9}$$

The field π represents a *configurational bulk tension* that performs work in conjunction with the addition of material at the boundary of a migrating control volume. Conversely, the relation 12.8 renders the theory consistent with the hypothesis of intrinsicality.

Summarizing, we have shown that the intrinsicality hypothesis is equivalent to the requirement that the configurational stress and expended power have the respective forms (12.8) and (12.9).

But more can be said if we account for the full set of migrational laws. A standard transport theorem asserts that, for $\mathcal{R}(t)$ a migrating control volume and $\Theta(\mathbf{x},t)$ a field on the body for all time,

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)} \Theta\,dv = \int\limits_{\mathcal{R}(t)} \dot{\Theta}\,dv + \int\limits_{\partial\mathcal{R}(t)} \Theta V_{\partial\mathcal{R}}\,da. \tag{12.10}$$

Thus we may rewrite (12.5) as

$$\int\limits_{\mathcal{R}(t)} \dot{\eta}\,dv + \int\limits_{\partial\mathcal{R}(t)} \eta V_{\partial\mathcal{R}}\,da \geq -\int\limits_{\partial\mathcal{R}(t)} \frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\,da + \int\limits_{\partial\mathcal{R}(t)} \frac{QV_{\partial\mathcal{R}}}{\theta}\,da. \tag{12.11}$$

On the other hand, we may use (12.9) and (12.10) to write balance of energy (12.4) in the form

$$\begin{aligned}\int\limits_{\mathcal{R}(t)} \dot{\epsilon}\,dv + \int\limits_{\partial\mathcal{R}(t)} \epsilon V_{\partial\mathcal{R}}\,da = \int\limits_{\partial\mathcal{R}(t)} \mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da + \int\limits_{\partial\mathcal{R}(t)} \pi V_{\partial\mathcal{R}}\,da - \int\limits_{\partial\mathcal{R}(t)} \mathbf{q}\cdot\boldsymbol{\nu}\,da \\ - \sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)} \mu^{\alpha}\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}\,da + \int\limits_{\partial\mathcal{R}(t)} \Big(Q + \sum_{\alpha=1}^{N}\mu^{\alpha}\rho^{\alpha}\Big)V_{\partial\mathcal{R}}\,da\end{aligned} \tag{12.12}$$

Given a time τ, it is possible to find a second migrating control volume $\mathcal{R}'(t)$ with $\mathcal{R}'(\tau) = \mathcal{R}(\tau)$, but with $V'_{\partial\mathcal{R}}$, the normal velocity of $\partial\mathcal{R}'$ at $t = \tau$, an *arbitrary scalar field* on $\partial\mathcal{R}'$; satisfaction of (12.11) and (12.12) for all such $V'_{\partial\mathcal{R}}$ implies that

$$Q = \eta\vartheta, \qquad \pi = \epsilon - \eta\vartheta - \sum_{\alpha=1}^{N} \mu^\alpha \rho^\alpha, \tag{12.13}$$

so that

$$\pi = \Psi - \sum_{\alpha=1}^{N} \mu^\alpha \rho^\alpha \tag{12.14}$$

with $\Psi = \epsilon - \theta\eta$ the free-energy. Thus (12.8) yields the *Eshelby relation*

$$\mathbf{C} = \Big(\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha\Big)\mathbf{1} - (\nabla\mathbf{u})^{\top}\mathbf{T}. \tag{12.15}$$

This relation, which applies to both unconstrained materials and substitutional alloys, plays a fundamental role in our discussion of evolving interfaces.

Note that, by (12.13), the accretive heating $QV_{\partial\mathcal{R}}$ coincides with the temperature times $\eta V_{\partial\mathcal{R}}$, a relation reminisent of the classical thermodynamic relation $d(heat) = (temperature)d(entropy)$.

12.3 Consistency of the migrational balance laws with classical forms of these laws

By (12.13), we may rewrite the migrational laws for energy and entropy in the form

$$\left.\begin{aligned}
\frac{d}{dt}\int\limits_{\mathcal{R}(t)} \epsilon\, dv - \int\limits_{\partial\mathcal{R}(t)} \epsilon V_{\partial\mathcal{R}}\, da &= \int\limits_{\partial\mathcal{R}(t)} (\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\, da - \int\limits_{\partial\mathcal{R}(t)} \mathbf{q}\cdot\boldsymbol{\nu}\, da \\
&\quad - \sum_{\alpha=1}^{N} \int\limits_{\partial\mathcal{R}(t)} \mu^\alpha \boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\, da - \int\limits_{\partial\mathcal{R}(t)} \Big(\Psi - \sum_{\alpha=1}^{N} \rho^\alpha\mu^\alpha\Big) V_{\partial\mathcal{R}}\, da, \\
\frac{d}{dt}\int\limits_{\mathcal{R}(t)} \eta\, dv - \int\limits_{\partial\mathcal{R}(t)} \eta V_{\partial\mathcal{R}}\, da &\ge - \int\limits_{\partial\mathcal{R}(t)} \frac{\mathbf{q}}{\theta}\cdot\boldsymbol{\nu}\, da.
\end{aligned}\right\} \tag{12.16}$$

The second of these and the atomic balance (12.3) are standard. On the other hand, balance of energy in the form $(12.16)_2$ is nonstandard, as it explicitly accounts for power expended by configurational forces, but we may use (12.9) and (12.14) to reduce $(12.16)_2$ to its classical form (12.2). *The migrational laws are therefore fully consistent with classical versions of these laws.*

12.4 Isothermal conditions. The free-energy imbalance

Assume now that *isothermal* conditions prevail, so that

$$\theta \equiv \text{constant}.$$

Multiplying the entropy imbalance $(12.16)_3$ by θ and subtracting the result from the energy balance $(12.16)_2$ then yields the (migrational) *free-energy imbalance*

$$\begin{aligned}\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\Psi\,dv \leq \int\limits_{\partial\mathcal{R}(t)}(\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}}+\mathbf{T}\boldsymbol{\nu}\cdot\overset{\circ}{\mathbf{u}})\,da \\ -\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da+\underbrace{\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha\rho^\alpha V_{\partial\mathcal{R}}\,da}_{\substack{\text{accretive flow of}\\ \text{chemical energy}}}. \qquad (12.17)\end{aligned}$$

This free-energy imbalance should be compared to its classical counterpart

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\Psi\,dv-\int\limits_{\partial\mathcal{R}(t)}\Psi V_{\partial\mathcal{R}}\,da \leq \int\limits_{\partial\mathcal{R}(t)}\mathbf{T}\boldsymbol{\nu}\cdot\dot{\mathbf{u}}\,da-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}\,da, \qquad (12.18)$$

which accounts for an accretive flow of free energy,

$$\int\limits_{\partial\mathcal{R}(t)}\Psi V_{\partial\mathcal{R}}\,da, \qquad (12.19)$$

but not for power expended by the configurational force system, nor for an accretive flow of chemical energy.

Finally, in view of the lattice constraint (5.1), $\mathbf{C}$ transforms according to

$$\mathbf{C}\to\mathbf{C}-c\rho^{\mathrm{sites}}\mathbf{1}$$

under the transformations $\mu^\alpha\to\mu^\alpha+c$ and, consequently, the free-energy imbalance (12.17) is invariant under such transformations.

12.5 Generic free-energy imbalance for migrating control volumes

The free-energy imbalance (12.17) has the generic form

$$\begin{aligned}&\frac{d}{dt}\{\text{free energy of }\mathcal{R}(t)\}\\ &\qquad\leq\{\text{power expended on }\mathcal{R}(t)\text{ by configurational and standard forces}\}\\ &\qquad\qquad+\{\text{energy flow into }\mathcal{R}(t)\text{ by atomic diffusion}\}\\ &\qquad\qquad\qquad+\{\text{accretive flow of chemical energy into }\mathcal{R}(t)\}. \qquad (12.20)\end{aligned}$$

With the exception of the next section, *the remainder of this work focuses on evolving interfaces neglecting thermal influences. Our discussion there is based on free-energy imbalances of the generic structure* (12.20) *with the role of a migrating control volume replaced by that of an interfacial pillbox* (§16).

13 Role and influence of constitutive equations

Until this point in our discussion of configurational forces, no use has been made of constitutive theory. Hence, the results are completely independent of constitutive equations and apply to broad classes of materials, allowing, for example, for plasticity, viscoelasticity, and other more complicated forms of dissipative material response that couple the mechanical and chemical degrees of freedom. We now consider the implications of assuming that the free energy, stress, and chemical potentials are given by thermocompatible constitutive equations depending upon the strain and the atomic density.

First note that, since $\big((\nabla\mathbf{u})^{\top}\mathbf{T}\big)_{ij} = T_{kj}\partial u_k/\partial x_i$, computing $\operatorname{div}\mathbf{C}$ using the Eshelby relation (12.15) gives

$$\frac{\partial C_{ij}}{\partial x_j} = \frac{\partial}{\partial x_i}\left(\Psi - \sum_{\alpha=1}^{N}\rho^{\alpha}\mu^{\alpha}\right) - T_{kj}\frac{\partial^2 u_k}{\partial x_j\partial x_i} - \frac{\partial T_{kj}}{\partial x_j}\frac{\partial u_k}{\partial x_i},$$

and therefore using the balance $\operatorname{div}\mathbf{T} = \mathbf{0}$, the symmetry of $\mathbf{T}$, and the strain-displacement relation (2.1), we find that the configurational body force $\mathbf{f}$ in the balance $\operatorname{div}\mathbf{C} + \mathbf{f} = \mathbf{0}$ has the decomposition

$$f_i = -\frac{\partial\Psi}{\partial x_i} + T_{kj}\frac{\partial E_{kj}}{\partial x_i} + \sum_{\alpha=1}^{N}\mu^{\alpha}\frac{\partial\rho^{\alpha}}{\partial x_i} + \sum_{\alpha=1}^{N}\rho^{\alpha}\frac{\partial\mu^{\alpha}}{\partial x_i}. \tag{13.1}$$

By (7.5),

$$\frac{\partial\Psi}{\partial x_i} = T_{kj}\frac{\partial E_{kj}}{\partial x_i} + \sum_{\alpha=1}^{N}\mu^{\alpha}\frac{\partial\rho^{\alpha}}{\partial x_i} \tag{13.2}$$

for an unconstrained material and therefore $\mathbf{f} = \sum_{\alpha=1}^{N}\rho^{\alpha}\nabla\mu^{\alpha}$. For a substitutional alloy the computation is similar, but a bit more complicated; the crucial step is noting that, by virtue of the lattice constraint (5.1), $\sum_{\alpha=1}^{N}\mu^{\alpha}(\partial\rho^{\alpha}/\partial x_i) = \sum_{\alpha=1}^{N}\mu^{\alpha\zeta}(\partial\rho^{\alpha}/\partial x_i)$ for any reference species ζ, so that, by (9.27),

$$\frac{\partial\Psi}{\partial x_i} = T_{kj}\frac{\partial E_{kj}}{\partial x_i} + \sum_{\alpha=1}^{N}\mu^{\alpha\zeta}\frac{\partial\rho^{\alpha}}{\partial x_i} = T_{kj}\frac{\partial E_{kj}}{\partial x_i} + \sum_{\alpha=1}^{N}\mu^{\alpha}\frac{\partial\rho^{\alpha}}{\partial x_i}. \tag{13.3}$$

Thus, for unconstrained materials and for substitutional alloys,

$$\mathbf{f} = \sum_{\alpha=1}^{N}\rho^{\alpha}\nabla\mu^{\alpha}, \tag{13.4}$$

showing that configurational body forces arise in response to spatial variations in the chemical potentials. We view $\mathbf{f}$ as an *internal* body force. If we had, from the outset, included an external body force $\mathbf{b}$ in the standard force system, so that $\operatorname{div}\mathbf{T} + \mathbf{b} = \mathbf{0}$, then we would get a concomitant *external* body force $-(\nabla\mathbf{u})^{\top}\mathbf{b}$ in the configurational system (cf. Eshelby, 1956; Maugin, 1993).

A major difference between the standard and configurational force systems is the presence of *internal configurational forces* such as $\mathbf{f}$. These forces are connected with the material structure of the body $\mathcal{B}$; corresponding to each configuration of $\mathcal{B}$ there are a distribution of material and internal configurational forces that act to hold the material in place in that configuration. Such forces characterize the resistance of the material to structural changes and are basic when discussing the kinetics of defects.

Finally, as is clear from (12.15) and (13.4), the configurational fields are completely determined by the fields $\mathbf{u}$, $\mathbf{T}$, Ψ, $\vec{\mu}$, and $\vec{\rho}$; there is no need for additional constitutive assumptions. As we shall see, this will not be so when we discuss evolving interfaces.

C INTERFACE KINEMATICS

We consider an *interface* $\mathcal{S}(t)$ separating bulk phases or grains; in the latter case we will often, but not always, refer to $\mathcal{S}$ as a *grain boundary*. To avoid cumbersome mathematical formality associated with surfaces,

we restrict attention to two space-dimensions;

the interface is then presumed to be a smooth curve $\mathcal{S}(t)$ that evolves smoothly with t.

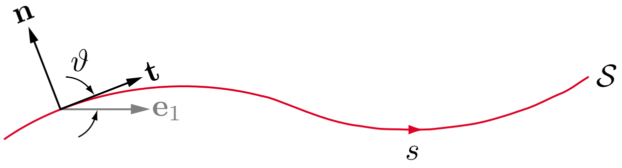

Figure 4: The interface $\mathcal{S}(t)$. Our convention is such that $K > 0$ on concave upward portions of $\mathcal{S}(t)$.

14 Definitions and basic results

This section contains mathematical results of a preliminary nature concerning the evolution of curves.[32]

14.1 Curvature. Normal velocity. Normal time-derivative

We use the following notation for quantities associated with $\mathcal{S}$: $\mathbf{t}(\mathbf{x},t)$ and $\mathbf{n}(\mathbf{x},t)$, respectively, denote the *tangent* and *normal* fields

$$\mathbf{t} = (\cos\vartheta, \sin\vartheta), \qquad \mathbf{n} = (-\sin\vartheta, \cos\vartheta), \tag{14.1}$$

with $\mathbf{n}$ directed outward from the region occupied by the $(-)$-phase, and with ϑ the counterclockwise angle from the (1,0) axis to $\mathbf{t}$ (Figure 4). Then (14.1) yield the *Frenet formulas*

$$\frac{\partial \mathbf{t}}{\partial s} = K\mathbf{n}, \qquad \frac{\partial \mathbf{n}}{\partial s} = -K\mathbf{t}, \tag{14.2}$$

with s the arclength and

$$K = \frac{\partial \vartheta}{\partial s} \tag{14.3}$$

the *curvature.*

We consistently use the term *interfacial field* for a scalar, vector, or tensor field $\varphi(\mathbf{x},t)$ defined on $\mathcal{S}(t)$ for all t.

Let $\mathbf{x} = \mathbf{r}(s,t)$ denote an arc-length parametrization of $\mathcal{S}(t)$ with s increasing in the direction of $\mathbf{t}$. Then

$$V = \frac{\partial \mathbf{r}}{\partial t} \cdot \mathbf{n} \tag{14.4}$$

---

[32] These results are taken from Angenent and Gurtin (1989). Cf. also Gurtin (1993, §§1,2), where a more detailed presentation may be found.

and

$$\mathbf{v} = V\mathbf{n} \tag{14.5}$$

denote the scalar and vector *normal velocities* of $\mathcal{S}$, while

$$v = -\frac{\partial \mathbf{r}}{\partial t} \cdot \mathbf{t}$$

is termed the *arc velocity.* Note that, since

$$\mathbf{t} = \frac{\partial \mathbf{r}}{\partial s}$$

and $\mathbf{t} \cdot \partial \mathbf{t}/\partial t = 0$, we may use $(14.2)_1$ and (14.4) to conclude that

$$\begin{aligned} \frac{\partial v}{\partial s} &= -\mathbf{t} \cdot \frac{\partial}{\partial t}\frac{\partial \mathbf{r}}{\partial s} - \frac{\partial \mathbf{r}}{\partial t} \cdot \frac{\partial \mathbf{t}}{\partial s} = -\frac{\partial \mathbf{r}}{\partial t} \cdot (K\mathbf{n}) \\ &= -KV. \end{aligned} \tag{14.6}$$

Given a point $\mathbf{x}_0$ on the interface at some time t_0, the *normal trajectory* through $\mathbf{x}_0$ at t_0 is the smooth curve $\mathbf{z}(t)$ defined as the solution of the initial-value problem

$$\frac{d\mathbf{z}(t)}{dt} = \mathbf{v}(\mathbf{z}(t), t), \qquad \mathbf{z}(t_0) = \mathbf{x}_0. \tag{14.7}$$

The normal trajectory $\mathbf{z}(t)$ may also be described uniquely in terms of arc length; indeed since the mapping $\mathbf{x} = \mathbf{r}(s, t)$ repesents a one-to-one correspondence between s and $\mathbf{x}$,[33] there is a function $s = S(t)$ such that $\mathbf{z}(t) = \mathbf{r}(S(t), t)$. Then, since the trajectory $\mathbf{z}(t)$ is normal,

$$\mathbf{t}(S(t), t) \cdot \frac{d\mathbf{r}(S(t), t)}{dt} = 0 \tag{14.8}$$

and hence $S(t)$ is a solution of the initial-value problem

$$\frac{dS(t)}{dt} = v(S(t), t), \qquad S(t_0) = s_0, \tag{14.9}$$

where $\mathbf{x}_0 = \mathbf{r}(s_0, t)$.

The *normal time-derivative* $\overset{\square}{\varphi}$ of an interfacial field $\varphi(\mathbf{x}, t)$ is the derivative of φ following the normal trajectories of $\mathcal{S}(t)$:[34]

$$\overset{\square}{\varphi}(\mathbf{x}_0, t_0) = \left.\frac{d\varphi(\mathbf{z}(t), t)}{dt}\right|_{t=t_0}. \tag{14.10}$$

The field $\varphi(\mathbf{x}, t)$ may equally well be described as a function $\varphi(s, t)$ of arc length and time. We refer to $\varphi(s, t)$ as the *arc-length description* of φ. In the arc-length description the normal time derivative has the equivalent form

$$\overset{\square}{\varphi}(s_0, t_0) = \left.\frac{d\varphi(S(t), t)}{dt}\right|_{t=t_0},$$

---

[33] The curve $\mathcal{S}(t)$ is presumed to be nonintersecting.

[34] The normal-time derivative is a counterpart, for the interface $\mathcal{S}$, of the time-derivative following the motion of the surface $\partial\mathcal{R}$ of a migrating control volume $\mathcal{R}$ (cf. §11.2).

so that, by (14.9),

$$\overset{\square}{\varphi} = \frac{\partial \varphi}{\partial t} + v \frac{\partial \varphi}{\partial s}, \tag{14.11}$$

where here and in what follows

$$\frac{\partial \varphi}{\partial t} \quad \text{denotes the partial derivative of } \varphi \text{ holding } s \text{ fixed.}$$

Basic to our discussion of constitutive equations is the *chain-rule for the normal time-derivative*: given a function

$$\varphi = \hat{\varphi}(\vec{\lambda}), \qquad \vec{\lambda} = (\lambda_1, \lambda_2, \dots, \lambda_N),$$

with each λ_n an interfacial field,

$$\overset{\square}{\varphi} = \sum_{n=1}^{N} \frac{\partial \hat{\varphi}(\vec{\lambda})}{\partial \lambda_n} \overset{\square}{\lambda}_n. \tag{14.12}$$

The verification of (14.12) is based on the definition of the normal time-derivative as specified in (14.10). Indeed,

$$\begin{aligned}
\overset{\square}{\varphi}(\mathbf{x}_0, t_0) &= \frac{d\varphi(\mathbf{z}(t), t)}{dt}\bigg|_{t=t_0} \\
&= \frac{d\hat{\varphi}(\vec{\lambda}(\mathbf{z}(t), t))}{dt}\bigg|_{t=t_0} \\
&= \sum_{n=1}^{N} \frac{\partial \hat{\varphi}(\vec{\lambda})}{\partial \lambda_n} \left[\frac{d\lambda_n(\mathbf{z}(t), t)}{dt}\right]_{t=t_0} && (14.13) \\
&= \sum_{n=1}^{N} \frac{\partial \hat{\varphi}(\vec{\lambda}(\mathbf{x}_0, t_0))}{\partial \lambda_n} \overset{\square}{\lambda}_n(\mathbf{x}_0, t_0). && (14.14)
\end{aligned}$$

14.2 Commutator and transport identities

Often in what follows it becomes necessary to interchange the differential operators $\partial/\partial s$ and $(\dots)^{\square}$. We now establish the commutator associated with such an interchange. Let φ be an interfacial field. Then, by (14.11),

$$\frac{\partial \overset{\square}{\varphi}}{\partial s} = \frac{\partial}{\partial s}\left(\frac{\partial \varphi}{\partial t} + v \frac{\partial \varphi}{\partial s}\right) = \frac{\partial^2 \varphi}{\partial t \partial s} + v \frac{\partial^2 \varphi}{\partial s^2} + \frac{\partial v}{\partial s}\frac{\partial \varphi}{\partial s},$$

so that, by (14.6), we have the *commutator relation*

$$\frac{\partial \overset{\square}{\varphi}}{\partial s} = \left(\frac{\partial \varphi}{\partial s}\right)^{\square} - KV \frac{\partial \varphi}{\partial s}. \tag{14.15}$$

Also important are the *transport identities*:

$$\left.\begin{aligned}
\overset{\square}{\vartheta} &= \frac{\partial V}{\partial s}, \\
\overset{\square}{K} &= \frac{\partial^2 V}{\partial s^2} + K^2 V, \\
\overset{\square}{\mathbf{t}} &= \overset{\square}{\vartheta}\mathbf{n}, \\
\overset{\square}{\mathbf{n}} &= -\overset{\square}{\vartheta}\mathbf{t}.
\end{aligned}\right\} \tag{14.16}$$

The identities $(14.16)_{3,4}$, follow from (14.1). Next, applying (14.11) with $\varphi = \mathbf{r}$,

$$\overset{\square}{\mathbf{r}} = \frac{\partial \mathbf{r}}{\partial t} + v\mathbf{t}, \tag{14.17}$$

so that, by (14.4) and (14.8),

$$\begin{aligned} \overset{\square}{\mathbf{r}} &= (\mathbf{n} \cdot \overset{\square}{\mathbf{r}})\mathbf{n} = \left(\mathbf{n} \cdot \frac{\partial \mathbf{r}}{\partial t}\right)\mathbf{n} \\ &= V\mathbf{n}. \end{aligned} \tag{14.18}$$

Therefore, by $(14.2)_2$,

$$\mathbf{n} \cdot \frac{\partial \overset{\square}{\mathbf{r}}}{\partial s} = \frac{\partial V}{\partial s}.$$

On the other hand, the commutator relation with $\varphi = \mathbf{r}$ yields

$$\mathbf{n} \cdot \frac{\partial \overset{\square}{\mathbf{r}}}{\partial s} = \mathbf{n} \cdot \overset{\square}{\mathbf{t}} = \overset{\square}{\vartheta}.$$

The last two relations imply $(14.16)_1$. Finally, since $K = \partial\vartheta/\partial s$, the commutator relation with $\varphi = \vartheta$ yields

$$\frac{\partial \overset{\square}{\vartheta}}{\partial s} = \overset{\square}{K} - K^2 V \tag{14.19}$$

and $(14.16)_2$ follows from $(14.16)_1$.

14.3 Evolving subcurves $\mathcal{C}(t)$ of $\mathcal{S}(t)$

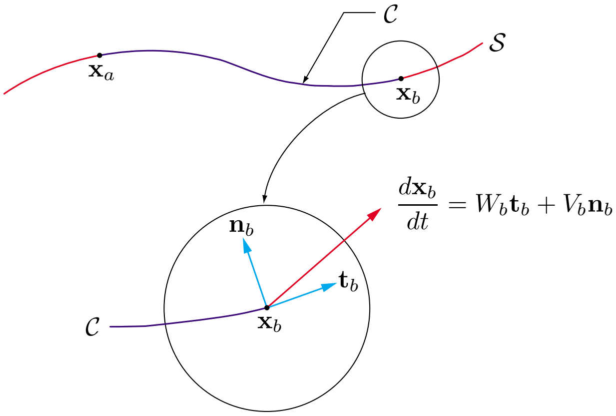

Figure 5: The subcurve $\mathcal{C}$ of $\mathcal{S}$ and the velocity of the endpoint $\mathbf{x}_b$. $W_b(t)$ is the tangential endpoint velocity of $\mathbf{x}_b$.

Throughout, $\mathcal{C}(t)$ denotes an arbitrary evolving subcurve of $\mathcal{S}(t)$. We consistently use the following notation: $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$, respectively, denote the initial and terminal points (in the sense of arc length) of the curve $\mathcal{C}(t)$; for any interfacial field $\varphi(\mathbf{x}, t)$,

$$\varphi_a(t) \equiv \varphi|_a(t) = \varphi(\mathbf{x}_a(t), t), \qquad \varphi_b(t) \equiv \varphi|_b(t) = \varphi(\mathbf{x}_b(t), t). \tag{14.20}$$

The endpoints of $\mathcal{C}(t)$ may also be marked by their arc-length values $S_a(t)$ and $S_b(t)$, where

$$\mathbf{x}_a(t) = \mathbf{r}(S_a(t), t), \qquad \mathbf{x}_b(t) = \mathbf{r}(S_b(t), t), \tag{14.21}$$

so that, using the arc-length description of φ,

$$\varphi_a(t) = \varphi(S_a(t), t), \qquad \varphi_b(t) = \varphi(S_b(t), t); \tag{14.22}$$

hence

$$\varphi\big|_a^b \equiv \varphi_b - \varphi_a = \int\limits_{\mathcal{C}} \frac{\partial\varphi}{\partial s}\, ds.$$

The functions $W_a(t)$ and $W_b(t)$ defined by

$$W_a = \mathbf{t}_a \cdot \frac{d\mathbf{x}_a}{dt}, \qquad W_b = \mathbf{t}_b \cdot \frac{d\mathbf{x}_b}{dt}$$

are the *tangential endpoint velocities* of $\mathcal{C}(t)$. Since the normal velocities of the endpoints must coincide with the normal velocity of $\mathcal{S}(t)$,

$$V_a = \mathbf{n}_a \cdot \frac{d\mathbf{x}_a}{dt}, \qquad V_b = \mathbf{n}_b \cdot \frac{d\mathbf{x}_b}{dt};$$

hence (Figure 5)

$$\frac{d\mathbf{x}_a}{dt} = W_a\mathbf{t}_a + V_a\mathbf{n}_a, \qquad \frac{d\mathbf{x}_b}{dt} = W_b\mathbf{t}_b + V_b\mathbf{n}_b. \tag{14.23}$$

On the other hand, by (14.21),

$$\frac{d\mathbf{x}_a}{dt} = \frac{\partial\mathbf{r}}{\partial t}\bigg|_a + \mathbf{t}_a\frac{dS_a}{dt},$$

so that, by (14.22),

$$\frac{d\mathbf{x}_a}{dt} = \overset{\scriptscriptstyle\square}{\mathbf{r}}\big|_a + \mathbf{t}_a\bigg(\frac{dS_a}{dt} - v_a\bigg), \tag{14.24}$$

and an analogous relation holds for the other endpoint. Thus, since $\mathbf{t}\cdot\overset{\scriptscriptstyle\square}{\mathbf{r}} = 0$,

$$W_a = \frac{dS_a}{dt} - v_a, \qquad W_b = \frac{dS_b}{dt} - v_b. \tag{14.25}$$

Given an interfacial field φ, the argument leading to (14.24) yields

$$\frac{d\varphi_a}{dt} = \overset{\scriptscriptstyle\square}{\varphi}\big|_a + \frac{\partial\varphi}{\partial s}\bigg|_a\bigg(\frac{dS_a}{dt} - v_a\bigg)$$

and similarly for the other endpoint. Therefore, by (14.25),

$$\frac{d\varphi_a}{dt} = \overset{\scriptscriptstyle\square}{\varphi}\big|_a + \frac{\partial\varphi}{\partial s}\bigg|_a W_a, \qquad \frac{d\varphi_b}{dt} = \overset{\scriptscriptstyle\square}{\varphi}\big|_b + \frac{\partial\varphi}{\partial s}\bigg|_b W_b, \tag{14.26}$$

and applying these relations with $\varphi = \vartheta$ yields, since $\partial\vartheta/\partial s = K$,

$$\frac{d\vartheta_a}{dt} = \overset{\scriptscriptstyle\square}{\vartheta}\big|_a + K_aW_a, \qquad \frac{d\vartheta_b}{dt} = \overset{\scriptscriptstyle\square}{\vartheta}\big|_b + K_bW_b. \tag{14.27}$$

14.4 Transport theorem for integrals

Let φ be an interfacial field. Then

$$\int\limits_{\mathcal{C}(t)} \varphi\, ds = \int\limits_{S_1(t)}^{S_2(t)} \varphi(s,t)\, ds.$$

Thus, writing

$$\big[\varphi S\big]_a^b = \varphi_b S_b - \varphi_a S_a \tag{14.28}$$

and suppressing the argument t where convenient, we may use (14.11) to conclude that

$$\frac{d}{dt}\int\limits_{\mathcal{C}(t)} \varphi\, ds = \int\limits_{\mathcal{C}} \frac{\partial \varphi}{\partial t}\, ds + \big[\varphi \dot{S}\big]_a^b = \int\limits_{\mathcal{C}} \left(\overset{\square}{\varphi} - v\frac{\partial \varphi}{\partial s}\right) ds + \big[\varphi \dot{S}\big]_a^b.$$

Thus if we integrate the term $v\,\partial\varphi/\partial s$ by parts and use (14.6) and (14.25), we arrive at the following theorem (Angenent and Gurtin, 1989):

> Transport Theorem for Integrals For $\mathcal{C}(t)$ a smoothly evolving subcurve of $\mathcal{S}(t)$ and $\varphi(\mathbf{x},t)$ a smooth interfacial field,
>
> $$\frac{d}{dt}\int\limits_{\mathcal{C}(t)} \varphi\, ds = \int\limits_{\mathcal{C}(t)} (\overset{\square}{\varphi} - \varphi K V)\, ds + \big[\varphi W\big]_a^b, \tag{14.29}$$
>
> with
>
> $$\big[\varphi W\big]_a^b = \varphi_b W_b - \varphi_a W_a. \tag{14.30}$$

Notation analogous to (14.30) (for endpoint differences) *will be used repeatedly throughout what follows.*

15 Deformation of the interface

We now turn to a discussion of deformation. We consider both solid-solid and solid-vapor phase transitions; in the former case we restrict attention to coherent interfaces.

15.1 Interfacial limits

We assume that the interface $\mathcal{S}(t)$ separates phases labelled (+) and (−), with the normal $\mathbf{n}$ pointing into the (+)-phase. When discussing solid-vapor interfaces, the (+)-phase always denotes the *vapor*.

Consider an arbitrary field $f(\mathbf{x},t)$ that is continuous up to $\mathcal{S}(t)$ from either side. Let $[\![f]\!]$ and $\langle\!\langle f\rangle\!\rangle$ designate the *jump* and *average* of f across the interface, while $f^{\pm}$ denote the limiting values of f; specifically, for $\mathbf{x}$ on $\mathcal{S}(t)$,

$$\left.\begin{aligned} [\![f]\!](\mathbf{x},t) &= f^{+}(\mathbf{x},t) - f^{-}(\mathbf{x},t), \\ \langle\!\langle f\rangle\!\rangle(\mathbf{x},t) &= \tfrac{1}{2}\big(f^{+}(\mathbf{x},t) + f^{-}(\mathbf{x},t)\big), \\ f^{\pm}(\mathbf{x},t) &= \lim_{\substack{\varepsilon\to 0\\ \varepsilon>0}} f(\mathbf{x}\pm\varepsilon\mathbf{n}(\mathbf{x},t),t). \end{aligned}\right\rbrace \tag{15.1}$$

Our discussion of solid-vapor interfaces is limited to situations in which the vapor may, in essence, be represented by the limiting values of its basic fields at the interface; bulk values of these fields away from the interface play no role. In this instance, the field f^+ simply represents the value of f in the vapor at the interface.

15.2 Interfacial-strain vector

(a) Solid-vapor interface

We assume that the *displacement* $\mathbf{u}(\mathbf{x}, t)$ is smooth up to the interface from the solid phase, so that the *interfacial strain*

$$\mathbf{e} = \frac{\partial \mathbf{u}}{\partial s} = (\nabla \mathbf{u})\mathbf{t} \tag{15.2}$$

is well defined on $\mathcal{S}$, as is the temporal derivative

$$\overset{\square}{\mathbf{u}} = \dot{\mathbf{u}} + (\nabla \mathbf{u})\mathbf{v}. \tag{15.3}$$

(b) Coherent solid-solid interface

In our discussion of solid-solid phase transitions we restrict attention to interfaces $\mathcal{S}$ that are *coherent* in the sense that $\mathbf{u}$ is continuous across the interface:[35]

$$[\![\mathbf{u}]\!] = \mathbf{0}. \tag{15.4}$$

We do not require that the derivatives of $\mathbf{u}$ be continuous across the interface, but we do require that all such derivatives be continuous up to the interface from either side, an assumption that allows us to compute the *interfacial strain*

$$\mathbf{e} = \frac{\partial \mathbf{u}}{\partial s} \tag{15.5}$$

using the limiting values of $\nabla \mathbf{u}$ on each side of the interface:

$$\mathbf{e} = (\nabla \mathbf{u})^+ \mathbf{t} = (\nabla \mathbf{u})^- \mathbf{t} = \langle\!\langle \nabla \mathbf{u} \rangle\!\rangle \mathbf{t}. \tag{15.6}$$

Similarly, for $\mathbf{x} = \mathbf{r}_{\mathrm{n}}(p, t)$ a normal parametrization of $\mathcal{S}(t)$,[36] we may use (14.10) and the chain-rule to compute $\overset{\square}{\mathbf{u}}$ as follows:

$$\overset{\square}{\mathbf{u}} = \dot{\mathbf{u}}^+ + (\nabla \mathbf{u})^+ \mathbf{v} = \dot{\mathbf{u}}^- + (\nabla \mathbf{u})^- \mathbf{v} = \langle\!\langle \dot{\mathbf{u}} \rangle\!\rangle + \langle\!\langle \nabla \mathbf{u} \rangle\!\rangle \mathbf{v}; \tag{15.7}$$

this yields the classical *compatibility condition*

$$[\![\dot{\mathbf{u}}]\!] + V [\![\nabla \mathbf{u}]\!] \mathbf{n} = \mathbf{0}. \tag{15.8}$$

(c) Identities involving the interfacial strain

It is convenient to introduce the *interfacial tensile and shear strains*, ε and γ, defined by

$$\mathbf{e} = \varepsilon \mathbf{t} + \gamma \mathbf{n}. \tag{15.9}$$

Then

$$\varepsilon = \mathbf{t} \cdot \frac{\partial \mathbf{u}}{\partial s}, \qquad \gamma = \mathbf{n} \cdot \frac{\partial \mathbf{u}}{\partial s}, \tag{15.10}$$

---

[35] Cf. Cermelli & Gurtin (1994a, b) for discussions of incoherent interfaces.

[36] That is, $\partial \mathbf{r}_{\mathrm{n}}/\partial t = V\mathbf{n} = \mathbf{v}$, with $\partial/\partial t$ the derivative holding p fixed.

so that, using the Frenet formulas (14.2),

$$\frac{\partial \varepsilon}{\partial s} = \mathbf{t}\cdot\frac{\partial^2 \mathbf{u}}{\partial s^2} + \Big(\mathbf{n}\cdot\frac{\partial \mathbf{u}}{\partial s}\Big)K, \qquad \frac{\partial \gamma}{\partial s} = \mathbf{n}\cdot\frac{\partial^2 \mathbf{u}}{\partial s^2} - \Big(\mathbf{t}\cdot\frac{\partial \mathbf{u}}{\partial s}\Big)K. \tag{15.11}$$

Next, the fields $\mathbf{u}$, $\overset{\square}{\mathbf{u}}$, and $\mathbf{e} = \partial\mathbf{u}/\partial s$ are, for each of the two types of phase transitions under consideration, well defined on the interface. We may therefore use the commutator relation (14.15) to conclude that

$$\frac{\partial \overset{\square}{\mathbf{u}}}{\partial s} = \overset{\square}{\mathbf{e}} - KV\mathbf{e}. \tag{15.12}$$

Let

$$\mathbf{e} = \varepsilon\mathbf{t} + \gamma\mathbf{n}; \tag{15.13}$$

ε and γ, respectively, represent *interfacial tensile and shear strains.* Then, by $(14.16)_{3,4}$, the *interfacial strain-rate* (following the motion of the interface) is given by

$$\overset{\square}{\mathbf{e}} = (\overset{\square}{\varepsilon} - \gamma\overset{\square}{\vartheta})\mathbf{t} + (\overset{\square}{\gamma} + \varepsilon\overset{\square}{\vartheta})\mathbf{n}. \tag{15.14}$$

Thus, interestingly, while the strain ε represents stretching of the interface, the *stretch rate*, as defined by $\mathbf{t}\cdot\overset{\square}{\mathbf{e}}$, is given by

$$\mathbf{t}\cdot\overset{\square}{\mathbf{e}} = \overset{\square}{\varepsilon} - \gamma\overset{\square}{\vartheta} \tag{15.15}$$

and hence involves the shear strain γ via a term arising from temporal changes in the orientation of the interface.

Let $\mathcal{C}(t)$, with endpoints $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$, be an arbitrary evolving subcurve of $\mathcal{S}(t)$, and let

$$\mathbf{u}_a(t) = \mathbf{u}(\mathbf{x}_a(t), t) \qquad \text{and} \qquad \mathbf{u}_b(t) = \mathbf{u}(\mathbf{x}_b(t), t)$$

denote the corresponding endpoint displacements (see Figure 5), so that

$$\frac{d\mathbf{u}_a}{dt} \qquad \text{and} \qquad \frac{d\mathbf{u}_b}{dt} \tag{15.16}$$

represent *motion velocities following these endpoints.* Then, by the vectorial counterpart of (14.26),

$$\frac{d\mathbf{u}_a}{dt} = \overset{\square}{\mathbf{u}}\big|_a + \mathbf{e}_a W_a, \qquad \frac{d\mathbf{u}_b}{dt} = \overset{\square}{\mathbf{u}}\big|_b + \mathbf{e}_b W_b. \tag{15.17}$$

$\big($These relations may also be derived using the chain-rule and, say (C4):

$$\frac{d\mathbf{u}_a}{dt} = (\dot{\mathbf{u}})_a + (\nabla\mathbf{u})_a\frac{d\mathbf{x}_a}{dt} = (\dot{\mathbf{u}})_a + (\nabla\mathbf{u})_a(W_a\mathbf{t}_a + V_a\mathbf{n}_a) = \overset{\square}{\mathbf{u}}\big|_a + \mathbf{e}_a W_a, \quad \text{etc.}\big)$$

16 Interfacial pillboxes

We will discuss interfaces separating grains, solid phases, and solid and vapor phases. For the purpose of this discussion, assume that the interface $\mathcal{S}(t)$ separates phases labelled $(+)$ and $(-)$, with the normal $\mathbf{n}$ pointing into the $(+)$-phase. Our discussion of configurational forces in bulk was based on the use of control volumes that migrate through the body. The counterpart of this notion for the interface $\mathcal{S} = \mathcal{S}(t)$ is an interfacial pillbox, which we now define.

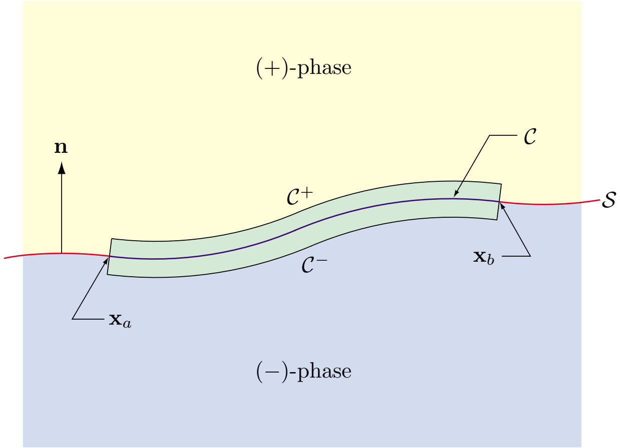

Figure 6: An interfacial pillbox separating (+) and (−) phases.

Consider an *arbitrary* evolving subcurve $\mathcal{C}(t)$ of $\mathcal{S}(t)$. Our discusion of basic laws views $\mathcal{C}$ as a *interfacial pillbox* of infinitesimal thickness containing a portion of $\mathcal{S}$, a view that allows us to isolate the physical processes in the individual phases that interact with $\mathcal{S}$. The geometric boundary of $\mathcal{C}$ consists of its endpoints $\mathbf{x}_a$ and $\mathbf{x}_b$. But $\mathcal{C}$ viewed as pillbox has a *pillbox boundary* consisting of (Figure 6):

- a surface $\mathcal{C}^+$ with unit normal $+\mathbf{n}$ that lies in the (+)-phase;
- a surface $\mathcal{C}^-$ with unit normal $-\mathbf{n}$ that lies in the (−)-phase;
- end faces represented by the endpoints $\mathbf{x}_a$ and $\mathbf{x}_b$ of $\mathcal{C}$.

The interaction of $\mathcal{C}$ with the bulk phases are then represented by tractions exerted on — and flows of atoms and energy across — the surfaces $\mathcal{C}^+$ and $\mathcal{C}^-$; the interaction of $\mathcal{C}$ with the remainder of $\mathcal{S}$ is represented by forces on — and flows of atoms and energy across — the endpoints of $\mathcal{C}$.

D GRAIN BOUNDARIES

We here consider a class of theories central to materials science. *These theories involve only configurational forces; deformation and standard forces are neglected.*[37]

17 Simple theory neglecting deformation and atomic transport

We here discuss an evolving grain boundary $\mathcal{S} = \mathcal{S}(t)$ neglecting deformation and atomic transport.[38]

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[37] Some workers who utilize the notion of configurational forces do not accept the notion of an independent configurational force balance, but consider the standard and configurational force balances to be "projections of a single equation onto two manifolds". The theories discussed in this part show that the configurational balance cannot, in general, be considered as a "projection" of the standard force balance, since in these theories *there are no standard forces; there are only configurational forces.*

[38] The results of this section are due to Angenent and Gurtin (1989); cf. also Gurtin (1993, 2000).

17.1 Configurational force balance

The configurational force system for the grain boundary consists of an *interfacial stress* (vector) $\mathbf{c}$, an *internal force density* $\mathbf{g}$, distributed continuously over $\mathcal{S}$, and contributions associated with the interaction of the bulk phases with the grain boundary (Figure 7). The stress $\mathbf{c}$ characterizes forces such as surface tension that act within $\mathcal{S}$; $\mathbf{g}$ represents internal forces associated with the exchange of atoms between grains at $\mathcal{S}$. Let $\mathcal{C} = \mathcal{C}(t)$ be an arbitrary interfacial pillbox. The portion of $\mathcal{S}$ external to $\mathcal{C}$ then exerts tractions $-\mathbf{c}_a$ and $\mathbf{c}_b$ at $\mathbf{x}_a$ and $\mathbf{x}_b$.[39] Further, the bulk material in the (+)-phase exerts a configurational traction $\mathbf{C}^+\mathbf{n}$ on $\mathcal{C}^+$, while that in the (−)-phase exerts a configurational traction $-\mathbf{C}^-\mathbf{n}$ on $\mathcal{C}^-$, so that the net configurational traction exerted at each point of $\mathcal{C}$ by the bulk phases is $\mathbf{C}^+\mathbf{n} - \mathbf{C}^-\mathbf{n} = [\![\mathbf{C}]\!]\mathbf{n}$. The *configurational force balance* for $\mathcal{C}$ therefore takes the form[40]

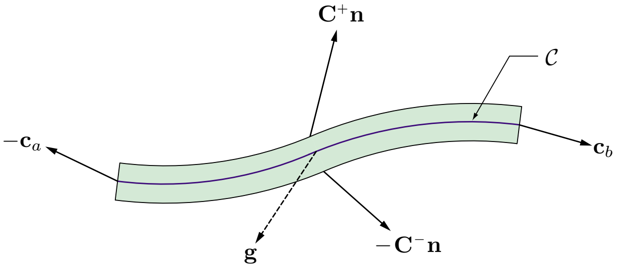

Figure 7: Configurational forces on an interfacial pillbox $\mathcal{C}$.

$$\mathbf{c}\Big|_a^b + \int_{\mathcal{C}} \mathbf{g}\,ds + \int_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\,ds = \mathbf{0}, \qquad \mathbf{c}\Big|_a^b = \mathbf{c}_b - \mathbf{c}_a, \tag{17.1}$$

and has the immediate consequence that

$$\mathbf{c} \;\text{ must be a continuous function of arc length.} \tag{17.2}$$

Further, since $\mathbf{c}_b - \mathbf{c}_a = \int_{\mathcal{C}} \partial\mathbf{c}/\partial s\,ds$, (17.1) yields the local balance

$$\frac{\partial \mathbf{c}}{\partial s} + \mathbf{g} + [\![\mathbf{C}]\!]\mathbf{n} = \mathbf{0}. \tag{17.3}$$

We define the *configurational surface tension* σ and *shear stress* τ through the decomposition

$$\mathbf{c} = \sigma\mathbf{t} + \tau\mathbf{n}. \tag{17.4}$$

Then, appealing to the Frenet formulas $\partial\mathbf{t}/\partial s = K\mathbf{n}$ and $\partial\mathbf{n}/\partial s = -K\mathbf{t}$,

$$\frac{\partial \mathbf{c}}{\partial s} = \left(\frac{\partial \sigma}{\partial s} - \tau K\right)\mathbf{t} + \left(\frac{\partial \tau}{\partial s} + \sigma K\right)\mathbf{n}, \tag{17.5}$$

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[39] I.e., e.g., $\mathbf{c}_a(t) = \mathbf{c}(\mathbf{x}_a, t)$.

[40] The balance (17.1) is an *interfacial* counterpart of the *bulk* configurational force-balance (11.1) for a part $\mathcal{P}$. The role of the net traction $\int_{\partial\mathcal{P}} \mathbf{C}\boldsymbol{\nu}\,da$ in (11.1) is played by $\mathbf{c}|_a^b + \int_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\,ds$, while that of the net internal force $\int_{\mathcal{P}} \mathbf{f}\,da$ is played by $\int_{\mathcal{C}} \mathbf{g}\,ds$.

whereby the normal component of (17.3), the *normal configurational force balance*, is given by

$$\sigma K + \frac{\partial \tau}{\partial s} + g + \mathbf{n} \cdot [\![\mathbf{C}]\!]\mathbf{n} = 0, \tag{17.6}$$

with

$$g = \mathbf{g} \cdot \mathbf{n} \tag{17.7}$$

the *normal internal force*. On the other hand, we shall find that $\mathbf{g} \cdot \mathbf{t}$ is *indeterminate*, thereby rendering the tangential component of (17.3), namely

$$\frac{\partial \sigma}{\partial s} - \tau K + \mathbf{g} \cdot \mathbf{t} + \mathbf{t} \cdot [\![\mathbf{C}]\!]\mathbf{n} = 0, \tag{17.8}$$

inconconsequential to the theory (cf. the discussion following (17.31)).

The bulk configurational stress $\mathbf{C}$ is determined by the Eshelby relation (12.15), which, since we neglect deformation and atomic transport, has the form $\mathbf{C} = \Psi\mathbf{1}$, with Ψ the bulk free energy; thus

$$[\![\mathbf{C}]\!] = [\![\Psi]\!]\mathbf{1}, \tag{17.9}$$

which we assume to be *constant.* The normal and tangential components of the configurational force balance therefore reduce to

$$\sigma K + \frac{\partial \tau}{\partial s} + g + [\![\Psi]\!] = 0 \tag{17.10}$$

and

$$\frac{\partial \sigma}{\partial s} - \tau K + \mathbf{g} \cdot \mathbf{t} = 0. \tag{17.11}$$

17.2 Power

(a) External expenditure of power

The configurational forces on an interfacial pillbox $\mathcal{C}$ are assumed to expend power in conjunction with the migration of the pillbox. The stress $\mathbf{c}$ exerts force at the endpoints $\mathbf{x}_a$ and $\mathbf{x}_b$ of $\mathcal{C}$, and we therefore take $d\mathbf{x}_a/dt$ and $d\mathbf{x}_b/dt$ as the corresponding power-conjugate velocities for $\mathbf{c}$. Analogously, the configurational tractions $\mathbf{C}^{+}\mathbf{n}$ and $-\mathbf{C}^{-}\mathbf{n}$ represent forces exerted on $\mathcal{C}^{+}$ and $\mathcal{C}^{-}$ and are therefore taken to be power-conjugate to the normal velocity $\mathbf{v} = V\mathbf{n}$ of $\mathcal{C}^{+}$ and $\mathcal{C}^{-}$. The (net) *power expended* on $\mathcal{C}$ therefore has the form

$$\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n} \cdot \mathbf{v}\, ds, \tag{17.12}$$

with

$$\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b = \mathbf{c}_b \cdot \frac{d\mathbf{x}_b}{dt} - \mathbf{c}_a \cdot \frac{d\mathbf{x}_a}{dt}.$$

(b) Internal expenditure of power. Power balance

By (14.23) and (17.4),

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b = \big[\sigma W + \tau V\big]_a^b, \tag{17.13}$$

while, by (14.5) and (17.9), $[\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v} = [\![\Psi]\!]V$; hence, the power expended on $\mathcal{C}$ has the form

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds = \big[\sigma W + \tau V\big]_a^b + \int\limits_{\mathcal{C}} [\![\Psi]\!]V\,ds. \tag{17.14}$$

Consider the term $\big[\tau V\big]_a^b$. Using the identity $\partial V/\partial s = \vartheta^{\square}$ (cf. $(14.16)_1$) and the normal configurational force balance (17.10), it follows that

$$\big[\tau V\big]_a^b = \int\limits_{\mathcal{C}} \Big(\tau\overset{\square}{\vartheta} + \frac{\partial\tau}{\partial s}V\Big)\,ds = \int\limits_{\mathcal{C}} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g + F)V\big]\,ds. \tag{17.15}$$

Combining (17.15) with (17.14) then yields the *power balance*

$$\underbrace{\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds}_{\text{power expended on }\mathcal{C}} = \underbrace{\big[\sigma W\big]_a^b + \int\limits_{\mathcal{C}} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g)V\big)\big]\,ds}_{\text{power expended within }\mathcal{C}}\,. \tag{17.16}$$

The individual terms comprising the internal power have the following physical interpretations (Figure 8):[41]

- The term $\big[\sigma W\big]_a^b$ represents power expended internally by the surface tension as material is added to $\mathcal{C}$ at its endpoints.
- The term $\tau\overset{\square}{\vartheta}$ represents an expenditure of power associated with changes in the orientation of the grain boundary.
- The term $-\sigma K V$ represents an expenditure of power associated with changes in interfacial length due to the curvature of the grain boundary.
- The term $-gV$ represents power expended in the exchange of material at the grain boundary; the negative sign signifies that g expends (positive) power when and only when it opposes motion of the grain boundary.

17.3 Free-energy imbalance

(a) Global imbalance

Guided by the arguments given in §12.4 in support of the free-energy imbalance (12.17) for a migrating control volume in *bulk*, and bearing in mind that the present theory

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[41] Gurtin (2000, pp. 71, 105). A complete catalog of internal power expenditures is possible only with the introduction of configurational forces within a structure that embodies the notion of *power.* Because they bypass such fundamental notions, ad hoc methods such as gradient-flow arguments obscure the underlying physics.

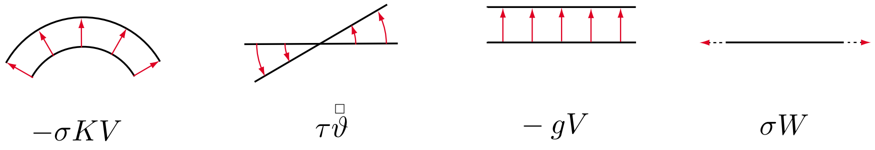

Figure 8: Power expenditures within an evolving grain boundary

does not allow for atomic transport, we posit a free-energy imbalance for each interfacial pillbox $\mathcal{C}(t)$ in the general form

$$\frac{d}{dt}\{\text{free energy of } \mathcal{C}(t)\} \le \{\text{power expended on } \mathcal{C}(t)\}. \tag{17.17}$$

As in our treatment of power expended on a migrating control volume, the right side does not account for flows of bulk and interfacial free-energy into the pillbox $\mathcal{C}(t)$ across its boundaries due to its migration, *but it is meant to include power expended on $\mathcal{C}(t)$ by configurational forces.*

Let ψ denote the *free energy* of the grain boundary, measured per unit length, so that

$$\int\limits_{\mathcal{C}(t)} \psi(\mathbf{x}, t)\, ds$$

represents the net free-energy of the interfacial pillbox $\mathcal{C}(t)$ at any time t. Thus, bearing in mind the expression (17.12) for the power expended by the configurational forces, we write the *free-energy imbalance* for $\mathcal{C}$ in the form

$$\frac{d}{dt}\int\limits_{\mathcal{C}} \psi\, ds \le \left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\, ds. \tag{17.18}$$

(b) Growth and decay of an isolated grain

The global free-energy imbalance has interesting consequences. Consider a grain isolated from all other grains, with $\mathcal{S}$ the closed curve that represents the grain boundary. Identify the grain with the $(-)$-phase, so that the normal $\mathbf{n}$ points into the surrounding matrix (Figure 9). Then, since $[\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v} = [\![\Psi]\!]V$ and $[\![\Psi]\!]$ is (assumed) constant,

$$\int\limits_{\mathcal{S}(t)} [\![\Psi]\!]V\, ds = [\![\Psi]\!]\dot{\mathcal{A}}(t),$$

where $\mathcal{A}(t)$ is the area enclosed by $\mathcal{S}(t)$ (that is, the area of the grain). Therefore

$$\frac{d}{dt}\left\{\int\limits_{\mathcal{S}(t)} \psi\, ds - [\![\Psi]\!]\mathcal{A}(t)\right\} \le 0, \tag{17.19}$$

and the quantity in braces decreases with time. If, for example, the bulk free energy of the matrix is strictly larger than that of the grain, then $[\![\Psi]\!]d\mathcal{A}/dt > 0$, so that, were interfacial energy neglegible, the area of the grain would increase with time, thereby lowering the net free energy of the bulk material. On the other hand, assuming that $\psi > 0$, for $[\![\Psi]\!]d\mathcal{A}/dt \le 0$ the area of the grain would decrease with time.

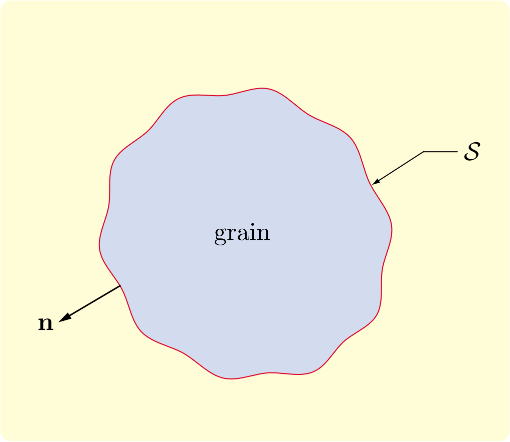

Figure 9: Depiction of an isolated grain.

If the grain and the surrounding matrix have equal free-energy densities, so that $[\![\Psi]\!] = 0$, then the total free-energy of the grain boundary must decrease with time. If, in addition, the grain-boundary energy $\psi > 0$ is constant, then

$$\frac{d}{dt}\big\{\text{length of } \mathcal{S}(t)\big\} \le 0$$

and the grain boundary must shorten with time.

(c) Indeterminacy of the tangential component of the internal force g

Note that there is no expenditure of power associated with "tangential motion" of the grain boundary $\mathcal{S}$ (which is to be expected, since only the normal motion of $\mathcal{S}$ is intrinsic). Consistent with a "constraint" of this type, we leave as *indeterminate* the tangential component $\mathbf{g}\cdot\mathbf{t}$ of the internal force. This assumption renders the tangential balance (17.8) irrelevant and allows us to restrict attention to the normal configurational force balance (17.10). This will be the case throughout what follows; for that reason, we will often leave the tangential configurational force balance unmentioned (cf. Remark 6 on page 6).

(d) Equality of surface tension and interfacial free energy

In view of the transport theorem (14.29) and the power balance (17.16), the free-energy imbalance for $\mathcal{C}$, namely (17.18), becomes

$$\int_{\mathcal{C}} (\overset{\square}{\psi} - \psi K V)\, ds + \overbrace{\big[(\psi - \sigma)W\big]_a^b}^{(\#)} \le \int_{\mathcal{C}} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g)V\big]\, ds. \tag{17.20}$$

Since $\mathcal{C}$ is arbitrary, so also are the tangential velocities W_a and W_b of the endpoints of $\mathcal{C}$; since the only term in (17.20) dependent on these velocities is the term (#), it follows that

$$\sigma = \psi. \tag{17.21}$$

There are many misconceptions concerning the relation between surface tension and interfacial free energy. Here surface tension enters the theory via a force balance, whereas free-energy enters via an energy imbalance; the fact that they coalesce is a consequence of the theory. *As we shall see, in more general theories allowing for interfacial torques, standard interfacial stress, or atomic transport accounting for atomic densities within the interface, the relation $\sigma = \psi$ is no longer valid.*

Note that, by (17.21), we may rewrite the normal configurational force balance (17.10) as

$$\psi K + \frac{\partial \tau}{\partial s} + g + [\![\Psi]\!] = 0. \tag{17.22}$$

(e) Dissipation inequality

By (17.21), the free-energy inequality (17.20) reduces to

$$\int\limits_{\mathcal{C}} (\overset{\square}{\psi} - \tau \overset{\square}{\vartheta} + gV)\, ds \le 0;$$

since $\mathcal{C}$ is arbitrary, we have the *dissipation inequality*

$$\overset{\square}{\psi} - \tau \overset{\square}{\vartheta} + gV \le 0. \tag{17.23}$$

17.4 Constitutive equations

As in our discussion of bulk behavior, we use the dissipation inequality (17.23) as a guide in the development of constitutive equations for the grain boundary. Moreover, we require that the local dissipation inequality hold in all "processes" related through the constitutive equations.

(a) Basic constitutive equations. Restrictions.

It would seem clear from the dissipation inequality (17.23) that, at bottom:

- ψ and τ should depend on ϑ, an assumption common to more classical theories (cf., e.g., Herring (1951));
- g should depend on V and, since classical theories display linear kinetics (cf., e.g., Mullins (1956)), this dependence might be linear; anisotropy would require a dependence of g also on ϑ.

We therefore begin with constitutive equations

$$\left.\begin{aligned} \psi &= \hat{\psi}(\vartheta), \\ \tau &= \hat{\tau}(\vartheta), \\ g &= -b(\vartheta)V. \end{aligned}\right\} \tag{17.24}$$

Here $b(\vartheta)$ is a *kinetic modulus* associated with the attachment kinetics of atoms at the grain boundary.

By the chain rule (14.12),

$$\overset{\square}{\psi} = \frac{d\hat{\psi}(\vartheta)}{d\vartheta} \overset{\square}{\vartheta}, \tag{17.25}$$

and since the constitutive relations (17.24) are independent of V, we may conclude, upon taking $V = 0$ in the dissipation inequality (17.23), that $\psi^{\square} - \tau\vartheta^{\square} \leq 0$. Thus compatibility with (17.23) requires that

$$\left\{ \frac{d\hat{\psi}(\vartheta)}{d\vartheta} - \hat{\tau}(\vartheta) \right\} \overset{\square}{\vartheta} \leq 0 \tag{17.26}$$

for all choices of the orientation field ϑ. We may therefore restrict attention to spatially uniform functions $\vartheta(t)$, so that $\vartheta^{\square} = \dot{\vartheta}$. Given any choice of the time t_0, we can always find a choice of $\vartheta(t)$ such that $\vartheta(t_0)$ and $\dot{\vartheta}(t_0)$ take on arbitrarily prescribed values. Thus, since $\vartheta^{\square}$ appears linearly in (17.26), its coefficient must vanish: $\hat{\tau} = \partial\hat{\psi}/\partial\vartheta$. The free energy must therefore determine the configurational shear through the relation

$$\tau = \frac{d\hat{\psi}(\vartheta)}{d\vartheta}. \tag{17.27}$$

Finally, by (17.27), the dissipation inequality reduces to $gV \leq 0$, which renders

$$b(\vartheta) \geq 0. \tag{17.28}$$

(b) Remarks

1. Anisotropy of the interface manifests itself in a nontrivial dependence of $\hat{\psi}(\vartheta)$ on ϑ. An interesting and important consequence of (17.27) is that, *for a grain boundary with anisotropic free energy, the surface shear cannot vanish.*[42]

2. By (17.4), (17.21), and (17.27), we may consider the configurational stress $\mathbf{c}$ as a function $\mathbf{c} = \mathbf{c}(\vartheta)$, with

$$\mathbf{c}(\vartheta) = \hat{\psi}(\vartheta)\mathbf{t}(\vartheta) + \frac{d\hat{\psi}(\vartheta)}{d\vartheta}\mathbf{n}(\vartheta). \tag{17.29}$$

3. The normal internal force g is a *dissipative force associated with the rearrangement of atoms at the grain boundary.* The term

$$\mathcal{D} \overset{\text{def}}{=} -gV = b(\vartheta)V^2$$

represents the *dissipation* per unit length of the interface, as its integral over $\mathcal{C}$ represents the right side of the free-energy imbalance (17.17) (the expended power) minus its left side (the net rate of change of free-energy); this dissipation is characterized by the kinetic modulus $b(\vartheta)$.

4. Were we to begin with constitutive relations of the form

$$\left.\begin{aligned} \psi &= \hat{\psi}(\vartheta, V), \\ \tau &= \hat{\tau}(\vartheta, V), \\ g &= \hat{g}(\vartheta, V), \end{aligned}\right\} \tag{17.30}$$

thereby satisfying equipresence, the dissipation inequality would render ψ and τ independent of V and consistent with (17.27), and would yield the reduced dissipation inequality $\hat{g}(\vartheta, V) \leq 0$; then, as in the discussion leading to $(17.24)_3$, linearity of $g = \hat{g}(\vartheta, V)$ in V would require an additional hypothesis.

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[42] Cf. Angenent and Gurtin (1989, eqt. 4.2), although this result is clear from the work of Herring (1951) in his discussion of the equilibrium theory within a variational framework.

5. More general constitutive equations are also possible. For example, a constitutive relation of the form

$$\tau = \frac{d\hat{\psi}(\vartheta)}{d\vartheta} - C(\vartheta)\overset{\square}{\vartheta}, \qquad C(\vartheta) > 0$$

   would be consisitent with the dissipation inequality.

6. Since, by (17.21) and (17.27), $\sigma = \psi$ and $\tau = \psi'(\vartheta)$,

$$\frac{\partial \sigma}{\partial s} = \tau \frac{\partial \vartheta}{\partial s} = \tau K,$$

   and we may conclude from the tangential configurational balance (17.8) that

$$\mathbf{g} \cdot \mathbf{t} = 0. \tag{17.31}$$

   Thus the tangential component of the internal force $\mathbf{g}$ vanishes. This result is a consequence of the special theory under consideration; as we shall see, for theories that account for the density of atoms within the interface the tangential force $\mathbf{g} \cdot \mathbf{t}$ is needed to balance spatial inhomogeneities on the interface induced by variations in chemical potential (cf. (13.4) and the discussion following (17.8)). For the theories discussed in §18 and §19, which account, respectively, for configurational torques and the diffusion of a single atomic species, it is also the case that $\mathbf{g} \cdot \mathbf{t} = 0$.

17.5 Evolution equation for the grain boundary. Parabolicity and backward parabolicity

We now return to our discussion of grain boundaries as described by the constitutive equations

$$\tau = \frac{d\hat{\psi}(\vartheta)}{d\vartheta}, \qquad g = -b(\vartheta)V,$$

assuming that $b(\vartheta) > 0$.

For any function $f(\vartheta)$ we write

$$f'(\vartheta) = \frac{df(\vartheta)}{d\vartheta},$$

and, when there is no danger of confusion, we write

$$\psi(\vartheta) = \hat{\psi}(\vartheta).$$

Then, since $K = \partial\vartheta/\partial s$, (17.27) yields $\partial\tau/\partial s = \psi''(\vartheta)K$; thus, by $(17.24)_3$, the normal configurational force balance reduces to the *curvature-flow equation*[43]

$$b(\vartheta)V = \big[\psi(\vartheta) + \psi''(\vartheta)\big]K + [\![\Psi]\!]. \tag{17.32}$$

Note that the larger the dissipation, as characterized by the modulus $b(\vartheta)$, the slower the motion of the interface.

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[43] Proposed by Uwaha (1987, eqt. 2) and independently by Gurtin (1988, eqt. 8.3). Cf. also Angenent and Gurtin (1989). Evolution according to (17.32) is studied by Angenent (1991), Chen, Giga, and Goto (1991), Barles, Soner, and Souganides (1993), and Soner (1993). A formulation of (17.32) using a variational definition of the curvature term is given by Taylor, Cahn, and Handwerker (1992), who give extensive references. The term $\psi(\vartheta) + \psi''(\vartheta)$ appears first in the study of Herring (1951), who shows that it represents the variational derivative of the net interfacial free-energy with respect to variations in the position of the interface.

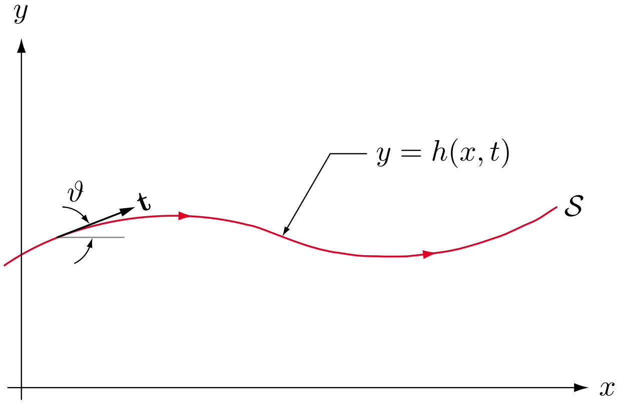

Figure 10: Sign conventions when the interface is a graph $y = h(x,t)$.

For an isotropic grain boundary both b and ψ are positive constants. Then, for $[\![\Psi]\!] = 0$ and, with an appropriate rescaling of space and time, (17.32) has the simple (and beautiful) form

$$V = K,$$

a parabolic partial differential equation with a large literature.[44] This equation, which was the forerunner of (17.32), was introduced by Burke and Turnbull (1952) and Mullins (1956) to study the motion of grain boundaries.

Locally the interface may be represented as the graph of a function $y = h(x,t)$, provided the x and y axes are chosen appropriately. Consider the choice indicated in Figure 10 (with orientation such that arc length increases with increasing x) and let

$$q = \frac{\partial h}{\partial x}.$$

Then, for $-\frac{\pi}{2} < \vartheta < \frac{\pi}{2}$,

$$q = \tan\vartheta, \qquad K = \frac{1}{(1+q^2)^{\frac{3}{2}}}\frac{\partial^2 h}{\partial x^2}, \qquad V = \frac{1}{\sqrt{1+q^2}}\frac{\partial h}{\partial t}, \tag{17.33}$$

and, assuming that $b(\vartheta) > 0$ for all such ϑ, we may use these relations to rewrite the evolution equation (17.32) in the form

$$\frac{\partial h}{\partial t} = A(q)\frac{\partial^2 h}{\partial x^2} + P(q), \tag{17.34}$$

with

$$A(q) = \frac{\psi(\vartheta) + \psi''(\vartheta)}{b(\vartheta)\cos\vartheta\,(1+\tan^2\vartheta)^{\frac{3}{2}}},$$

$$P(q) = \frac{F}{b(\vartheta)\cos\vartheta}, \qquad q = \tan\vartheta.$$

For the angle range $-\frac{\pi}{2} < \vartheta < \frac{\pi}{2}$ under consideration, $\operatorname{sgn} A(q) = \operatorname{sgn}\big[\psi(\vartheta) + \psi''(\vartheta)\big]$. Thus the evolution equation ((17.34) and hence) (17.32) is:[45]

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[44] Cf. Gurtin (2000) for references.

[45] Angenent and Gurtin (1989).

(i) *parabolic* on any angle interval over which $\psi(\vartheta) + \psi''(\vartheta) > 0$;

(ii) *backward parabolic* (and hence unstable as a partial differential equation) on any angle interval over which $\psi(\vartheta) + \psi''(\vartheta) < 0$.

Let

$$\phi(\vartheta) \overset{\text{def}}{=} \psi(\vartheta) + \psi''(\vartheta). \tag{17.35}$$

Materials scientists often refer to $\phi(\vartheta)$ as the *interfacial stiffness.* When $\phi(\vartheta) > 0$ for all ϑ, (17.32), being parabolic, exhibits behavior that is not much different than that for $V = K$, and is well understood.[46] What makes (17.32) nonstandard is the possibility of backward parabolicity for interfacial free-energy densities that satisfy $\phi(\vartheta) < 0$ for certain angle-intervals. Such energy densities are not mathematical curiosities: materials scientists give strong arguments in support of free-energy densities with $\phi(\vartheta) < 0$ for some angles ϑ.[47]

17.6 Backward parabolicity. Facets and wrinklings

In analyzing energies with backward-parabolic angle-intervals an important concept is the *Frank diagram* $\mathcal{F}$,[48] which is the graph in polar coordinates of the function $r = 1/\psi(\vartheta)$: $\mathcal{F}$ is locally strictly convex where $\phi(\vartheta) > 0$ and locally strictly concave where $\phi(\vartheta) < 0$. One method of dealing with the backward-parabolic intervals is to allow the interface to contain corners (jumps in tangent angle) that exclude the backward-parabolic ranges of ϑ. In the presence of a corner, the evolution equation (17.32) does not by itself characterize the motion of the interface; there is an additional condition (17.2) requiring that the configurational stress

$$\mathbf{c}(\vartheta) = \psi(\vartheta)\mathbf{t}(\vartheta) + \frac{d\psi(\vartheta)}{d\vartheta}\mathbf{n}(\vartheta) \quad \text{be a continuous function of arc length}$$

(cf. (17.29)). Thus for a corner corresponding to an angle jump from ϑ_1 to ϑ_2 we must have

$$\mathbf{c}(\vartheta_1) = \mathbf{c}(\vartheta_2),$$

a condition that has important consequences. One can show that: (i) the tangent line to $\mathcal{F}$ at ϑ_1 must also be a tangent line to $\mathcal{F}$ at ϑ_2 (that is, ϑ_1 and ϑ_2 must be angles of *bitangency* for $\mathcal{F}$); and (ii) there is exactly one (maximal) angle interval between ϑ_1 and ϑ_2 on which $\phi(\vartheta) < 0$. Thus, by restricting attention to an interface with corners such that there is one corner for each backward parabolic interval and such that across each corner the tangent angle jumps between bitangency angles of the Frank diagram, one arrives at an interface whose evolution is governed by a parabolic equation (Angenent and Gurtin, 1993). This procedure leads to to a free-boundary problem, since the positions of the corners vary with time.

The presence of unstable angle-intervals allows for *facets* (flat sections) and *wrinklings*, which are interfacial sections consisting of facets whose tangent angle is ϑ_1 alternating with facets whose tangent angle is ϑ_2 (Figure 11). Because $K \equiv 0$ on each facet, facets with tangent angle ϑ_1 must, by (17.32), have constant normal velocity $V \equiv V_1 = F/b(\vartheta_1)$, while $V \equiv V_2 = F/b(\vartheta_2)$ for those with angle ϑ_2. Then, by compatibility, the wrinkling must evolve as a rigid body with velocity $\mathbf{w}$ defined by $\mathbf{w} \cdot \mathbf{n}(\vartheta_i) = F/b(\vartheta_i)$, $i = 1, 2$.[49]

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[46] Cf. Angenent (1991), Chen, Giga, and Goto (1991), Barles, Soner, and Souganides (1993), and Soner (1993)

[47] Cf. Gjostein (1963) and Cahn and Hoffman (1974).

[48] Frank (1963).

[49] Cf. Gurtin (1993, §11) for a thorough discussion of wrinklings and related phenomena.

Figure 11: A wrinkled portion $\mathcal{C}$ of the grain boundary $\mathcal{S}$. The angles ϑ_1 and ϑ_2 associated with the facet-tangents $\mathbf{t}_1$ and $\mathbf{t}_2$ must be bitangency angles of the Frank diagram.

17.7 Junctions

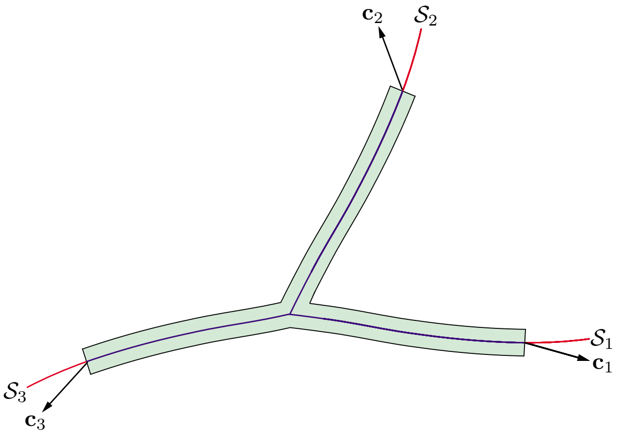

Figure 12: A triple-junction with a corresponding junction pillbox. Only the interfacial tractions on the pillbox are shown.

In the two-dimensional theory under consideration, grain boundaries meet at junctions such as the one shown in Figure 12. This figure shows the pillbox used to determine the configurational force balance for the junction; this figure omits the forces exerted by the bulk material on the pillbox as well as the internal forces exerted on the grain boundaries; we assume that these forces approach zero as the pillbox collapses to the junction. For the case in which N grain boundaries, labelled $n = 1, 2, \ldots, N$, meet at a junction, and for which the individual grain boundaries are oriented so that the unit tangent field of each is directed away from the junction, the configurational force balance for the junction has the form

$$\sum_{n=1}^{N} \mathbf{c}_n + \{\text{net force exerted on the pillbox by the bulk material}\} \\ + \{\text{net internal force exerted on the pillbox}\} = \mathbf{0}, \qquad (17.36)$$

where $\mathbf{c}_n$ denotes the force exerted on the pillbox by the portion of grain-boundary n that lies outside the pillbox. Assuming that the two terms written $\{\ldots\}$ tend to zero as the pillbox tends to the junction, we arrive at *Herring's junction balance* (1951):[50]

$$\sum_{n=1}^{N} \mathbf{c}_n = \mathbf{0}, \tag{17.37}$$

or, equivalently,

$$\sum_{n=1}^{N} (\sigma_n \mathbf{t}_n + \tau_n \mathbf{n}_n) = \mathbf{0}.$$

A classical consequence of the junction balance is that, for a triple junction, if the free energies of the grain boundaries are constant and equal, then the angles between adjacent boundaries are equal, with $\frac{2\pi}{3}$ the common angle.

17.8 Digression: general theory of interfacial constitutive relations with essentially linear dissipative response

In our development of constitutive equations for grain-boundaries, we used the dissipation inequality $\psi^{\square} - \tau\vartheta^{\square} + gV \le 0$ (and experience with classical theories) to motivate constitutive relations giving ψ and τ as functions of ϑ together with a relation giving g as a function of ϑ and V. This procedure will be used repeatedly in this article, where each of the individual theories is based on a *dissipation inequality* of the form

$$\overset{\square}{\psi} - \sum_{m=1}^{N} \tau_n \overset{\square}{\vartheta}_n + \sum_{m=1}^{N} g_m V_m \le 0. \tag{17.38}$$

In these theories we use the terms

$$\overset{\square}{\psi} - \sum_{m=1}^{N} \tau_n \overset{\square}{\vartheta}_n, \qquad \sum_{m=1}^{N} g_m V_m,$$

respectively, to motivate constitutive relations giving[51]

$$\psi,\ \vec{\tau}\ \text{ as functions of }\ \vec{\vartheta}, \qquad \vec{g}\ \text{ as a function of }\ (\vec{\vartheta}, \vec{V}\,), \tag{17.39}$$

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[50] In describing the forces on the junction, we neglected the internal configurational force $\mathbf{g}^*$ on the junction, which if included would appear on the left side of (17.37). If we neglect junction energy, then the appropriate free-energy imbalance for the junction would lead to the inequality $\mathbf{g}^* \cdot \mathbf{v}^* \le 0$, where $\mathbf{v}^*$ is the junction velocity. In this manner we would be led to a constitutive equation

$$\mathbf{g}^* = -\mathbf{B}\mathbf{v}^*$$

with $\mathbf{B}$ a positive semi-definite tensorial modulus that may depend on the junction angles of the grain boundaries as well as the mismatch angles of the grains. In this manner, we would arrive at the balance $\sum_n \mathbf{c}_n = \mathbf{B}\mathbf{v}^*$. Cf. Simha and Bhattacharya (1998); Gurtin (2000, Part H); cf. also Suo (1997, eqt. (2.17)), whose analysis is restricted to isotropic surface energies and to a junction between two grains and a vapor, a situation of great interest in discussing grain-boundary grooving (cf. Mullins (1957)).

[51] This structure cannot include theories involving temporal derivatives (or past histories) of the independent constitutive variables, nor can it include theories whose constitutive equations involve variables not present in the dissipation inequality. But it does include constitutive theories that we believe to be appropriate for the class of applications under consideration, without encumbering the presentation with lengthy arguments involving thermodynamical reductions of general constitutive theories. Moreover, as is clear from Remark C.1 above, the a priori splitting presumed in (17.39), in which ψ and $\vec{\tau}$ are taken to be independent of $\vec{V}$, may, in come cases, be unnecessary (e.g., in §18). But in discussions involving surface diffusion, spatial derivatives of chemical potentials enter the list $\vec{V}$.

where

$$\vec{\tau} = (\tau_1, \tau_2, \dots, \tau_N), \qquad \vec{\vartheta} = (\vartheta_1, \vartheta_2, \dots, \vartheta_N),$$
$$\vec{g} = (g_1, g_2, \dots, g_M), \qquad \vec{V} = (V_1, V_2, \dots, V_M).$$

and where neither of the fields $\vec{\vartheta}$ and $\vec{V}$ involves temporal derivatives of the other.

In view of the chain-rule (14.12), thermodynamic compatibility requires that, for any choice of the fields $\vec{\vartheta}$ and $\vec{V}$,

$$\sum_{n=1}^{N} \left\{ \frac{\partial\hat{\psi}(\vec{\vartheta})}{\partial\vartheta_n} - \hat{\tau}_n(\vec{\vartheta}\,) \right\} \overset{\scriptscriptstyle\square}{\vartheta}_n + \sum_{m=1}^{M} \hat{g}_m(\vec{\vartheta}, \vec{V}\,) V_m \le 0. \tag{17.40}$$

It is always possible to find an interfacial field $\vec{\vartheta}$ whose values *and whose (normal) time-derivative-values* at any given time are arbitrary. Thus, since the inequality (17.40) is *linear* in the variables $\vartheta_n^{\square}$, we must have $\hat{\tau}_n = \partial\hat{\psi}/\partial\vartheta_n$ (for all n). We therefore have the following *thermodynamic restrictions*:

- ψ must determine $\vec{\tau}$ through the relations
$$\tau_n = \frac{\partial\hat{\psi}(\vec{\vartheta}\,)}{\partial\vartheta_n}; \tag{17.41}$$
- the constitutive response function for $\vec{g}$ must be consistent with the *reduced dissipation inequality*
$$\sum_{m=1}^{M} \hat{g}_m(\vec{\vartheta}, \vec{V}\,) V_m \le 0. \tag{17.42}$$

In the special cases we shall consider,

$$\mathcal{D} \overset{\text{def}}{=} -\sum_{m=1}^{M} \hat{g}_m(\vec{\vartheta}, \vec{V}\,) V_m$$

represents the *dissipation.* Of special interest here are constitutive equations giving $\vec{g}$ as a linear function of $\vec{V}$ for each fixed value of $\vec{\vartheta}$:

$$g_m = -\sum_{j=1}^{M} A_{mj}(\vec{\vartheta}\,) V_j; \tag{17.43}$$

in this case we refer to the constitutive equations as having *essentially linear dissipative response*. (The term "essential" refers to the fact that (17.43) is linear in the primary variable $\vec{V}$, but the dependence on $\vec{\vartheta}$ is unrestricted). In addition, if

$$A_{mj} = 0 \quad \text{for} \quad m \ne j, \tag{17.44}$$

so that, writing $A_m = A_{mm}$,

$$\left.\begin{aligned} g_1 &= A_1(\vec{\vartheta}\,) V_1, \\ g_2 &= A_2(\vec{\vartheta}\,) V_2, \\ &\vdots \\ g_N &= A_N(\vec{\vartheta}\,) V_N, \end{aligned}\right\} \tag{17.45}$$

we refer to the constitutive equations as having *uncoupled* essentially linear dissipative response.

Returning to the uncoupled relations (17.42), the reduced dissipation inequality requires that the coefficients $A_{mj}(\vec{\vartheta})$ form a positive semi-definite matrix. The dissipation corresponding to the constitutive relations (17.43) has the form

$$\mathcal{D} = \sum_{m,j=1}^{M} A_{mj}(\vec{\vartheta}) V_m V_j. \tag{17.46}$$

18 Interfacial couples. Allowance for an energetic dependence on curvature

Within the theory for grain boundaries presented above, facets are modeled as sharp corners. That crystalline solids may exhibit departures from this idealization was recognized by Herring (1951),[52] who argued that, when the radius of curvature of a crystal surface is sufficiently small, the free energy of that surface should depend not only on orientation but also on curvature. A theory which allows for such dependence has numerous benefits. The procedure discussed in §17.6 cannot, by itself, characterize the nucleation of facets and wrinklings, nor can it be used for an initial-value problem in which the initial interface has angle intervals for which $\psi(\vartheta) + \psi''(\vartheta) < 0$. To analyze behavior within such angle-intervals, a regularization of the evolution equation (17.32) is needed. Such a regularization, proposed by Angenent and Gurtin (1989) and developed by DiCarlo, Gurtin, and Podio-Guidugli (1992),[53] entails a curvature-dependent free energy. Within the present framework, a curvature-dependent free energy requires (configurational) interfacial couples together with a configurational balance for torques. A theory including these ingredients provides a *physically-based regularization* of the evolution equation (17.32), in contrast to the pragmatic alternative of simply adding to such an equation supplemental terms involving higher-order derivatives.

18.1 Configurational torque balance

We now expand the configurational force system discussed in Section §17.1 to include a (scalar) *interfacial couple-stress* M and a (scalar) *internal couple* m distributed continuously over $\mathcal{S}$ (Figure 13). Let $\mathcal{C} = \mathcal{C}(t)$ be an arbitrary interfacial pillbox $\mathcal{S}$. The portion of $\mathcal{S}$ external to $\mathcal{C}$ then exerts torques $-M_a - (\mathbf{x}_a - \mathbf{0})\times\mathbf{c}_a$ and $M_b(\mathbf{x}_b - \mathbf{0})\times\mathbf{c}_b$ at $\mathbf{x}_a$ and $\mathbf{x}_b$.[54] In addition to the interfacial couple m distributed uniformly over $\mathcal{C}$, there is the torque $(\mathbf{x}-\mathbf{0})\times\mathbf{g}$ associated with the internal force $\mathbf{g}$. Further, the bulk material in the $(+)$-phase exerts a torque $(\mathbf{x}-\mathbf{0})\times\mathbf{C}^{+}\mathbf{n}$ on $\mathcal{C}^{+}$, while that in the $(-)$-phase exerts a torque $-(\mathbf{x}-\mathbf{0})\times\mathbf{C}^{-}\mathbf{n}$ on $\mathcal{C}^{-}$, so that the net configurational torque exerted at each point of $\mathcal{C}$ by the bulk phases is $(\mathbf{x}-\mathbf{0})\times(\mathbf{C}^{+}\mathbf{n} - \mathbf{C}^{-}\mathbf{n}) = (\mathbf{x}-\mathbf{0})\times[\![\mathbf{C}]\!]\mathbf{n}$. The *configurational*

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[52] Cf., also, Gjostein (1963) and Cahn and Hoffman (1974).

[53] Cf. Stewart and Goldenfeld (1992), who define the chemical potential as the variational derivative of the interfacial energy with respect to changes in the location of the surface and, starting with a mass balance that includes surface diffusion and evaporation terms, derive an evolution equation which, after linearization, yields conditions for the onset of instabilities (and the subsequent formation of facets along the surface). Cf. also Golovin, Davis, and Nepomnyashchy (1998, 1999), who use variational arguments to obtain an evolution equation for an interface $z = h(x,t)$ (respectively, $z = h(x,y,t)$) with a curvature-dependent surface tension, assuming that dh/dx is small (respectively, $\partial h/\partial x$ and $\partial h/\partial y$ are small).

[54] Here the "×" denotes the (scalar) two-dimensional cross-product; in components $\mathbf{p}\times\mathbf{k} = p_1k_2 - p_2k_1$.

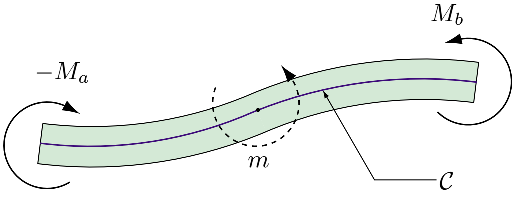

Figure 13: Configurational *couples* on on an interfacial pillbox $\mathcal{C}$. In the configurational torque balance these couples are supplemented by torques exerted by the configurational force system.

torque balance for $\mathcal{C}$ therefore takes the form

$$\big[M + (\mathbf{x}-\mathbf{0})\times\mathbf{c}\big]_a^b + \int\limits_{\mathcal{C}} m\,ds + \int\limits_{\mathcal{C}} \big[(\mathbf{x}-\mathbf{0})\times(\mathbf{g}+[\![\mathbf{C}]\!]\mathbf{n})\big]\,ds = 0. \tag{18.1}$$

This balance supplements the configurational force balance (17.1).

Consider the term $\big[M+(\mathbf{x}-\mathbf{0})\times\mathbf{c}\big]_a^b$. Since $\partial\mathbf{x}/\partial s = \mathbf{t}$, and since, by (17.4), $\mathbf{t}\times\mathbf{c} = \tau$,

$$\big[M + (\mathbf{x}-\mathbf{0})\times\mathbf{c}\big]_a^b = \int\limits_{\mathcal{C}} \left(\frac{\partial M}{\partial s} + \tau + (\mathbf{x}-\mathbf{0})\times\frac{\partial \mathbf{c}}{\partial s}\right) ds.$$

Thus, by the local consequence (17.3), namely $\partial\mathbf{c}/\partial s + \mathbf{g} + [\![\mathbf{C}]\!]\mathbf{n} = \mathbf{0}$, of the configurational force balance (17.1), the torque balance (18.1) reads

$$\int\limits_{\mathcal{C}} \left(\frac{\partial M}{\partial s} + m + \tau\right) ds = 0;$$

since $\mathcal{C}$ is arbitrary, this yields the *local torque balance*

$$\frac{\partial M}{\partial s} + m + \tau = 0. \tag{18.2}$$

Differentiating each term of (18.2) with respect to s and using the normal configurational force balance (17.6) to give an expression for $\partial\tau/\partial s$, it follows that

$$\frac{\partial^2 M}{\partial s^2} + \frac{\partial m}{\partial s} - \sigma K - g - \mathbf{n}\cdot[\![\mathbf{C}]\!]\mathbf{n} = 0, \tag{18.3}$$

or equivalently, granted $\mathbf{C} = \Psi\mathbf{1}$ as in the theory without couples, that

$$\frac{\partial^2 M}{\partial s^2} + \frac{\partial m}{\partial s} - \sigma K - g - [\![\Psi]\!] = 0, \tag{18.4}$$

with $[\![\Psi]\!]$ assumed constant. This balance is basic to what follows.

18.2 Power

(a) External expenditure of power

Let $\mathcal{C} = \mathcal{C}(t)$ be an interfacial pillbox. In addition to the power expended by configurational forces, we must now account for power expended by the couple stress M. This stress acts at the endpoints of $\mathcal{C}$ and the corresponding torques M_a and M_b should be power-conjugate to the angle-rates $d\vartheta_a/dt$ and $d\vartheta_b/dt$ at these endpoints (cf. (14.22)). Thus

$$\left[M\frac{d\vartheta}{dt}\right]_a^b \equiv M_b\frac{d\vartheta_b}{dt} - M_a\frac{d\vartheta_a}{dt}$$

represents the power expended on $\mathcal{C}$ by the couple stress, and the (net) power expended on $\mathcal{C}$ has the form

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + M\frac{d\vartheta}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds. \tag{18.5}$$

By (14.27),

$$\left[M\frac{d\vartheta}{dt}\right]_a^b = \big[M(\overset{\square}{\vartheta} + KW)\big]_a^b, \tag{18.6}$$

so that, using (14.19),

$$\begin{aligned}\left[M\frac{d\vartheta}{dt}\right]_a^b &= \big[MKW\big]_a^b + \int\limits_{\mathcal{C}} \left(M\frac{\partial\overset{\square}{\vartheta}}{\partial s} + \frac{\partial M}{\partial s}\overset{\square}{\vartheta}\right) ds \\ &= \big[MKW\big]_a^b + \int\limits_{\mathcal{C}} \left(M(\overset{\square}{K} - K^2V) + \frac{\partial M}{\partial s}\overset{\square}{\vartheta}\right) ds.\end{aligned}$$

On the other hand, (17.16) (which holds here also) and (18.2) yield

$$\begin{aligned}\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds &= \big[\sigma W\big]_a^b + \int\limits_{\mathcal{C}(t)} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g)V\big]\,ds \\ &= \big[\sigma W\big]_a^b - \int\limits_{\mathcal{C}} \left((\sigma K + g)V + \left(\frac{\partial M}{\partial s} + m\right)\overset{\square}{\vartheta}\right) ds.\end{aligned}$$

Adding the last two relations, we arrive at the *power balance*

$$\begin{aligned}&\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + M\frac{d\vartheta}{dt}\right]_a^b + \int\limits_{\mathcal{C}} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds \\ &\qquad = \big[(\sigma + MK)W\big]_a^b + \int\limits_{\mathcal{C}} \big[M\overset{\square}{K} - m\overset{\square}{\vartheta} - \big((\sigma + MK)K + g\big)V\big]\,ds,\end{aligned} \tag{18.7}$$

which bears comparison to (17.16). Note that here:

- The term $\big[(\sigma + MK)W\big]_a^b$ (rather than $\big[\sigma W\big]_a^b$) represents power expended internally as material is added to $\mathcal{C}$ at its endpoints.
- The term $M\overset{\square}{K}$ represents an expenditure of power associated with changes in the curvature of the grain boundary.
- The term $-m\overset{\square}{\vartheta}$ (rather than $\tau\overset{\square}{\vartheta}$) represents the expenditure of power associated with changes in the orientation of the grain boundary.

- The term $-(\sigma + MK)KV$ (rather than $-\sigma KV$) represents the expenditure of power associated with changes in interfacial area due to the curvature of the grain boundary.

As before, the *tangential* component of $\mathbf{g}$ expends no power internally, but now, interestingly, neither does the shear τ, as its role in the power balance is replaced by the internal torque m. This is consistent with the theory without couples, since, by (18.2), $\tau = -m$ when $M = 0$. Classically, forces that expend no power internally are presumed to be indeterminate; for that reason, τ joins $\mathbf{g}\cdot\mathbf{t}$ as an indeterminate field, an assumption that allows us to consider the torque balance (18.2) as a defining relation for τ. Note that, granted τ is defined by the torque balance, the balance (18.4) is equivalent to the normal configurational force balance (17.10) of the theory without couples.

18.3 Free-energy imbalance

(a) Global imbalance

As before, we let ψ denote the free energy of the grain boundary; the *free-energy imbalance* for $\mathcal{C}$ then takes the form

$$\frac{d}{dt}\int\limits_{\mathcal{C}(t)} \psi\,ds \le \left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + M\frac{d\vartheta}{dt}\right]_a^b + \int\limits_{\mathcal{C}(t)} [\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds. \tag{18.8}$$

Note that, since $[\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v} = [\![\Psi]\!]V$, with $[\![\Psi]\!]$ (assumed) constant, the decay relation (17.19) and its consequences remain valid within this more general theory.

(b) Dissipation inequality

In view of the transport identity (14.29) and the power balance (18.7), the free-energy inequality (18.8) becomes

$$\int\limits_{\mathcal{C}} (\overset{\square}{\psi} - \psi KV)\,ds + \overbrace{\big[\big(\psi - (\sigma + MK)\big)W\big]_a^b}^{(\#)} \le \int\limits_{\mathcal{C}} \big[M\overset{\square}{K} - m\overset{\square}{\vartheta} - \big((\sigma + MK)K + g\big)V\big]\,ds. \tag{18.9}$$

Since $\mathcal{C}$ is arbitrary, so also are the tangential velocities W_a and W_b of the endpoints of $\mathcal{C}$; thus, since the only term in (18.9) dependent on these velocities is the term (#), we have the relation

$$\sigma = \psi - MK; \tag{18.10}$$

thus, in contrast to classical theories, the present theory requires that the correspondence between surface tension and interfacial free energy be generalized to account for the influence of the interfacial couple-stress M. Using (18.10), we may rewrite the normal configurational force balance (17.10) as

$$(\psi - MK)K + \frac{\partial\tau}{\partial s} + g + [\![\Psi]\!] = 0. \tag{18.11}$$

Next, by (18.10), the free-energy inequality (18.9) reduces to

$$\int\limits_{\mathcal{C}} (\overset{\square}{\psi} + m\,\overset{\square}{\vartheta} - M\overset{\square}{K} + gV)\,ds \le 0, \tag{18.12}$$

and this yields the *dissipation inequality*

$$\overset{\square}{\psi} + m\,\overset{\square}{\vartheta} - M\overset{\square}{K} + gV \le 0. \tag{18.13}$$

18.4 Constitutive equations

Guided by (18.13) and the discussion of §17.4 for the theory without configurational moments, we consider constitutive equations giving

$$\left.\begin{aligned} \psi,\ m,\ M \ \ &\text{as functions of}\ \ (\vartheta, K),\\ g \ \ &\text{as a function of}\ \ (\vartheta, K, V). \end{aligned}\right\} \tag{18.14}$$

Then, appealing to the general constitutive theory discussed in §17.8, we find, as a consequence of thermocompatibility and an assumption of essentially linear dissipative response, that:

- the free energy determines the internal couple and the interfacial couple-stress through the relations

$$\left.\begin{aligned} m &= -\frac{\partial\hat{\psi}(\vartheta, K)}{\partial\vartheta},\\ M &= \frac{\partial\hat{\psi}(\vartheta, K)}{\partial K}. \end{aligned}\right\} \tag{18.15}$$

- the normal internal force is given by the linear relation

$$g = -b(\vartheta, K)V, \tag{18.16}$$

  with *kinetic modulus* $b(\vartheta, K) \ge 0$.

18.5 Evolution equation for the grain boundary

The basic equations of the theory consist of the balance (18.4) with $\sigma = \psi - MK$, viz.,

$$\frac{\partial^2 M}{\partial s^2} + \frac{\partial m}{\partial s} - (\psi - MK)K - g - [\![\Psi]\!] = 0, \tag{18.17}$$

supplemented by the constitutive relations (18.15) and (18.16). In general, the coupling between orientation and curvature induced by the constitutive relation for the free energy renders the resulting evolution complicated. But, for small curvatures, a quadratic dependence on curvature should provide a reasonable approximation and, as we shall see, such an energy provides a parabolic regularization to the evolution equation (17.32).

We therefore consider the simple constitutive equation

$$\hat{\psi}(\vartheta, K) = \psi_0(\vartheta) + \tfrac{1}{2}\lambda K^2, \tag{18.18}$$

with $\lambda > 0$ constant. The restrictions (18.15) then yield the specific relations

$$m = -\psi_0'(\vartheta), \qquad M = \lambda K;$$

thus, assuming that $b = b(\vartheta) > 0$, (18.16) and (18.17) yield the evolution equation

$$b(\vartheta)V = \big[\psi_0(\vartheta) + \psi_0''(\vartheta)\big]K - \lambda\bigg(\frac{\partial^2 K}{\partial s^2} + \tfrac{1}{2}K^3\bigg) + [\![\Psi]\!]. \tag{18.19}$$

For the interface a graph $y = h(x,t)$, we can use (17.33) to rewrite the evolution equation (18.19) in a form analogous to (17.34). The right side of the resulting equation then contains a term of the form

$$-(\dots)\frac{\partial^4 h}{\partial x^4},$$

and all other terms as well as the coefficient (...) depend on partial derivatives of h with respect to x of order strictly less than four. Moreover, the coefficient (...) is strictly positive. Thus the evolution equation (18.19) is equivalent to a fourth-order parabolic partial differential equation. In that sense, (18.19) with λ small *represents a parabolic regularization of the evolution equation* (17.32). This regularization should be useful in analyzing situations for which the interfacial stiffness is negative and (17.32) is backward parabolic for certain angle intervals.

In a sense, the regularized equation (18.19) represents a counterpart for interfaces of the classical Cahn-Hilliard equation (Cahn and Hilliard, 1958, 1959, 1971), as discussed by DiCarlo, Gurtin, and Podio-Guidugli (1992).[55]

19 Grain-vapor interfaces with atomic transport

In this section we consider an interface $\mathcal{S} = \mathcal{S}(t)$ that separates a grain from a vapor environment. We include atomic transport in bulk, on the interface, and from the vapor, but neglect deformation of the grain and flow in the vapor.[56] For simplicity, *we restrict attention to a single atomic species.* We model the vapor as a reservoir whose sole interaction with the grain is through the evaporation of atoms from — and the condensation of atoms on — the grain boundary.

19.1 Configurational force balance

We assume that the configurational stress in the vapor vanishes:[57] considering the vapor to be the (+)-phase, the grain the (−)-phase, it follows that $\mathbf{C}^+ = \mathbf{0}$.

Apart from this restriction, the discussion of configurational forces is identical to that presented for a grain-grain interface. Thus, writing $\mathbf{C} = \mathbf{C}^-$, the configurational force balance (17.1) takes the form

$$\mathbf{c}\big|_a^b + \int\limits_{\mathcal{C}} \mathbf{g}\,ds - \int\limits_{\mathcal{C}} \mathbf{C}\mathbf{n}\,ds = \mathbf{0}, \tag{19.1}$$

---

[55] Cf. Watson, Otto, Rubinstein and Davis (2003) and Watson (2003).

[56] Cf. Spencer, Voorhees, and Davis (1991, 1993), Spencer and Meiron (1994), Guyer and Voorhees (1996, 1998), and Spencer, Voorhees, and Tersoff (2000), who investigate the morphological stability of epitaxially strained single-component and alloy thin films in the presence of surface diffusion and an isotropic surface free-energy. See also Zhang and Bower (1999, 2001), who examine shape changes of strained islands on lattice-mismatched substrates due to surface diffusion in the presence of both isotropic and anisotropic surface energies.

[57] Tacit are the following assumptions: the free energy of the grain is reckoned relative to that of the vapor; the atomic density of the vapor and the vapor pressure are negligible.

and this yields the *normal configurational force balance*

$$\sigma K + \frac{\partial \tau}{\partial s} + g - \mathbf{n} \cdot \mathbf{C}\mathbf{n} = 0, \tag{19.2}$$

with σ and τ defined by (17.4) and $g = \mathbf{g} \cdot \mathbf{n}$, as before.

The bulk configurational force $\mathbf{C}$ is determined by the Eshelby relation (12.15), which, since deformation is neglected here, has the form

$$\mathbf{C} = (\Psi - \rho\mu)\mathbf{1}, \tag{19.3}$$

with μ, the bulk chemical-potential, assumed continuous up to the grain boundary. The normal configurational force balance (19.1) therefore takes the form

$$\rho\mu = \Psi - \sigma K - \frac{\partial \tau}{\partial s} - g \tag{19.4}$$

and the normal configurational force balance provides a relation for the chemical potential of the grain boundary. Finally, the tangential component of the configurational force balance reduces to (17.11).

19.2 Power

Consistent with the requirement that the configurational stress vanishes in the vapor and the notational convention $\mathbf{C} = \mathbf{C}^-$, the (net) *power expended* on a migrating pillbox $\mathcal{C}$ has the form

$$\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b - \int_{\mathcal{C}} \mathbf{C}\mathbf{n} \cdot \mathbf{v}\, ds. \tag{19.5}$$

By (17.13), (14.5), and the Eshelby relation (19.3), $\mathbf{C}\mathbf{n} \cdot \mathbf{v} = (\Psi - \rho\mu)V$; hence, the power expended on $\mathcal{C}$ has the form

$$\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b - \int_{\mathcal{C}} \mathbf{C}\mathbf{n} \cdot \mathbf{v}\, ds = \big[\sigma W + \tau V\big]_a^b - \int_{\mathcal{C}} (\Psi - \rho\mu)V\, ds \tag{19.6}$$

which, by (17.15) and the normal configurational force balance (19.4), yields the power balance

$$\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b - \int_{\mathcal{C}} \mathbf{C}\mathbf{n} \cdot \mathbf{v}\, ds = \big[\sigma W\big]_a^b + \int_{\mathcal{C}} \big[\tau \overset{\square}{\vartheta} - (\sigma K + g)V\big]\, ds. \tag{19.7}$$

19.3 Atomic flows due to diffusion, evaporation-condensation, and accretion. Atomic balance

In addition to the bulk atomic density ρ and bulk atomic flux $\jmath$, we account for an *atomic supply* r from the vapor and for a (*scalar*) *interfacial atomic flux*[58] h. Without loss of generality, we write $\rho = \rho^-$ and $\jmath = \jmath^-$ for the interfacial limits of the density and atomic flux in the grain. While we account for the transport of adatoms along the interface through the flux h, we assume that the adatom density is negligibly small.

Let $\mathcal{C} = \mathcal{C}(t)$ be an interfacial pillbox. Then surface diffusion in the portion of $\mathcal{S}$ exterior to $\mathcal{C}$ results in fluxes h_a and $-h_b$ of atoms into $\mathcal{C}$ across $\mathbf{x}_a$ and $\mathbf{x}_b$; (since $\mathbf{n}$ points into the vapor) bulk diffusion results in a flow $\jmath \cdot \mathbf{n}$ of atoms into $\mathcal{C}$ across

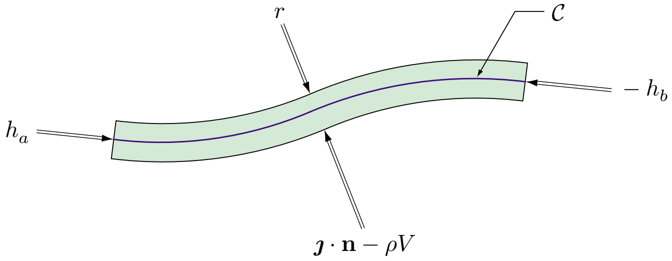

Figure 14: Atomic fluxes and supplies to an interfacial pillbox $\mathcal{C}$.

$\mathcal{C}^-$ from the solid; r represents the rate at which atoms are supplied from the vapor (Figure 14). Hence, the net rate at which atoms are added to $\mathcal{C}$ by diffusive transport and by evaporation-condensation is

$$-h\big|_a^b + \int\limits_{\mathcal{C}} (\boldsymbol{\jmath}\cdot\mathbf{n} + r)\,ds. \tag{19.8}$$

Atoms are also carried into $\mathcal{C}$ as it migrates. Since we neglect the adatom density, the only such accretive flow is $-\rho V$ across $\mathcal{C}^-$ into $\mathcal{C}$ (Figure 14), so that the net rate at which atoms are added to $\mathcal{C}$ by accretion is

$$-\int\limits_{\mathcal{C}} \rho V\,ds. \tag{19.9}$$

Thus, the *atomic balance* for $\mathcal{C}$ takes the form

$$-h\big|_a^b + \int\limits_{\mathcal{C}} (\boldsymbol{\jmath}\cdot\mathbf{n} - \rho V + r)\,ds = 0; \tag{19.10}$$

since $\mathcal{C}$ is arbitrary, this yields the local balance

$$\rho V = -\frac{\partial h}{\partial s} + \boldsymbol{\jmath}\cdot\mathbf{n} + r. \tag{19.11}$$

19.4 Free-energy imbalance

The general free-energy imbalance (17.17) is now modified to include energy flow into the pillbox $\mathcal{C}(t)$ by atomic transport:

$$\frac{d}{dt}\{\text{free energy of }\mathcal{C}(t)\} \le \{\text{power expended on }\mathcal{C}(t)\} + \{\text{energy flow into }\mathcal{C}(t)\text{ by atomic transport}\}. \tag{19.12}$$

To discuss this inequality, we let μ_v denote the *chemical potential of the vapor*.

We assume that *the chemical potential μ of the solid at the surface is the limiting value $\mu = \mu^-$ of the bulk chemical potential; μ therefore represents the chemical potential for surface diffusion*. Since we attribute no specific structure to the vapor, μ_v represents the chemical potential of the vapor at the grain boundary. In general, we admit the possibility that μ differs from μ_v.

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[58] The vectorial flux is represented by $h\mathbf{t}$.

(a) Energy flows due to diffusion, evaporation-condensation, and accretion

Atomic transport induces energy flows associated with diffusion, evaporation-condensation, and accretion. The diffusion of atoms within the interface results in energy fluxes $-\mu_a h_a$ and $\mu_b h_b$ across $\mathbf{x}_a$ and $\mathbf{x}_b$; the diffusion of atoms within the solid results in an energy flow $\mu\boldsymbol{\jmath}\cdot\mathbf{n}$ across $\mathcal{C}^-$; the supply r of atoms from the vapor results in an energy flow $\mu_v r$. Hence, the net rate at which energy is added to $\mathcal{C}$ by diffusion and evaporation-condensation is

$$-\big[\mu h\big]_a^b+\int\limits_{\mathcal{C}}(\mu\boldsymbol{\jmath}\cdot\mathbf{n}+\mu_v r)\,ds. \tag{19.13}$$

The motion of the interface results in an energy flow $-\rho\mu V$ associated with accretive transport of atoms from the grain across $\mathcal{C}^-$, so that the rate at which energy is added to $\mathcal{C}$ by the accretive transport of atoms is

$$-\int\limits_{\mathcal{C}}\rho\mu V\,ds. \tag{19.14}$$

(b) Global imbalance

As before, we let ψ denote the free energy of the grain boundary; in view of (19.13) and (19.14), the free-energy imbalance for an arbitrary interfacial pillbox then takes the form[59]

$$\underbrace{\frac{d}{dt}\int\limits_{\mathcal{C}(t)}\psi\,ds}_{\text{free energy}}\le\underbrace{\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b-\int\limits_{\mathcal{C}(t)}\mathbf{Cn}\cdot\mathbf{v}\,ds}_{\substack{\text{power expended}\\ \text{by configurational forces}}}+\underbrace{\int\limits_{\mathcal{C}(t)}\big(\mu(\boldsymbol{\jmath}\cdot\mathbf{n}-\rho V)+\mu_v r\big)\,ds-\big[\mu h\big]_a^b}_{\text{energy flow by atomic transport}}. \tag{19.15}$$

(c) Dissipation inequality

Next, by (19.7) and the transport theorem (14.29), the free-energy imbalance (19.15) becomes

$$\int\limits_{\mathcal{C}}(\overset{\square}{\psi}-\psi KV)\,ds+\overbrace{\big[(\psi-\sigma)W\big]_a^b}^{(\#)}$$
$$\le\int\limits_{\mathcal{C}}(\tau\overset{\square}{\vartheta}-(\sigma K+g)V)+\mu(\boldsymbol{\jmath}\cdot\mathbf{n}-\rho V)+\mu_v r)\,ds-\big[\mu h\big]_a^b. \tag{19.16}$$

We must therefore have $\sigma=\psi$, as before, and hence

$$\int\limits_{\mathcal{C}}\overset{\square}{\psi}\,ds\le\int\limits_{\mathcal{C}}(\tau\overset{\square}{\vartheta}-gV+\mu(\boldsymbol{\jmath}\cdot\mathbf{n}-\rho V)+\mu_v r)\,ds-\big[\mu h\big]_a^b. \tag{19.17}$$

Next, using the atomic balance (19.11),

$$\big[\mu h\big]_a^b=\int\limits_{\mathcal{C}}\left(\mu\frac{\partial h}{\partial s}+h\frac{\partial\mu}{\partial s}\right)ds=\int\limits_{\mathcal{C}}\left(\mu(\boldsymbol{\jmath}\cdot\mathbf{n}-\rho V+r)+h\frac{\partial\mu}{\partial s}\right)ds.$$

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[59] Cf. Davì and Gurtin (1990).

Thus, (19.17) reduces to

$$\int\limits_{\mathcal{C}} \left(\overset{\square}{\psi} - \tau \overset{\square}{\vartheta} + h \frac{\partial \mu}{\partial s} + (\mu - \mu_v) r + gV \right) ds \leq 0;$$

since $\mathcal{C}$ is arbitrary, we have the *dissipation inequality*

$$\overset{\square}{\psi} - \tau \overset{\square}{\vartheta} + h \frac{\partial \mu}{\partial s} + (\mu - \mu_v) r + gV \leq 0. \tag{19.18}$$

19.5 Constitutive equations

Our discussion of constitutive equations follows the format set out in §17.8. We consider constitutive equations giving

$$\left. \begin{array}{c} \psi, \ \tau \ \text{ as functions of } \ \vartheta \\[1ex] h, \ r, \ g \ \text{ as functions of } \ \left(\vartheta, \dfrac{\partial \mu}{\partial s}, \mu - \mu_v, V \right). \end{array} \right\} \tag{19.19}$$

Then, appealing to the discussion of §17.8 we find, as a consequence of thermocompatibility and an *assumption of essentially linear dissipative response*, that the free energy determines the shear through the relation

$$\tau = \psi'(\vartheta), \tag{19.20}$$

that the constititutive equations for h, r, and g have the specific form[60]

$$\left. \begin{aligned} h &= -L(\vartheta) \frac{\partial \mu}{\partial s} - \breve{\ell}(\vartheta)(\mu - \mu_v) - \ell(\vartheta) V, \\ r &= -K(\vartheta) \frac{\partial \mu}{\partial s} - \breve{k}(\vartheta)(\mu - \mu_v) - k(\vartheta) V, \\ g &= -B(\vartheta) \frac{\partial \mu}{\partial s} - \breve{b}(\vartheta)(\mu - \mu_v) - b(\vartheta) V, \end{aligned} \right\} \tag{19.21}$$

and that, for each ϑ, the coefficients that define the linear relations (19.21) form a positive semi-definite matrix.

It is the purpose of this section to discuss more classical theories in which the linear relations (19.21) are uncoupled. We therefore assume that

- surface diffusion is given by Fick's law (Herring, 1951; Mullins, 1957),

  $$h = -L(\vartheta) \frac{\partial \mu}{\partial s}, \tag{19.22}$$

  with $L(\vartheta) \geq 0$ a modulus that describes the *mobility* of the atoms on the interface;

- evaporation-condensation is described by the relation

  $$r = -k(\vartheta)(\mu - \mu_v), \tag{19.23}$$

  with $k(\vartheta) \geq 0$ an *evaporation modulus*;

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[60] Cf. Davì and Gurtin (1990), who neglect the internal force g and hence do not include dependences on V.

- kinetics is defined by the relation

  $$g = -b(\vartheta)V, \tag{19.24}$$

  with $b(\vartheta) \geq 0$.

The dissipation then has the form

$$\mathcal{D} = \underbrace{L(\vartheta)\left(\frac{\partial\mu}{\partial s}\right)^2}_{\substack{\text{dissipation induced}\\ \text{by surface diffusion}}} + \underbrace{k(\vartheta)(\mu - \mu_v)^2 + b(\vartheta)V^2}_{\substack{\text{dissipation accompanying the}\\ \text{attachment of vapor atoms}}} \tag{19.25}$$

and results in two terms, $k(\vartheta)(\mu - \mu_v)^2$ and $b(\vartheta)V^2$, associated with the attachment of vapor atoms to the lattice. One might expect the *dynamical* term $b(\vartheta)V^2$ to be negligible for standard evaporation-condensation, and, in fact, theories discussed by materials scientists typically do not include the kinetic term $g = -b(\vartheta)V$.[61]

19.6 Basic equations

The basic equations for the interface consist of the normal configurational force-balance (19.4) (with $\sigma = \psi$) and the atomic balance

$$\begin{aligned} \rho\mu &= \Psi - \psi K - \frac{\partial\tau}{\partial s} - g, \\ \rho V &= -\frac{\partial h}{\partial s} + \boldsymbol{\jmath}\cdot\mathbf{n} + r, \end{aligned}$$

supplemented by the constitutive equations $\psi = \hat{\psi}(\vartheta)$, (19.20), and (19.22)–(19.23):

$$\left.\begin{aligned} \rho\mu &= \Psi - \big[\psi(\vartheta) + \psi''(\vartheta)\big]K + b(\vartheta)V, \\ \rho V &= \frac{\partial}{\partial s}\left(L(\vartheta)\,\frac{\partial\mu}{\partial s}\right) + \boldsymbol{\jmath}\cdot\mathbf{n} + k(\vartheta)(\mu_v - \mu). \end{aligned}\right\} \tag{19.26}$$

These equations are coupled to the bulk atomic balance

$$\dot{\rho} = -\mathrm{div}\,\boldsymbol{\jmath} \tag{19.27}$$

and the bulk constitutive equations

$$\mu = \hat{\mu}(\rho) = \frac{d\hat{\Psi}(\rho)}{d\rho} \tag{19.28}$$

and

$$\boldsymbol{\jmath} = -\mathbf{M}(\rho)\nabla\mu \tag{19.29}$$

($(7.5)_2$), or equivalently,

$$\boldsymbol{\jmath} = -\mathbf{D}(\rho)\nabla\rho, \qquad \mathbf{D}(\rho) = \frac{d\hat{\mu}(\rho)}{d\rho}\mathbf{M}(\rho). \tag{19.30}$$

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[61] Cf. §26.3 for a detailed discussion of this kinetic term.

19.7 Nearly flat interface at equilibrium

For a *flat interface at equilibrium*, $K = V = 0$ and the normal configurational force balance (19.26) implies that

$$\Psi - \rho\mu = 0, \tag{19.31}$$

which is the familiar assertion that, *in equilibrium, the grand canonical potential $\Psi - \rho\mu$ of the solid must coincide with that of the vapor*, here normalized to be zero (cf. Larché and Cahn 1985).

Let the constants Ψ_0, ρ_0, and μ_0 denote the values of the bulk free-energy, bulk atomic-density, and chemical potential when the grain and vapor are in equilibrium, with the interface flat; then

$$\Psi_0 = \hat{\Psi}(\rho_0), \qquad \mu_0 = \hat{\mu}(\rho_0) = \left.\frac{d\hat{\Psi}}{d\rho}\right|_0,$$

where the subscript zero denotes evaluation at $\rho = \rho_0$. Then, by (19.31),

$$\Psi_0 - \mu_0\rho_0 = 0.$$

Thus $\Psi - \rho\mu$, considered as a function of ρ, has the following expansion for ρ close to ρ_0:

$$\begin{aligned}\Psi - \rho\mu &= \left.\frac{d\hat{\Psi}}{d\rho}\right|_0(\rho-\rho_0) - \mu_0(\rho-\rho_0) - \rho_0\left.\frac{d\hat{\mu}}{d\rho}\right|_0(\rho-\rho_0) + \mathrm{o}(|\rho-\rho_0|)\\ &= -\rho_0\left.\frac{d\hat{\mu}}{d\rho}\right|_0(\rho-\rho_0) + \mathrm{o}(|\rho-\rho_0|).\end{aligned}$$

On the other hand,

$$\mu = \mu_0 + \left.\frac{d\hat{\mu}}{d\rho}\right|_0(\rho-\rho_0) + \mathrm{o}(|\rho-\rho_0|),$$

so that

$$\Psi - \rho\mu = -\rho_0(\mu-\mu_0) + o(|\rho-\rho_0|). \tag{19.32}$$

If, in addition, we assume that *the vapor is not supersaturated*, then its chemical potential must coincide with the equilibrium potential of the grain:

$$\mu_v = \mu_0. \tag{19.33}$$

Thus, neglecting the term of $\mathrm{o}(|\rho-\rho_0|)$ in (19.32), we may write the normal configurational balance and the interfacial atomic balance, (19.26), with the approximation $\rho V = \rho_0 V$, in the form[62]

$$\left.\begin{aligned}\rho_0(\mu-\mu_0) &= -\phi(\vartheta)K + b(\vartheta)V,\\ \rho_0 V &= \frac{\partial}{\partial s}\left(L(\vartheta)\frac{\partial\mu}{\partial s}\right) + \boldsymbol{\jmath}\cdot\mathbf{n} - k(\vartheta)(\mu-\mu_0),\end{aligned}\right\} \tag{19.34}$$

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[62] In statical situations the configurational balance $(19.34)_1$ reduces to the classical relation

$$\rho_0(\mu-\mu_0) = -\phi(\vartheta)K$$

due to Herring (1951), whose derivation utilizes virtual variations of the position of the interface (cf. (i) of §1.1).

with ϕ as defined in (17.35). These equations, when combined, form a single equation for the interface

$$\rho_0^2 V = \left(\frac{\partial}{\partial s} L(\vartheta) \frac{\partial}{\partial s} - k(\vartheta)\right)(-\phi(\vartheta)K + b(\vartheta)V) + \rho_0\, \jmath \cdot \mathbf{n}. \tag{19.35}$$

Similarly, to within a term of $\mathrm{o}(|\rho - \rho_0|)$, we may rewrite Fick's law (19.30) as

$$\jmath = -\mathbf{D}_0 \nabla\rho, \tag{19.36}$$

and the bulk atomic balance has the approximate form

$$\dot{\rho} = \mathrm{div}\,(\mathbf{D}_0 \nabla\rho), \tag{19.37}$$

or, for D_{ij} the components of $\mathbf{D}_0$,

$$\dot{\rho} = D_{ij} \frac{\partial^2 \rho}{\partial x_i \partial x_j}.$$

Note the presence of two terms in the interface system (19.34) involving the velocity V:

- $b(\vartheta)V$, a dissipative term associated with the attachment kinetics of atoms at the free surface;
- $\rho_0 V$, a nondissipative term associated with the accretive transport of atoms to and from the bulk material at the interface.

The equations (19.34)–(19.37) govern the motion of the interface assuming small departures from equilibrium and a non-supersaturated vapor. These equations are complicated; two important special cases are described below.[63] For the remainder of this section we restrict attention to behavior close to equilibrium with vapor not supersaturated, and therefore work with the approximations (19.34) and (19.37).

(a) Interface motion by surface diffusion

The equations simplify considerably when bulk diffusion, evaporation-condensation, and kinetics are neglected. In this instance we omit the bulk diffusion equation (19.37), take $\jmath \cdot \mathbf{n} = 0$ at the interface, and take $b(\vartheta) = k(\vartheta) = 0$. Then (19.35) reduces to

$$\rho_0^2 V = -\frac{\partial}{\partial s}\Big(L(\vartheta) \frac{\partial}{\partial s}\Big(\phi(\vartheta)K\Big)\Big). \tag{19.38}$$

If we neglect the dependences of the coefficients on ϑ (that is, if we assume that the material response of the interface is well-approximated as isotropic), then this equation has the simple form

$$V = -A\, \frac{\partial^2 K}{\partial s^2}, \tag{19.39}$$

with

$$A = \frac{L\psi}{\rho_0^2},$$

and represents a fourth-order parabolic equation for the evolution of the interface.

---

[63] For an isotropic material, linearized versions of (19.39) and (19.40) (with $b = 0$) are discussed by Mullins (1957) in his discussion of thermal grooving. Cf. Davì and Gurtin (1990), who work within the present framework.

(b) Interface motion by evaporation-condensation and kinetics

If we neglect surface and bulk diffusion, and hence take $L(\vartheta) = 0$, drop the bulk diffusion equation (19.37), and take $\jmath \cdot \mathbf{n} = 0$ at the interface, then (19.34) combine to give

$$B(\vartheta)V = \big[\psi(\vartheta) + \psi''(\vartheta)\big]K, \tag{19.40}$$

with

$$B(\vartheta) = b(\vartheta) + \frac{\rho_0^2}{k(\vartheta)}.$$

Thus the equations reduce to the curvature-flow equation (17.32) (with $F = 0$), but now the kinetic term consists of two parts as represented by the constants $b(\vartheta)$ and $\rho_0^2/k(\vartheta)$. Note that the limit $k \to 0$ yields $B \to \infty$ and hence $V \to 0$, which is consistent with the underlying assumptions and the balances (19.34); in this limit the first of (19.34) yields $\rho_0(\mu - \mu_0) = -\phi(\vartheta)K$.

E Strained solid-vapor interfaces. Epitaxy

We now broadly generalize certain aspects of the discussion of solid-vapor interfaces presented in §19 to account for deformation, standard interfacial stress, multiple species of atoms, and adatoms. The inclusion of deformation is of particlar importance in discussions of epitaxy (Figure 15), as differences in lattice parameters between film and substrate can induce large stresses in the film.[64] Further, as discussed by Shchukin and Bimberg (1999) and demonstrated in the first-principles calculations of Van de Walle, Asta, and Voorhees (2002), standard interfacial stress may strongly influence the formation of surface patterns.[65]

We begin by characterizing the solid-vapor interaction through prescribed supplies of vapor atoms to the solid surface, a characterization that would seem appropriate to molecular beam epitaxy; later sections discuss more general constitutive relations for the solid-vapor interface.[66]

20 Configurational and standard forces

When considering the configurational forces that act on an isolated portion $\mathcal{P}$ of a body, it is generally necessary to account not only for forces that describe interactions between $\mathcal{P}$ and the remainder of the body but also for *internal forces* within $\mathcal{P}$, as such internal forces are of importance in the generation and evolution of defects. The situation for standard forces is quite different. There, internal forces are typically of little importance.

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[64] See, for example, the reviews of Stringfellow (1982), Cammarata and Sieradzki (1994), Ibach (1997), Politi, Grenet, Marty, Ponchet and Villain (2000), and Spaepen (2000). For sufficiently thick films, stresses may be induced by dislocations and other defects — even in the absence of a lattice mismatch between film and substrate. See Freund (1993) and Gao and Nix (1999) for studies of defects in films.

[65] Andreussi and Gurtin (1977) show that a decreasing dependence of standard surface stress on tensile surface strain leads to the wrinkling of a free surface. See, also, Shenoy and Freund (2002), who demonstrate the existence of an instability induced solely by surface strain, more precisely, by a compressive-strain induced nonconvexity in the dependence of surface energy on orientation.

[66] The results of Part E are small-deformation counterparts of those obtained by Fried and Gurtin (2003).

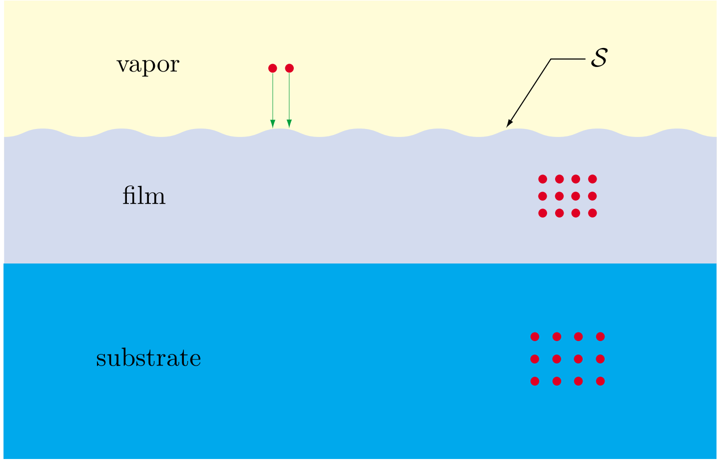

Figure 15: Schematic describing epitaxy. Undulations of the film-vapor interface typically result from instabilities induced, for example, by stresses arising from a mismatch in lattice parameters between film and substrate.

20.1 Configurational forces

For an interface separating solid and vapor phases, the configurational forces acting on a pillbox are identical to those arising in our discussion of grain-vapor interfaces. Thus, the configurational force balance (19.1) and its local consequences remain valid. In particular, we have the *normal configurational force balance*

$$\sigma K + \frac{\partial \tau}{\partial s} + g - \mathbf{n} \cdot \mathbf{C}\mathbf{n} = 0. \tag{20.1}$$

20.2 Standard forces

In addition to the standard stress $\mathbf{T}$ distributed over the solid, we allow for a *standard interfacial stress* $\mathbf{s}$ distributed continuously over the interface. We assume that the standard stress in the vapor vanishes: considering the solid as the $(-)$-phase and the vapor as the $(+)$-phase, it follows that $\mathbf{T}^+ = \mathbf{0}$. Thus we may, without danger of confusion, write $\mathbf{T} = \mathbf{T}^-$ for the interfacial limit of the stress in the solid.

Let $\mathcal{C} = \mathcal{C}(t)$ be an arbitrary interfacial pillbox. The portion of $\mathcal{S}$ exterior to $\mathcal{C}$ then exerts standard forces $-\mathbf{s}_a$ and $\mathbf{s}_b$ at $\mathbf{x}_a$ and $\mathbf{x}_b$,[67] while the solid exerts a traction $-\mathbf{T}\mathbf{n}$ on $\mathcal{C}$ across $\mathcal{C}^-$ (Figure 16). The standard torques acting on a pillbox are determined analogously.

In view of the preceding discussion, the *standard force and torque balances for* $\mathcal{C}$ take the form

$$\left.\begin{aligned} \mathbf{s}\Big|_a^b - \int\limits_{\mathcal{C}} \mathbf{T}\mathbf{n}\,ds &= \mathbf{0}, \\ \big[(\mathbf{x}-\mathbf{0}) \times \mathbf{s}\big]_a^b - \int\limits_{\mathcal{C}} (\mathbf{x}-\mathbf{0}) \times \mathbf{T}\mathbf{n}\,ds &= \mathbf{0}, \end{aligned}\right\} \tag{20.2}$$

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[67] I.e., e.g., $\mathbf{s}_a(t) = \mathbf{s}(\mathbf{x}_a(t), t)$

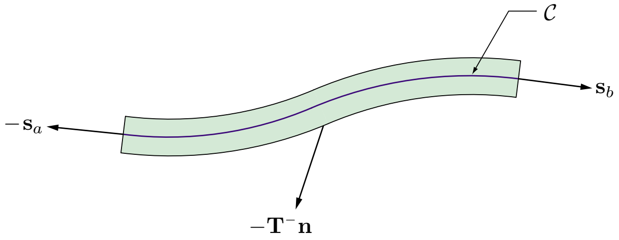

Figure 16: Standard forces on an interfacial pillbox $\mathcal{C}$ for a solid-vapor interface. The tangency of $\mathbf{s}_a$ and $\mathbf{s}_b$ follows from balance of torques.

which, since $\mathcal{C}$ is arbitrary, yield the interfacial force and torque balances (cf. Footnote 96, page 137

$$\frac{\partial \mathbf{s}}{\partial s} = \mathbf{Tn}, \qquad \mathbf{t} \times \mathbf{s} = \mathbf{0}. \tag{20.3}$$

The torque balance $(20.3)_2$ renders the stress vector $\mathbf{s}$ *tangent to the interface*; hence there is a scalar field $\bar{\sigma}$ such that

$$\mathbf{s} = \bar{\sigma}\mathbf{t}; \tag{20.4}$$

$\bar{\sigma}$ represents the *standard scalar interfacial stress*. Since $\partial\mathbf{t}/\partial s = K\mathbf{n}$, we can rewrite the interface condition $(20.3)_1$ as

$$\bar{\sigma}K\mathbf{n} + \frac{\partial \bar{\sigma}}{\partial s}\mathbf{t} = \mathbf{Tn}, \tag{20.5}$$

or equivalently, as

$$\bar{\sigma}K = \mathbf{n}\cdot\mathbf{Tn}, \qquad \frac{\partial \bar{\sigma}}{\partial s} = \mathbf{t}\cdot\mathbf{Tn}. \tag{20.6}$$

The first of (20.6) represents a counterpart, for a solid-vapor interface, of the classical Laplace–Young relation for a liquid-vapor interface.

21 Power

21.1 External power expenditures

Our discussion of power follows the discussions leading to (11.9) and (17.14). Consider an arbitrary interfacial pillbox $\mathcal{C} = \mathcal{C}(t)$. The configurational and standard stresses $\mathbf{c}$ and $\mathbf{s}$ act at the endpoints $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$ of $\mathcal{C}(t)$. As in our discussion of grain boundaries (cf. §17.2), we take $d\mathbf{x}_a/dt$ and $d\mathbf{x}_b/dt$ as the power-conjugate velocities for $\mathbf{c}$. For $\mathbf{s}$, we reason by analogy to our treatment of the power expended by standard tractions on a migrating control volume and take as power-conjugate velocities the motion velocities $d\mathbf{u}_a/dt$ and $d\mathbf{u}_b/dt$ following the evolution of the endpoints $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$ (cf. (15.17)). The portion $\mathcal{C}^-$ of the pillbox boundary adjacent to the solid is acted on by the tractions $-\mathbf{Cn}$ and $-\mathbf{Tn}$. As in our discussion of grain-vapor interfaces (cf. §19), we assume that the configurational traction $-\mathbf{Cn}$ is power-conjugate to the normal velocity $\mathbf{v}$. Further, consistent with our treatment of the power expended by standard tractions on a migrating control volume, we use as a power-conjugate velocity for $-\mathbf{Tn}$ the motion velocity $\overset{\square}{\mathbf{u}}$ following $\mathcal{S}(t)$ (cf. 11.8). Finally, the configurational force $\mathbf{g}$, being internal, expends no external power. The (net) *external power expended* on $\mathcal{C}(t)$ therefore has the form (cf. (19.5))

$$\Big[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}+\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b-\int\limits_{\mathcal{C}}\big(\mathbf{Cn}\cdot\mathbf{v}+\mathbf{Tn}\cdot\overset{\square}{\mathbf{u}}\big)\,ds. \tag{21.1}$$

21.2 Internal power expenditures. Power balance

First of all, using the identity $\partial V/\partial s=\overset{\square}{\vartheta}$ and the normal configurational force balance (20.1), it follows that (cf. (17.13) and (17.15))

$$\Big[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\Big]_a^b=\big[\sigma W+\tau V\big]_a^b=\big[\sigma W\big]_a^b+\int\limits_{\mathcal{C}}\big[\tau\overset{\square}{\vartheta}-(\sigma K+g-\mathbf{n}\cdot\mathbf{Cn})V\big]\,ds; \tag{21.2}$$

thus, since $\mathbf{v}=V\mathbf{n}$,

$$\Big[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\Big]_a^b-\int\limits_{\mathcal{C}}\mathbf{Cn}\cdot\mathbf{v}\,ds=\big[\sigma W\big]_a^b+\int\limits_{\mathcal{C}}\big[\tau\overset{\square}{\vartheta}-(\sigma K+g)V\big]\,ds. \tag{21.3}$$

Further, since $\mathbf{s}=\bar{\sigma}\mathbf{t}$ and $\varepsilon=\mathbf{t}\cdot\mathbf{e}$ (cf. 15.13)), we may use (15.17) to obtain

$$\Big[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b=\big[\mathbf{s}\cdot\overset{\square}{\mathbf{u}}+\bar{\sigma}\varepsilon W\big]_a^b. \tag{21.4}$$

Thus, since $\partial\overset{\square}{\mathbf{u}}/\partial s=\overset{\square}{\mathbf{e}}-KV\mathbf{e}$ (cf. (15.12))

$$\Big[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b=\big[\bar{\sigma}\varepsilon W\big]_a^b+\int\limits_{\mathcal{C}}\Big(\frac{\partial\mathbf{s}}{\partial s}\cdot\overset{\square}{\mathbf{u}}+\mathbf{s}\cdot(\overset{\square}{\mathbf{e}}-KV\mathbf{e})\Big)\,ds. \tag{21.5}$$

On the other hand, since $\mathbf{s}=\bar{\sigma}\mathbf{t}$ and $\mathbf{t}\cdot\overset{\square}{\mathbf{e}}=\overset{\square}{\varepsilon}-\gamma\overset{\square}{\vartheta}$ (cf. (15.15)),

$$\mathbf{s}\cdot\overset{\square}{\mathbf{e}}=\bar{\sigma}(\overset{\square}{\varepsilon}-\gamma\overset{\square}{\vartheta}); \tag{21.6}$$

therefore

$$\Big[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b=\big[\bar{\sigma}\varepsilon W\big]_a^b+\int\limits_{\mathcal{C}}\Big(\frac{\partial\mathbf{s}}{\partial s}\cdot\overset{\square}{\mathbf{u}}+\bar{\sigma}(\overset{\square}{\varepsilon}-\gamma\overset{\square}{\vartheta})-\bar{\sigma}\varepsilon KV\Big)\,ds \tag{21.7}$$

and, using the standard force balance $(20.3)_1$,

$$\Big[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b-\int\limits_{\mathcal{C}}\mathbf{Tn}\cdot\overset{\square}{\mathbf{u}}\,ds=\big[\bar{\sigma}\varepsilon W\big]_a^b+\int\limits_{\mathcal{C}}\big[\bar{\sigma}(\overset{\square}{\varepsilon}-\gamma\overset{\square}{\vartheta})-\bar{\sigma}\varepsilon KV\big]\,ds. \tag{21.8}$$

Combining (29.9) and (21.8) then yields the *power balance*

$$\begin{aligned}\Big[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}+\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\Big]_a^b&-\int\limits_{\mathcal{C}}\big(\mathbf{Cn}\cdot\mathbf{v}+\mathbf{Tn}\cdot\overset{\square}{\mathbf{u}}\big)\,ds\\&=\big[(\sigma+\bar{\sigma}\varepsilon)W\big]_a^b+\int\limits_{\mathcal{C}}\big[\bar{\sigma}\overset{\square}{\varepsilon}+\bar{\tau}\overset{\square}{\vartheta}-\big((\sigma+\bar{\sigma}\varepsilon)K+g\big)V\big]\,ds,\end{aligned} \tag{21.9}$$

where we have introduced the *reduced configurational shear*

$$\bar{\tau} = \tau - \bar{\sigma}\gamma. \tag{21.10}$$

The contributions to the internal power-expenditure, which should be compared with those (cf. §17.2) for a grain boundary, therefore have the form:

- The term $\big[(\sigma + \bar{\sigma}\varepsilon)W\big]_a^b$ (rather than $\big[\sigma W\big]_a^b$) represents power expended internally as material is added to $\mathcal{C}$ at its endpoints.
- The term $\bar{\sigma}\overset{\square}{\varepsilon}$ represents an expenditure of power associated with interfacial stretching.
- The term $\bar{\tau}\overset{\square}{\vartheta}$ (rather than $\tau\overset{\square}{\vartheta}$) represents an expenditure of power associated with changes in the orientation of the interface.[68]
- The term $-(\sigma + \bar{\sigma}\varepsilon)KV$ (rather than $-\sigma KV$) represents the expenditure of power associated with changes in interfacial length due to the curvature of the interface.

The expenditure $-gV$ is as discussed following (17.16).

22 Atomic transport

22.1 Atomic balance

As in our treatment of bulk atomic transport, we consider N species of atoms, labelled $\alpha = 1, 2, \ldots, N$. In addition to atomic densities ρ^α and fluxes $\boldsymbol{\jmath}^\alpha$ distributed over the solid, we account for *interfacial atomic densities* δ^α, (*scalar*) *interfacial atomic fluxes* h^α, and a prescribed supply r^α of atoms from the vapor to the solid surface. As before, we write $\rho^\alpha = \rho^{\alpha-}$ and $\boldsymbol{\jmath}^\alpha = \boldsymbol{\jmath}^{\alpha-}$ for the appropriate interfacial limits.

Let $\mathcal{C} = \mathcal{C}(t)$ be an arbitrary interfacial pillbox. Then surface diffusion in the portion of $\mathcal{S}$ exterior to $\mathcal{C}$ results in fluxes h_a^α and $-h_b^\alpha$ of α-atoms across $\mathbf{x}_a$ and $\mathbf{x}_b$, bulk diffusion results in a flow $\boldsymbol{\jmath}^\alpha \cdot \mathbf{n}$ of α-atoms from the solid into $\mathcal{C}$ across $\mathcal{C}^-$, and there is a flow r^α of α-atoms into $\mathcal{C}$ across $\mathcal{C}^+$ from the vapor (Figure 17). Hence, the net rate at which atoms are added to $\mathcal{C}$ by diffusive transport and through the vapor supply is

$$-h^\alpha\big|_a^b + \int\limits_{\mathcal{C}} (\boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha)\, ds. \tag{22.1}$$

Accretion of the portion of the interface exterior to $\mathcal{C}$ results in fluxes $-\delta_a^\alpha W_a$ and $\delta_b^\alpha W_b$ of α-atoms across $\mathbf{x}_a$ and $\mathbf{x}_b$,[69] while accretion of $\mathcal{C}$ results in a flow $-\rho^\alpha V$ of

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[68] One might, at first sight, be surprised at the term $\bar{\sigma}\gamma$ in the power expenditure $\bar{\tau}\vartheta^\square = (\tau - \bar{\sigma}\gamma)\vartheta^\square$. The presence of this term is a consequence of the fact that the interfacial stress $\mathbf{s}$ is tangent to the interface, but the interfacial strain-rate $\mathbf{e}^\square$ is not; because of this dichotomy the standard interfacial stress power is given by (21.6). In the *finite-strain theory* the interfacial stress $\mathbf{s}$ is tangent to the *deformed interface*; i.e., $\mathbf{s} = \bar{\sigma}\bar{\mathbf{t}}$ with $\bar{\mathbf{t}}$ the unit tangent to the deformed interface. If in that theory we let $\mathbf{u}$ denote the displacement relative to the reference configuration and consider ∇ and $\partial/\partial s$ as "material" operators and $(\ldots)^\square$ as the time-derivative following the interface as described materially, then, defining $\mathbf{e} = \partial\mathbf{u}/\partial s$, it follows, as before, that $\mathbf{e}^\square = (\varepsilon^\square - \gamma\vartheta^\square)\mathbf{t} + (\gamma^\square + \varepsilon\vartheta^\square)\mathbf{n}$. Thus in the finite-strain theory the interfacial stress power has the form $\mathbf{s}\cdot\mathbf{e}^\square = \bar{\sigma}(\varepsilon^\square - \gamma\vartheta^\square)(\bar{\mathbf{t}}\cdot\mathbf{t}) + (\gamma\bar{\mathbf{t}}\cdot + \varepsilon\vartheta^\square)(\bar{\mathbf{t}}\cdot\mathbf{n})$ and hence reduces to that used in the "small-deformation theory" in the small-strain limit, where $\bar{\mathbf{t}} \to \mathbf{t}$ and $\bar{\mathbf{n}} \to \mathbf{n}$. This lends further credence to the form of the power expenditures described here.

[69] I.e., e.g., $\delta_a^\alpha(t)W_a(t) = \delta^\alpha(\mathbf{x}_a(t), t)W_a(t)$.

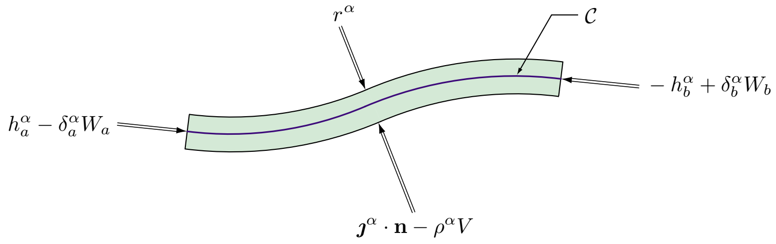

Figure 17: Transport of α-atoms into an interfacial pillbox $\mathcal{C}$.

α-atoms into $\mathcal{C}$ across $\mathcal{C}^-$ (Figure 17). Hence, the net rate at which atoms are added to $\mathcal{C}$ by accretive transport is

$$\big[\delta^\alpha W\big]_a^b - \int\limits_{\mathcal{C}} \rho^\alpha V\, ds. \tag{22.2}$$

In view of (22.1) and (22.2), the *atomic balance* for $\mathcal{C}$ takes the form

$$\frac{d}{dt}\int\limits_{\mathcal{C}(t)} \delta^\alpha\, ds = -\big[h^\alpha - \delta^\alpha W\big]_a^b + \int\limits_{\mathcal{C}(t)} (\boldsymbol{\jmath}^\alpha \cdot \mathbf{n} - \rho^\alpha V + r^\alpha) ds, \tag{22.3}$$

for each species α, and by virtue of the integral transport theorem (14.29), we have the local balance[70]

$$\overset{\square}{\delta}{}^\alpha + (\rho^\alpha - \delta^\alpha K)V = -\frac{\partial h^\alpha}{\partial s} + \boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha \tag{22.4}$$

on the interface for each species α.

22.2 Net atomic balance

Defining the net bulk and adatom densities and the *atomic volume* Ω through

$$\rho = \sum_{\beta=1}^{N} \rho^\beta, \qquad \delta = \sum_{\beta=1}^{N} \delta^\beta, \qquad \Omega = \frac{1}{\rho}, \tag{22.5}$$

and the net fluxes and supply through

$$\boldsymbol{\jmath} = \sum_{\beta=1}^{N} \boldsymbol{\jmath}^\beta, \qquad h = \sum_{\beta=1}^{N} h^\beta, \qquad r = \sum_{\beta=1}^{N} r^\beta, \tag{22.6}$$

we see that (22.4), when summed over all atomic species, yields the *net atomic balance*

$$\overset{\square}{\delta} + (\rho - \delta K)V = -\frac{\partial h}{\partial s} + \boldsymbol{\jmath} \cdot \mathbf{n} + r. \tag{22.7}$$

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[70] Comparison of the interfacial atomic balance (22.4) with its bulk counterpart (3.2) reveals several formal similarities and differences. The adatom densities and fluxes enter (22.4) in a manner completely analogous to that in which the bulk atomic densities and fluxes enter (3.2). Aside from the curvature term and the term accounting for the supply of atoms from the vapor, what most distinguishes (22.4) from (3.2) is the presence of interaction terms that account for the accretion and the flow of atoms between the interface and the bulk.

If adatom densities are neglected, then this net balance reduces to an equation for the normal velocity:

$$V = \Omega\Big(- \frac{\partial h}{\partial s} + \boldsymbol{\jmath} \cdot \mathbf{n} + r\Big). \tag{22.8}$$

For a substitutional alloy the lattice constraint (5.1) and the substitutional flux constraint (5.4) imply that $\rho = \rho^{\rm sites}$ and $\boldsymbol{\jmath} = \mathbf{0}$; hence the net atomic balance (22.7) takes the form

$$\overset{\square}{\delta} - \delta K V + \rho^{\rm sites} V = -\frac{\partial h}{\partial s} + r \tag{22.9}$$

whose sole coupling with the remaining field equations is through the kinematical terms V and K and, possibly, through the net flux h via additional constitutive information. If adatom densities are neglected, then (22.9) reduces to

$$V = \Omega\Big(- \frac{\partial h}{\partial s} + r\Big), \tag{22.10}$$

with

$$\Omega = \frac{1}{\rho^{\rm sites}}$$

constant. Thus, *when both adatom densities and surface diffusion are neglected, the evolution of an interface between a substitutional alloy and a vapor is governed solely by the atomic supply r.*

23 Free-energy imbalance

23.1 Energy flows due to atomic transport. Global imbalance

We assume that, if the material is unconstrained, then, for each species α, the chemical potential μ^α of the solid at its surface is the limiting value $\mu^{\alpha-}$ of the bulk chemical potential. For a substitutional alloy, the individual chemical potentials are not well defined in bulk; the relative chemical potentials must be used. We assume that, for any two species α and β, the limiting value $\mu^{\alpha\beta-}$ of the relative chemical potential is equal to the difference $\mu^\alpha - \mu^\beta$ of chemical potentials of the solid at its surface. Thus we have the *chemical interface-conditions*:

$$\left.\begin{aligned} \mu^\alpha &= \mu^{\alpha-} && \text{for an unconstrained material,} \\ \mu^\alpha - \mu^\beta &= \mu^{\alpha\beta-} && \text{for a substitutional alloy.} \end{aligned}\right\} \tag{23.1}$$

Motivated by the desire to describe processes such as molecular beam epitaxy, where atoms are *supplied directly at the film surface* and the vapor cannot simply be modeled as a reservoir, we introduce for each species α an external supply r^α of α-atoms, with concomitant supply $\mu^\alpha r^\alpha$ of energy. Therefore, in contrast to the discussion of more classical evaporation-condensation in §19, *we do not find it necessary to endow the vapor with a chemical potential.*[71] However, in §28 we will discuss a different class of vapor-interaction equations in which the vapor is considered as a reservoir for atoms endowed

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[71] The discussion of evaporation-condensation (§19, for a single species) was based on the tacit assumption that there exist an infinitesimally thin transition-layer across which there is flow r of atoms from a quiescent reservoir at chemical potential μ_v to the solid at potential μ, a flow proportional to $\mu_v - \mu$.

with chemical potentials μ_v^α, and for which r^α is no longer arbitrarily prescribed, but is, instead, a constitutive variable.

The energy flow into a migrating pillbox $\mathcal{C}$ due to atomic transport includes contributions associated with diffusion, accretion, and the supply of atoms from the vapor. The diffusion of α-atoms within the interface results in energy fluxes $\mu_a^\alpha h_a^\alpha$ and $-\mu_b^\alpha h_b^\alpha$ across $\mathbf{x}_a$ and $\mathbf{x}_b$; the diffusion of α-atoms in the solid results in an energy flow $\mu^\alpha \boldsymbol{\jmath}^\alpha \cdot \mathbf{n}$ across $\mathcal{C}^-$; the supply r^α of α-atoms from the vapor results in an energy flow $\mu^\alpha r^\alpha$. The net rate at which energy is supplied to $\mathcal{C}$ by diffusion and evaporation-condensation is hence given by (cf. (19.13))

$$-\sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha (\boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha)\, ds. \tag{23.2}$$

The motion of the interface results in energy fluxes $-\mu_a^\alpha \delta_a^\alpha W_a$ and $\mu_b^\alpha \delta_b^\alpha W_b$ associated with the accretive transport of α-atoms across the endpoints $\mathbf{x}_a$ and $\mathbf{x}_b$ of $\mathcal{C}$. In addition, the motion of the interface results in an energy flow $-\mu^\alpha \rho^{\alpha-} V$ associated with the accretive transport of α-atoms from the solid across $\mathcal{C}^-$. Hence, the net rate at which energy is added to $\mathcal{C}$ by the accretive transport of atoms is

$$\sum_{\alpha=1}^{N} \big[\mu^\alpha \delta^\alpha W\big]_a^b - \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha \rho^\alpha V\, ds. \tag{23.3}$$

Letting ψ denote the free energy of the interface and bearing in mind (21.1), (23.2), and (23.3), the *free-energy imbalance* for an arbitrary interfacial pillbox $\mathcal{C} = \mathcal{C}(t)$ takes the form

$$\begin{aligned}\underbrace{\frac{d}{dt}\int\limits_{\mathcal{C}} \psi\, ds}_{\text{free energy}} \;\le\; & \underbrace{\left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \mathbf{C}\mathbf{n} \cdot \mathbf{v}\, ds}_{\substack{\text{power expended}\\ \text{by configurational forces}}} + \underbrace{\left[\mathbf{s} \cdot \frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \mathbf{T}\mathbf{n} \cdot \overset{\square}{\mathbf{u}}\, ds}_{\substack{\text{power expended}\\ \text{by standard forces}}} \\ & + \underbrace{\sum_{\alpha=1}^{N} \big[\mu^\alpha(-h^\alpha + \delta^\alpha W)\big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha (\boldsymbol{\jmath}^\alpha \cdot \mathbf{n} - \rho^\alpha V + r^\alpha)\, ds}_{\text{energy flow by atomic transport}}. \end{aligned} \tag{23.4}$$

23.2 Dissipation inequality

In view of (21.9), (22.4), and the integral transport theorem (14.29), the free-energy imbalance (23.4) for $\mathcal{C}$ becomes

$$\begin{aligned} \int\limits_{\mathcal{C}} (\overset{\square}{\psi} - \psi K V)\, ds + \overbrace{\left[\Big(\psi - \sum_{\alpha=1}^{N} \mu^\alpha \delta^\alpha - \bar{\sigma}\varepsilon - \sigma\Big) W\right]_a^b}^{(\#)} & \\ \le \int\limits_{\mathcal{C}} \bigg(\bar{\sigma}\overset{\square}{\varepsilon} + \bar{\tau}\overset{\square}{\vartheta} - \Big(\sigma + \sum_{\alpha=1}^{N} \mu^\alpha \delta^\alpha + \bar{\sigma}\varepsilon\Big) K V - g V\bigg)\, ds & \\ - \sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha \Big(\overset{\square}{\delta}{}^\alpha + \frac{\partial h^\alpha}{\partial s}\Big)\, ds. & \end{aligned} \tag{23.5}$$

Since $\mathcal{C}$ is arbitrary, so also are the tangential velocities W_a and W_b of the endpoints of $\mathcal{C}$; thus, since the only term in (23.5) dependent on these velocities is the term (#), we have the *interfacial Eshelby relation*[72]

$$\sigma = \psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha - \bar{\sigma}\varepsilon, \tag{23.6}$$

which is an analog of the bulk Eshelby relation (12.15).

Since

$$\sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b = \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \left(\mu^\alpha \frac{\partial h^\alpha}{\partial s} + h^\alpha \frac{\partial \mu^\alpha}{\partial s} \right) ds, \tag{23.7}$$

we may use (23.6) to rewrite (23.5) as

$$\int\limits_{\mathcal{C}} \left(\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N} \left(\mu^\alpha \overset{\square}{\delta}{}^\alpha - h^\alpha \frac{\partial \mu^\alpha}{\partial s} \right) + gV \right) ds \le 0; \tag{23.8}$$

since $\mathcal{C}$ is arbitrary, this yields the *interfacial dissipation inequality*

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N} \left(\mu^\alpha \overset{\square}{\delta}{}^\alpha - h^\alpha \frac{\partial \mu^\alpha}{\partial s} \right) + gV \le 0. \tag{23.9}$$

When adatom densities are neglected, the "constraint" $\vec{\delta} = \vec{0}$ renders (23.9) independent of the chemical potentials μ^α; in this case, as in classical theories of continua, the chemical potentials μ^α on $\mathcal{S}$ should be considered as *indeterminate* (not constitutively determinate).

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[72] In the absence of standard interfacial stress, the configurational stress within the interface has the form $\mathbf{c} = \sigma\mathbf{t} + \tau\mathbf{n}$, wit $\sigma = \psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha$. This result, which, like the relation $\sigma = \psi$ arising in our discussion of grain boundaries (cf. (17.21)), has a purely energetic structure. In this case it is legitimate to view σ as an interfacial tension. But when standard stress is taken into account this interpretation is no longer valid. To explain this, consider the three-dimensional theory. There the interface is a *surface* $\mathcal{S}$ and the interfacial stresses are tensorial. The standard stress $\mathbf{T}$ is a symmetric, tangential tensor field on $\mathcal{S}$: in terms of Cartesian coordinates with subscripts 1 and 2 associated with the tangent plane at a point $\mathbf{x}$ on $\mathcal{S}$, the component matrix of $\mathbf{T}(\mathbf{x})$ has the form

$$\begin{bmatrix} T_{11} & T_{12} & 0 \\ T_{12} & T_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(cf., e.g., Gurtin and Murdoch (1975) and the review of Shchukin and Bimberg (1999)). On the other hand, the configurational surface stress is a tensor field with both normal and tangential parts; the tangential part, which is the part relevant to a discussion of surface tension and which might be compared to the vector field $\mathbf{c}$ of the two-dimensional theory, has the form

$$\mathbf{C}_{\tan} = \left(\psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha \right) \mathbf{P} - (\nabla_{\mathcal{S}} \mathbf{u})^\top \mathbf{T},$$

where $\nabla_{\mathcal{S}}$ is the surface gradient on $\mathcal{S}$, and $\mathbf{P}$, the projector onto $\mathcal{S}$, has component matrix at $\mathbf{x}$ of the form

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Only in the absence of standard surface stress does $\mathbf{C}_{\tan}$ take the form $\mathbf{C}_{\tan} = \big(\psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha\big)\mathbf{P}$ of a pure tension; otherwise, $\mathbf{C}_{\tan}$ *is a generic tangential tensor field.* One could, of course, think of $\psi - \delta^\alpha \mu^\alpha$ as a surface tension, and this is often done (cf. Shchukin and Bimberg, 1999), but what is more cogent is the form of $\mathbf{C}_{\tan}$, which should be compared with the form $\mathbf{C} = \big(\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha\big)\mathbf{1} - (\nabla \mathbf{u})^\top \mathbf{T}$ of the bulk Eshelby tensor established in §12, a comparison that identifies $\mathbf{C}_{\tan}$ as an *Eshelby tensor* for the surface $\mathcal{S}$ (cf. Gurtin, 1995, 2000).

24 Normal configurational force balance revisited

24.1 Mechanical potential $\mathcal{F}$

Since we account for deformation and atomic transport, the bulk configurational stress $\mathbf{C}$ is determined by the Eshelby relation (12.15):

$$\mathbf{C} = \Bigl(\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha\Bigr)\mathbf{1} - (\nabla\mathbf{u})^\top\mathbf{T}.$$

Thus, in view of the interfacial Eshelby relation (23.6), we may write the normal configurational force balance (20.1) in a form,

$$\sum_{\alpha=1}^{N} (\rho^\alpha - \delta^\alpha K)\mu^\alpha = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - (\psi - \bar\sigma\varepsilon)K - \frac{\partial\tau}{\partial s} - g, \tag{24.1}$$

which equates terms representing transport to those that are purely mechanical. Thus, for

$$\mathcal{F} \overset{\text{def}}{=} \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - (\psi - \bar\sigma\varepsilon)K - \frac{\partial\tau}{\partial s} - g, \tag{24.2}$$

we may rewrite the normal configurational force balance in the form

$$\sum_{\alpha=1}^{N} (\rho^\alpha - \delta^\alpha K)\mu^\alpha = \mathcal{F}; \tag{24.3}$$

we refer to $\mathcal{F}$ as the *mechanical potential*.

When $g = 0$, $\mathcal{F}$ represents the variational derivative of the total free energy with respect to variations of the position of the interface, holding the composition fixed. This field appears first in the works of Wu (1996), Freund (1998), and Norris (1998), who, working within a framework that does not explicitly account for atomic species, follow Herring (1951) (cf. our discussion of (1.1)) in viewing the surface gradient of this potential as the driving force for surface diffusion.[73] That (24.3) is compatible with this point of view follows upon neglecting adatom densities and restricting attention to a single species. A useful alternative form for $\mathcal{F}$ follows upon noting that, since $\tau = \bar\sigma\gamma + \bar\tau$ (cf. (21.10)) and $\partial\bar\sigma/\partial s = \mathbf{t}\cdot\mathbf{Tn} = \mathbf{n}\cdot\mathbf{Tt}$ (cf. (20.6)),

$$\frac{\partial\tau}{\partial s} = \frac{\partial\bar\sigma}{\partial s}\gamma + \bar\sigma\frac{\partial\gamma}{\partial s} + \frac{\partial\bar\tau}{\partial s} = \gamma\mathbf{n}\cdot\mathbf{Tt} + \bar\sigma\frac{\partial\gamma}{\partial s} + \frac{\partial\bar\tau}{\partial s}; \tag{24.4}$$

hence

$$\mathcal{F} = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt} - (\psi - \bar\sigma\varepsilon)K - \bar\sigma\frac{\partial\gamma}{\partial s} - \frac{\partial\bar\tau}{\partial s} - g. \tag{24.5}$$

Another form for $\mathcal{F}$ and one that we find interesting, but do not use, is

$$\mathcal{F} = \Phi + \varepsilon\,\mathrm{tr}\,\mathbf{T} - \psi K - \bar\sigma\frac{\partial\gamma}{\partial s} - \frac{\partial\bar\tau}{\partial s} - g, \tag{24.6}$$

with Φ the free enthalpy (cf. (7.15)). The verification of (24.6) involves the relations $\mathbf{1} = \mathbf{t}\otimes\mathbf{t} + \mathbf{n}\otimes\mathbf{n}$, $\mathbf{e} = (\nabla\mathbf{u})\mathbf{t} = \varepsilon\mathbf{t} + \gamma\mathbf{n}$, and $\bar\sigma K = \mathbf{n}\cdot\mathbf{Tn}$.

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[73] Related studies are those of Asaro and Tiller (1972), Rice and Chuang (1981), and Spencer, Voorhees, and Davis (1991), who restrict attention to a surface free-energy that is constant. See, also, Freund and Jonsdottir (1993), Grilhe (1993), Gao (1994), Freund (1995), Spencer and Meiron (1994), Yang and Srolovitz (1994), Suo and Wang (1997), Wang and Suo (1997), Xia, Bower, Suo and Shih (1997), Léonard and Desai (1998), Gao and Nix (1999), Shchukin and Bimberg (1999), Danescu (2001), Spencer, Voorhees, and Tersoff (2001), Xiang and E (2002).

24.2 Substitutional alloys. Interfacial chemical potentials μ^α in terms of the relative chemical-potentials $\mu^{\alpha\beta}$

For a substitutional alloy the bulk densities ρ^α are subject to the lattice constraint (5.1). As a consequence of this constraint, the individual chemical potentials μ^α in bulk *away from the interface* are not well-defined; only the relative chemical potentials $\mu^{\alpha\beta}$ have meaning. At the interface the limiting values of these relative potentials are related to the chemical potentials of the solid at the interface through the chemical interface-conditions (23.1), $\mu^\alpha - \mu^\beta = \mu^{\alpha\beta-}$. Thus, limiting our discussion to the interface and writing $\mu^{\alpha\beta} = \mu^{\alpha\beta-}$, we have the interface condition

$$\mu^\alpha - \mu^\beta = \mu^{\alpha\beta}. \tag{24.7}$$

On the other hand,

there is no lattice constraint for the diffusion of adatoms

and, as is clear from (24.1), it is the individual chemical potentals μ^α that enter the basic equations on $\mathcal{S}$. In accord with this, we now show that the individual chemical potentials on $\mathcal{S}$ are uniquely determined — by what is essentially the normal configurational force balance — when the relative chemical potentials are known in the film.

If we define *effective densities*

$$\rho^\alpha_{\text{ef}} = \rho^\alpha - \delta^\alpha K, \tag{24.8}$$

then (24.3) becomes

$$\rho^\alpha_{\text{ef}}\mu^\alpha = \mathcal{F}. \tag{24.9}$$

It is convenient to define an *effective net density* ρ_{ef}, *effective concentrations* c^α_{ef}, and an *effective net atomic volume* Ω_{ef} through

$$\rho_{\text{ef}} = \sum_{\alpha=1}^{N} \rho^\alpha_{\text{ef}}, \qquad c^\alpha_{\text{ef}} = \frac{\rho^\alpha_{\text{ef}}}{\rho_{\text{ef}}}, \qquad \Omega_{\text{ef}} = \frac{1}{\rho_{\text{ef}}}. \tag{24.10}$$

Then, choosing an atomic species α arbitrarily, we may use an argument of Larché and Cahn[74] to express μ^α in terms of the $N-1$ relative chemical-potentials $\mu^{\alpha\beta}$ and the sum $\rho^\beta_{\text{ef}}\mu^{\beta\alpha}$. Since $\mu^\beta = \mu^\alpha - \mu^{\alpha\beta}$,

$$\sum_{\beta=1}^{N} \rho^\beta_{\text{ef}}\mu^\beta = \sum_{\beta=1}^{N} \rho^\beta_{\text{ef}}(\mu^\alpha - \mu^{\alpha\beta}) = \rho_{\text{ef}}\mu^\alpha - \sum_{\beta=1}^{N} \rho^\beta_{\text{ef}}\mu^{\alpha\beta},$$

and the normal configurational force balance (24.9) yields an identity,

$$\begin{aligned}\mu^\alpha &= \sum_{\beta=1}^{N} c^\beta_{\text{ef}}\mu^{\alpha\beta} + \Omega_{\text{ef}}\mathcal{F} \\ &= \sum_{\beta=1}^{N} c^\beta_{\text{ef}}\mu^{\alpha\beta} + \Omega_{\text{ef}}\left\{\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - (\psi - \bar{\sigma}\varepsilon)K - \frac{\partial\tau}{\partial s} - g\right\},\end{aligned} \tag{24.11}$$

which, for a substitutional alloy, gives the individual chemical potential μ^α of each species α in terms of the chemical-potentials $\mu^{\alpha\zeta}$ of α relative to all other species ζ. We refer to (24.11) as the *configurational-chemistry relations*.

Conversely, if (24.11) holds for all α, then $\mu^{\alpha\beta} = \mu^\alpha - \mu^\beta$ and (24.9) is satisfied. Thus we have the following result:

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[74] Larché and Cahn (1985, Appendix 1).

EQUIVALENCY THEOREM FOR SUBSTITUTIONAL ALLOYS The configurational-chemistry relations,

$$\mu^{\alpha} = \sum_{\beta=1}^{N} c_{\mathrm{ef}}^{\beta} \mu^{\alpha\beta} + \Omega_{\mathrm{ef}} \mathcal{F}, \qquad \alpha = 1, 2, \dots, N, \tag{24.12}$$

are satisfied if and only if *both* the normal configurational force balance,

$$\sum_{\alpha=1}^{N} (\rho^{\alpha} - \delta^{\alpha} K) \mu^{\alpha} = \mathcal{F},$$

and the relative chemical-potential relations,

$$\mu^{\alpha\beta} = \mu^{\alpha} - \mu^{\beta}, \qquad \alpha, \beta = 1, 2, \dots, N,$$

are satisfied.

Thus, *when discussing substitutional alloys we may equally well use the normal configurational force balance or the onfigurational-chemistry relations, provided that in the former case we account also for the relative chemical-potential relations.* This result is central to what follows.

25 Constitutive equations for the interface

Since there is no lattice constraint for the diffusion of adatoms along the interface, the discussion of this section is valid whether or not the associated bulk material is subject to a lattice constraint.

25.1 General relations

Our discussion of constitutive equations is guided by the interfacial dissipation inequality (23.9), viz.,

$$\overset{\square}{\psi} - \bar{\sigma} \overset{\square}{\varepsilon} - \bar{\tau} \overset{\square}{\vartheta} - \sum_{\alpha=1}^{N} \left(\mu^{\alpha} \overset{\square}{\delta}{}^{\alpha} - h^{\alpha} \frac{\partial \mu^{\alpha}}{\partial s} \right) + gV \leq 0,$$

and follows the format set out in §17.8.

Let

$$\vec{\delta} = (\delta^{1}, \delta^{2}, \dots, \delta^{N}), \qquad \vec{\mu} = (\mu^{1}, \mu^{2}, \dots, \mu^{N}).$$

Granted essentially linear dissipative response, we consider constitutive equations giving[75]

$$\psi, \ \bar{\sigma}, \ \bar{\tau}, \ \vec{\mu} \ \text{ as functions of } \ (\varepsilon, \vartheta, \vec{\delta}\,)$$

in conjunction with constititutive equations for h^{α} and g of the specific form

$$\left. \begin{aligned} h^{\alpha} &= -\sum_{\beta=1}^{N} L^{\alpha\beta} \frac{\partial \mu^{\beta}}{\partial s} - \ell^{\alpha} V, \\ g &= -\sum_{\alpha=1}^{N} B^{\alpha} \frac{\partial \mu^{\alpha}}{\partial s} - bV, \end{aligned} \right\} \tag{25.1}$$

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[75] Since $\varepsilon = \mathbf{t} \cdot (\nabla \mathbf{u}) \mathbf{t}$ is invariant for transformations of the form $\nabla \mathbf{u} \mapsto \nabla \mathbf{u} + \mathbf{W}$, with $\mathbf{W}$ an arbitrary skew-symmetric tensor, the constitutive equations considered here have the requisite invariance under infinitesimal changes of observer.

with coefficients possibly dependent on $(\varepsilon, \vartheta, \vec{\delta}\,)$.[76]

Then, appealing to the discussion of §17.8, we find that the free energy determines the standard scalar interfacial stress, the reduced shear, and the chemical potentials through the relations

$$\left.\begin{aligned} \bar{\sigma} &= \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \varepsilon}, \\ \bar{\tau} &= \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \vartheta}, \\ \mu^{\alpha} &= \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)}{\partial \delta^{\alpha}}, \end{aligned}\right\} \tag{25.2}$$

and that the coefficient matrix of the equations (25.1) must be positive semi-definite.

In view of (21.10), $\tau = \bar{\sigma}\gamma + \bar{\tau}$ and $(25.2)_{1,2}$ yield an auxiliary constitutive relation showing that the configurational shear τ depends also on the interfacial shear-strain γ. An increased understanding of $\bar{\tau}$ is achieved by introducing

$$\tilde{\psi}(\mathbf{e}, \vartheta, \vec{\delta}\,) = \hat{\psi}(\mathbf{e}\cdot\mathbf{t}, \vartheta, \vec{\rho}\,) = \hat{\psi}(\varepsilon, \vartheta, \vec{\rho}\,). \tag{25.3}$$

Specifially, differentiating with respect to ϑ, we obtain

$$\frac{\partial \tilde{\psi}(\mathbf{e}, \vartheta, \vec{\delta}\,)}{\partial \vartheta} = \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\rho}\,)}{\partial \varepsilon}\,\frac{\partial (\mathbf{e}\cdot\mathbf{t})}{\partial \vartheta} + \frac{\partial \hat{\psi}(\varepsilon, \vartheta, \vec{\rho}\,)}{\partial \vartheta}, \tag{25.4}$$

which, by $(25.2)_{1,2}$, (14.1), the definition $(15.10)_2$ of γ, and the relation $\tau = \bar{\sigma}\gamma + \bar{\tau}$ gives

$$\frac{\partial \tilde{\psi}(\mathbf{e}, \vartheta, \vec{\rho}\,)}{\partial \vartheta} = \tau. \tag{25.5}$$

Thus, whereas $\bar{\tau}$ accounts for configurational shear arising solely from changes of interfacial orientation, τ accounts also for configurational shear generated by tensile stretching of the interface.

Within the context of small deformations, it is reasonable to restrict attention to free energies that are quadratic in the tensile strain ε and, thus, have the form

$$\hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,) = \psi_0(\vartheta, \vec{\delta}\,) + w(\varepsilon, \vartheta, \vec{\delta}\,), \tag{25.6}$$

with strain energy w of the form

$$w(\varepsilon, \vartheta, \vec{\delta}\,) = \bar{\sigma}_0(\vartheta, \vec{\delta}\,)\varepsilon + \tfrac{1}{2}k(\vartheta, \vec{\delta}\,)\varepsilon^2. \tag{25.7}$$

Here, $\psi_0(\vartheta, \vec{\delta}\,)$ is the strain-free surface energy, $\bar{\sigma}_0(\vartheta, \vec{\delta}\,)$ is the residual surface stress, and $k(\vartheta, \vec{\delta}\,)$ is the surface elasticity. Because atoms on the free surface are not bonded to the maximum number of nearest neighboring atoms, a residual surface stress is to be expected (Shchukin and Bimberg, 1999).

The expressions for $\bar{\sigma}$, $\bar{\tau}$, and μ^{α} determined by (25.2) under this specialization are straightforward. However, the final field equations are cumbersome. For this reason, we work with the generic expression $\psi = \hat{\psi}(\varepsilon, \vartheta, \vec{\delta}\,)$.

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[76] The experiments of Barvosa-Carter and Aziz (2001) and first-principles calculations of Van de Walle, Asta, and Voorhees (2002) suggest that strain dependence of the mobilities may be important.

25.2 Uncoupled relations for h^α and g

A simplified form of (25.1) would take the classical Fickean form

$$h^\alpha = -\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s} \tag{25.8}$$

in conjunction with the simple kinetic relation

$$g = -bV \tag{25.9}$$

that formed the basis of our discussion of grain boundaries. Here the coefficients $L^{\alpha\beta}$, which represent the mobility of the atoms on the interface, are presumed to form a positive semi-definite matrix, while $b \geq 0$. The dissipation then has the form

$$\mathcal{D} = \underbrace{\sum_{\alpha,\beta=1}^{N} L^{\alpha\beta}(\varepsilon,\vartheta,\vec{\delta}\,)\frac{\partial\mu^\alpha}{\partial s}\frac{\partial\mu^\beta}{\partial s}}_{\text{dissipation induced by surface diffusion}} \quad + \underbrace{b(\varepsilon,\vartheta,\vec{\delta}\,)V^2}_{\substack{\text{dissipation accompany-}\\\text{ing the attachment}\\\text{of vapor atoms}}} \quad . \tag{25.10}$$

We henceforth work with the uncoupled relations (25.8) *and* (25.9). This choice is made for convenience only; the generalization of the resulting equations to situations involving the more general coupled relations (25.1) is straightforward. An argument in support of the uncoupled relations is that (25.8) represents the flow of atoms *within the interface*, while (25.9) represents *an interaction of the solid surface with the vapor environment.* But we do believe that there might be situations in which there is *coupling* between the diffusive adatom-flow described by $\vec{h}$ and the solid-vapor interaction as described by g. Such coupling might be especially important when studying film growth, since the kinetics of the deposition process and the small length scales involved render this process of a nature far different than the processes leading, for example, to relations that describe classical surface diffusion.

26 Governing equations at the interface

26.1 Equations with adatom densities included

While generally considered negligible, adatom densities would seem important in describing the segregation of atomic species at a solid-vapor interface.[77] Moreover, the parabolic nature of the atomic balances when adatom densities are included might serve to regularize the overall system of partial differential equations, which is typically unstable. Regardless of whether adatom *densities* are included or neglected, our theory accounts for the presence of adatoms and their diffusion via the interfacial atomic balances.

(a) General relations

The basic interfacial balances are the standard force-balance, the atomic balance, and the normal configurational force balance; for the case of a substitutional alloy, the configurational balance with the relations for the relative chemical potentials together are

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[77] Spencer, Voorhees, and Tersoff (2001) assert that: "surface segregation can make the surface composition differ from the bulk and the overall surface density of components could be nonuniform." See also Lu and Suo (2001, 2002), who use a Cahn–Hilliard type theory to study segregation of a planar two-phase monolayer on a strained substrate.

equivalent to the configurational-chemistry relations together with the relations for the relative chemical potentials. The standard force and atomic balances are (cf. §20.2, §22)

$$\left.\begin{aligned}\mathbf{Tn} &= \bar{\sigma}K\mathbf{n} + \frac{\partial\bar{\sigma}}{\partial s}\mathbf{t},\\ \overset{\square}{\delta}{}^{\alpha} + (\rho^{\alpha} - \delta^{\alpha}K)V &= -\frac{\partial h^{\alpha}}{\partial s} + \boldsymbol{\jmath}^{\alpha}\cdot\mathbf{n} + r^{\alpha},\end{aligned}\right\} \tag{26.1}$$

while the normal configurational force balance and the configurational-chemistry relations for substitutional alloys take the respective forms

$$\sum_{\alpha=1}^{N}(\rho^{\alpha} - \delta^{\alpha}K)\mu^{\alpha} = \mathcal{F}, \qquad \mu^{\alpha} = \sum_{\beta=1}^{N} c_{\mathrm{ef}}^{\beta}\mu^{\alpha\beta} + \Omega_{\mathrm{ef}}\mathcal{F} \tag{26.2}$$

(cf. (24.3), (24.5), (24.12)), with

$$\mathcal{F} = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt} - (\psi - \bar{\sigma}\varepsilon)K - \bar{\sigma}\,\frac{\partial\gamma}{\partial s} - \frac{\partial\bar{\tau}}{\partial s} - g. \tag{26.3}$$

As asserted in the equivalency theorem for substitutional alloys (page 98), for such materials imposing $(26.2)_2$ ensures satisfaction of both $(26.2)_1$ and the relations $\mu^{\alpha\beta} = \mu^{\alpha} - \mu^{\beta}$.

The balances are coupled to the constitutive relations

$$\bar{\sigma} = \frac{\partial\hat{\psi}(\varepsilon,\vartheta,\vec{\delta}\,)}{\partial\varepsilon}, \qquad \bar{\tau} = \frac{\partial\hat{\psi}(\varepsilon,\vartheta,\vec{\delta}\,)}{\partial\vartheta}, \qquad \mu^{\alpha} = \frac{\partial\hat{\psi}(\varepsilon,\vartheta,\vec{\delta}\,)}{\partial\delta^{\alpha}} \tag{26.4}$$

(cf. §25.2) and

$$h^{\alpha} = -\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^{\beta}}{\partial s}, \qquad g = -bV. \tag{26.5}$$

In (26.5) the constitutive moduli $L^{\alpha\beta}$ and g are possibly dependent on $(\varepsilon,\vartheta,\vec{\delta}\,)$.

By (26.4), writing

$$\psi(\varepsilon,\vartheta,\vec{\delta}\,) = \hat{\psi}(\varepsilon,\vartheta,\vec{\delta}\,)$$

and omitting the arguments $(\varepsilon,\vartheta,\vec{\delta}\,)$, we find that

$$\begin{aligned}&(\psi - \bar{\sigma}\varepsilon)K + \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{\tau}}{\partial s}\\ &\qquad = \left(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\right)K + \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\,\frac{\partial\varepsilon}{\partial s} + \frac{\partial\psi}{\partial\varepsilon}\,\frac{\partial\gamma}{\partial s} + \sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^{\beta}\partial\vartheta}\,\frac{\partial\delta^{\beta}}{\partial s},\end{aligned} \tag{26.6}$$

Thus, combining the interfacial balances and the constitutive relations, we arrive at the standard force and atomic balances

$$\left.\begin{aligned}\mathbf{Tn} &= \frac{\partial\psi}{\partial\varepsilon}K\mathbf{n} + \left(\frac{\partial^2\psi}{\partial\varepsilon^2}\,\frac{\partial\varepsilon}{\partial s} + \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}K + \sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\varepsilon\partial\delta^{\beta}}\,\frac{\partial\delta^{\beta}}{\partial s}\right)\mathbf{t},\\ \overset{\square}{\delta}{}^{\alpha} + (\rho^{\alpha} - \delta^{\alpha}K)V &= \frac{\partial}{\partial s}\left(\sum_{\beta=1}^{N} L^{\alpha\beta}\,\frac{\partial\mu^{\beta}}{\partial s}\right) + \boldsymbol{\jmath}^{\alpha}\cdot\mathbf{n} + r^{\alpha},\end{aligned}\right\} \tag{26.7}$$

and find that the mechanical potential $\mathcal{F}$ used in describing the normal configurational force balance and configurational-chemistry relations (26.2) has the form

$$\begin{aligned}\mathcal{F} &= \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}\\ &\quad - \Big(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\Big)K - \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\frac{\partial\varepsilon}{\partial s} - \frac{\partial\psi}{\partial\varepsilon}\frac{\partial\gamma}{\partial s} - \sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s} + bV. \qquad (26.8)\end{aligned}$$

Consider the atomic balance $(26.7)_2$. If we define moduli

$$\kappa_{\mathrm{ad}}^{\alpha\beta} = \frac{\partial^2\psi}{\partial\delta^\alpha\partial\delta^\beta}, \qquad D_{\mathrm{ad}}^{\alpha\beta} = \sum_{\gamma=1}^{N} L^{\alpha\gamma}\kappa_{\mathrm{ad}}^{\gamma\beta}, \tag{26.9}$$

with $D_{\mathrm{ad}}^{\alpha\beta}$ the *surface diffusivity of* α *relative to* β, then the interfacial-diffusion term in (26.7) has the form

$$\frac{\partial}{\partial s}\bigg(\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\bigg) = \frac{\partial}{\partial s}\bigg\{\sum_{\beta=1}^{N} D_{\mathrm{ad}}^{\alpha\beta}\frac{\partial\delta^\beta}{\partial s} + \sum_{\beta=1}^{N} L^{\alpha\beta}\bigg(\frac{\partial^2\psi}{\partial\delta^\beta\partial\varepsilon}\frac{\partial\varepsilon}{\partial s} + \frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\vartheta}{\partial s}\bigg)\bigg\}. \tag{26.10}$$

Thus, bearing in mind the term $(\delta^\alpha)^{\Box}$ in $(26.7)_2$, we note that if the matrix with entries $D_{\mathrm{ad}}^{\alpha\beta}$ is positive definite, then $(26.7)_2$, as a system of partial differential equations for the adatoms δ^α (considering the remaining fields as fixed), is *parabolic* and as such should have a *regularizing* effect on the evolution of the interface.

(b) Chemical potentials at the surface. Chemical compatibility

For an *unconstrained material*, the chemical potentials μ^α of the surface, needed in the normal configurational force balance $(26.2)_1$, may be determined directly through the limit relation

$$\mu^\alpha = \mu^{\alpha-}. \tag{26.11}$$

On the other hand, these chemical potentials are given by the relations $\mu^\alpha = \partial\psi/\partial\delta^\alpha$ and by the limit relations (26.11) supplemented by the bulk constitutive relations (7.17):

$$\mu^\alpha = \frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\alpha} = \frac{\partial\tilde\Phi(\mathbf{T},\vec\rho\,)}{\partial\rho^\alpha}. \tag{26.12}$$

Similarly, for a *substitutional alloy*, the relative chemical potentials $\mu^{\alpha\beta}$ on the solid surface may be determined through the limit relation

$$\mu^{\alpha\beta} = \mu^{\alpha\beta-}, \tag{26.13}$$

and, in addition, (9.36) yields

$$\mu^{\alpha\beta} = \frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\alpha} - \frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\beta} = \frac{\partial\tilde\Phi^{(\beta)}(\mathbf{T},\vec\rho\,)}{\partial\rho^\alpha}; \tag{26.14}$$

Granted a knowledge of these relative chemical potentials, the surface values of the chemical potentials μ^α are given by the configurational-chemistry relations $(26.2)_2$, a procedure that ensures satisfaction of the normal configurational force balance.

Equations (26.12) and (26.14) might be termed *chemical-compatibility relations* as they represent compatibility between the composition of the interface and that of the bulk material. When

$$\left(\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^1},\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^2},\ldots,\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^N}\right)$$

is an invertible function of $\vec\delta$, (26.12) furnishes explicit relations giving the adatom densities as functions of the bulk densities (as well as ε, ϑ, and $\mathbf{T}$).[78] A similar assertion cannot be made for (26.14). Note that, for *mechanically simple materials*, (26.12) and (26.14) have the respective forms (cf. (7.34), (9.63), (9.64))

$$\mu^\alpha=\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\alpha}=\mu_0^\alpha(\vec\rho\,)-\mathbf{N}^\alpha\cdot\mathbf{T} \tag{26.15}$$

and

$$\mu^{\alpha\beta}=\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\alpha}-\frac{\partial\hat\psi(\varepsilon,\vartheta,\vec\delta\,)}{\partial\delta^\beta}=\mu_0^\alpha(\vec\rho\,)-\mu_0^\beta(\vec\rho\,)-\mathbf{N}^{\alpha\beta}\cdot\mathbf{T}. \tag{26.16}$$

(c) Equations neglecting standard surface stress ($\mathbf{s}\equiv\mathbf{0}$)

In this case $\psi=\psi(\vartheta,\vec\delta\,)$ and the standard force-balance $(26.7)_1$ has the simple form

$$\mathbf{Tn}=\mathbf{0}, \tag{26.17}$$

asserting that the solid-vapor interface be (standard) *traction-free*, and the atomic balance $(26.7)_2$ becomes

$$\overset{\scriptscriptstyle\square}{\delta}{}^\alpha+(\rho^\alpha-\delta^\alpha K)V=\frac{\partial}{\partial s}\left(\sum_{\beta=1}^{N}L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\right)+\boldsymbol{\jmath}^\alpha\cdot\mathbf{n}+r^\alpha. \tag{26.18}$$

Further, the normal configurational force balance (26.8) for unconstrained materials and the configurational-chemistry relations for substitutional alloys have the respective forms

$$\sum_{\alpha=1}^{N}(\rho^\alpha-\delta^\alpha K)\mu^\alpha=\Psi-\left(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}\right)K-\sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s}+bV \tag{26.19}$$

and

$$\mu^\alpha=\sum_{\beta=1}^{N}c_{\rm ef}^\beta\mu^{\alpha\beta}+\Omega_{\rm ef}\left\{\Psi-\left(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}\right)K-\sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s}+bV\right\}. \tag{26.20}$$

We now specialize the normal configurational force balance and the configurational-chemistry relations to mechanically simple materials. For such materials the relation (7.31) for the free energy and the Gibbs relation (8.3) yield

$$\Psi=\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]+\sum_{\alpha=1}^{N}\rho^\alpha\mu_0^\alpha(\vec\rho\,); \tag{26.21}$$

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[78] Spencer, Voorhees and Tersoff (2001) do not consider a dependence of interfacial free-energy on adatom densities, but instead posit constitutive relations of the form $\delta^\alpha=\lambda\rho^\alpha$, with λ constant. For a nondeformable, unconstrained material, relations of this form would follow from (26.12), granted interfacial and bulk free-energies of the form $\psi=\frac{1}{2}\Lambda\sum_{\alpha=1}^{N}(\delta^\alpha)^2$ and $\Psi=\frac{1}{2}\lambda\Lambda\sum_{\alpha=1}^{N}(\rho^\alpha)^2$, with Λ constant.

hence the normal configurational force balance (26.19) for an *unconstrained, mechanically simple material* takes the form

$$\sum_{\beta=1}^{N}(\rho^\alpha-\delta^\alpha K)\mu^\alpha=\sum_{\alpha=1}^{N}\rho^\alpha\mu_0^\alpha+\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]$$
$$-\Big(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}\Big)K-\sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s}+bV. \quad (26.22)$$

The analogous result for a substitutional alloy is not as simple to derive. To begin with, we assume there are no vacancies; the relations $(9.65)_{1,3}$ and (9.58) for the free energy and chemical potentials and the free-energy conditions at zero-stress, (9.45), then imply that

$$\left.\begin{aligned}\Psi&=\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]+\sum_{\alpha=1}^{N}\rho^\alpha\mu_0^\alpha(\vec{\rho}),\\ \mu^{\alpha\beta}&=\mu_0^\alpha(\vec{\rho})-\mu_0^\beta(\vec{\rho})-\mathbf{N}^{\alpha\beta}\cdot\mathbf{T}.\end{aligned}\right\} \quad (26.23)$$

Thus, writing

$$R=-\Big(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}\Big)K-\sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s}+bV,$$

we may use (24.8), (24.10), and (26.20) to show that

$$\begin{aligned}\rho_{\rm ef}\,\mu^\alpha&=\sum_{\beta=1}^{N}\rho_{\rm ef}^\beta\mu^{\alpha\beta}+\Psi+R\\ &=\rho_{\rm ef}\,\mu_0^\alpha-\sum_{\beta=1}^{N}\rho_{\rm ef}^\beta\mu_0^\beta-\sum_{\beta=1}^{N}\rho_{\rm ef}^\beta\mathbf{N}^{\alpha\beta}\cdot\mathbf{T}+\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]+\sum_{\beta=1}^{N}\rho^\beta\mu_0^\beta+R\\ &=\rho_{\rm ef}\,\mu_0^\alpha+\sum_{\beta=1}^{N}\delta^\beta\mu_0^\beta K-\sum_{\beta=1}^{N}\rho_{\rm ef}^\beta\mathbf{N}^{\alpha\beta}\cdot\mathbf{T}+\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]+R.\end{aligned}$$

The configurational-chemistry relations (26.20) for a *mechanically simple, substitutional alloy without vacancies* therefore takes the form

$$\mu^\alpha-\mu_0^\alpha=\sum_{\beta=1}^{N}c_{\rm ef}^\beta\mathbf{N}^{\beta\alpha}\cdot\mathbf{T}+\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}]$$
$$-\Big(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}-\sum_{\beta=1}^{N}\delta^\beta\mu_0^\beta\Big)K-\sum_{\beta=1}^{N}\frac{\partial^2\psi}{\partial\delta^\beta\partial\vartheta}\frac{\partial\delta^\beta}{\partial s}+bV. \quad (26.24)$$

26.2 Equations when adatom densities are neglected

(a) Balances

The basic interfacial balances are (26.1) and (26.2) with the terms involving adatoms deleted. The balances for standard forces and atoms therefore take the form

$$\left.\begin{aligned}\mathbf{Tn}&=\bar{\sigma}K\mathbf{n}+\frac{\partial\bar{\sigma}}{\partial s}\mathbf{t},\\ \rho^\alpha V&=-\frac{\partial h^\alpha}{\partial s}+\boldsymbol{\jmath}^\alpha\cdot\mathbf{n}+r^\alpha,\end{aligned}\right\} \quad (26.25)$$

while the normal configurational force balance and the configurational-chemistry relations (for substitutional alloys) take the respective forms

$$\sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha = \mathcal{F}, \qquad \mu^\alpha = \sum_{\beta=1}^{N} c^\beta \mu^{\alpha\beta} + \Omega\,\mathcal{F}, \tag{26.26}$$

with mechanical potential $\mathcal{F}$, as before, given by (26.3). In writing (26.26) we have used the fact that, for $\vec{\delta} \equiv 0$, the defining relations for Ω_{ef} in (24.8) and c^β_{ef} in (24.10) take the respective forms

$$\Omega_{\text{ef}} = \Omega = \frac{1}{\rho^{\text{sites}}}, \qquad c^\beta_{\text{ef}} = c^\beta = \frac{\rho^\beta}{\rho^{\text{sites}}}, \tag{26.27}$$

with Ω the *atomic volume* and c^β the *concentration of species* β.

(b) Constitutive relations. Indeterminacy of the chemical potentials

The treatment of chemical potentials in the absence of an accounting of adatom densities is somewhat delicate: since $\mu^\alpha(\delta^\alpha)^\square = 0$ for each α, the interfacial dissipation inequality (23.9) reduces to

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} + \sum_{\alpha=1}^{N} h^\alpha \frac{\partial \mu^\alpha}{\partial s} + gV \le 0; \tag{26.28}$$

the absence of a field conjugate to the surface chemical potentials μ^α renders them *indeterminate* on $\mathcal{S}$; that is, not viable as independent variables in the constitutive relations for the interface. Thus, in view of the dissipation inequality (26.28), arguing as for (26.4) and (26.5), we are led to the constitutive relations

$$\bar{\sigma} = \frac{\partial \hat{\psi}(\varepsilon, \vartheta)}{\partial \varepsilon}, \qquad \bar{\tau} = \frac{\partial \hat{\psi}(\varepsilon, \vartheta)}{\partial \vartheta}, \tag{26.29}$$

and

$$h^\alpha = -\sum_{\beta=1}^{N} L^{\alpha\beta} \frac{\partial \mu^\beta}{\partial s}, \qquad g = -bV, \tag{26.30}$$

with moduli $L^{\alpha\beta}$ and g allowed to depend on (ε, ϑ).

By (26.29), writing $\psi(\varepsilon, \vartheta) = \hat{\psi}(\varepsilon, \vartheta)$, we find that

$$(\psi - \bar{\sigma}\varepsilon)K + \bar{\sigma}\,\frac{\partial \gamma}{\partial s} + \frac{\partial \bar{\tau}}{\partial s} = \left(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2} - \varepsilon \frac{\partial \psi}{\partial \varepsilon}\right)K + \frac{\partial^2 \psi}{\partial \varepsilon \partial \vartheta}\frac{\partial \varepsilon}{\partial s} + \frac{\partial \psi}{\partial \varepsilon}\frac{\partial \gamma}{\partial s}. \tag{26.31}$$

Thus, if we combine the interfacial balances and the constitutive relations, we arrive at the standard force and atomic balances

$$\left.\begin{aligned} \mathbf{Tn} &= \frac{\partial \psi}{\partial \varepsilon} K\mathbf{n} + \left(\frac{\partial^2 \psi}{\partial \varepsilon^2}\,\frac{\partial \varepsilon}{\partial s} + \frac{\partial^2 \psi}{\partial \varepsilon \partial \vartheta} K\right)\mathbf{t}, \\ \rho^\alpha V &= \frac{\partial}{\partial s}\left(\sum_{\beta=1}^{N} L^{\alpha\beta}\,\frac{\partial \mu^\beta}{\partial s}\right) + \boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha. \end{aligned}\right\} \tag{26.32}$$

Further, the normal configurational force balance and the configurational-chemistry relations for substitutional alloys are given by (26.26) with mechanical potential

$$\begin{aligned}\mathcal{F} &= \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}\\ &\qquad - \Big(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\Big)K - \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\frac{\partial\varepsilon}{\partial s} - \frac{\partial\psi}{\partial\varepsilon}\frac{\partial\gamma}{\partial s} + bV,\end{aligned} \tag{26.33}$$

which is simply (26.8) with the term involving adatoms dropped.

(b) Equations based on a quadratic strain-energy

A theory that might be useful in accessing the effects of surface stress might be based on a free energy of the form (cf. $(26.4)_1$)

$$\psi = \psi_0(\vartheta) + w(\varepsilon,\vartheta), \tag{26.34}$$

with quadratic strain-energy

$$w(\varepsilon) = \bar\sigma_0(\vartheta)\varepsilon + \tfrac{1}{2}k(\vartheta)\varepsilon^2. \tag{26.35}$$

In this case, the scalar surface stress and reduced configurational shear are

$$\bar\sigma = \bar\sigma_0(\vartheta) + k(\vartheta)\varepsilon, \qquad \bar\tau = \psi_0'(\vartheta) + \bar\sigma_0'(\vartheta)\varepsilon + \tfrac{1}{2}k_0'(\vartheta)\varepsilon^2. \tag{26.36}$$

Further, by (15.10) and (15.11), the normal and tangential components $(20.6)_1$ and $(20.6)_2$ of the standard force balance reduce to

$$\mathbf{n}\cdot\mathbf{Tn} = \Big(\bar\sigma_0(\vartheta) + k(\vartheta)\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)K \tag{26.37}$$

and

$$\mathbf{t}\cdot\mathbf{Tn} = \Big(\bar\sigma_0'(\vartheta) \;+ k(\vartheta)\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s} + k'(\vartheta)\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)K + k(\vartheta)\mathbf{t}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2}, \tag{26.38}$$

while the mechanical potential becomes

$$\begin{aligned}\mathcal{F} = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \Big\{&\psi_0(\vartheta) + \psi_0''(\vartheta) - \big(\bar\sigma_0(\vartheta) - \bar\sigma_0''(\vartheta)\big)\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s} + 2\bar\sigma_0'(\vartheta)\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\\ &+ k(\vartheta)\Big(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)^2 - \tfrac{1}{2}\big(3k(\vartheta) - k''(\vartheta)\big)\Big(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)^2 + 2k'(\vartheta)\Big(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)\Big(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)\Big\}K\\ &- \Big(\bar\sigma_0(\vartheta)\mathbf{n} + \bar\sigma_0'(\vartheta)\mathbf{t} + k(\vartheta)\Big\{\Big(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)\mathbf{n} + \Big(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)\mathbf{t}\Big\} + k'(\vartheta)\Big(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)\mathbf{t}\Big)\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} + bV.\end{aligned} \tag{26.39}$$

A simplifying assumption of potential value for assessing the importance of surface stress might be to take the residual stress and elasticity for the surface to be constant. Then, (26.37) and (26.38) simplify slightly to

$$\mathbf{n}\cdot\mathbf{Tn} = \Big(\bar\sigma_0 + k\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)K \tag{26.40}$$

and

$$\mathbf{t}\cdot\mathbf{Tn} = \left(k\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)K + k\mathbf{t}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2}, \tag{26.41}$$

while (26.42) reduces to

$$\begin{aligned}\mathcal{F} = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \left(\psi_0(\vartheta) + \psi_0''(\vartheta) - \tfrac{3}{2}k\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)^2 + k\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)^2 - \bar{\sigma}_0\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)K \\ - \left(\bar{\sigma}_0\mathbf{n} + k\left\{\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{n} + \left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{t}\right\}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} + bV. \end{aligned}\tag{26.42}$$

so that even within this drastically simplified theory the standard force balance, the normal configurational force balance, and, for a substitutional alloy, the configurational-chemistry relations are quite complicated.

Alternatively, consistent with the view of Shchukin and Bimberg (1999), we might allow the free energy to be anisotropic but ignore interfacial elasticity, so that

$$\left.\begin{aligned}\psi &= \psi_0(\vartheta) + \bar{\sigma}_0(\vartheta)\varepsilon, \\ \bar{\sigma} &= \bar{\sigma}_0(\vartheta), \\ \bar{\tau} &= \psi_0'(\vartheta) + \bar{\sigma}_0'(\vartheta)\varepsilon. \end{aligned}\right\}\tag{26.43}$$

Then, the appropriately simplified versions of (26.37) and (26.38) combine to yield

$$\mathbf{Tn} = \bar{\sigma}_0(\vartheta)K\mathbf{n} + \bar{\sigma}_0'(\vartheta)K\mathbf{t}; \tag{26.44}$$

thus, writing

$$\frac{\partial\mathbf{u}}{\partial n} = (\nabla\mathbf{u})\mathbf{n},$$

it follows that

$$\mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} = \bar{\sigma}_0(\vartheta)K\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n} + \bar{\sigma}_0'(\vartheta)K\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial n} \tag{26.45}$$

and we may replace (26.42) by

$$\begin{aligned}\mathcal{F} = \Psi - \left(\psi_0(\vartheta) + \psi_0''(\vartheta) + \big(\bar{\sigma}_0(\vartheta) + 2\bar{\sigma}_0'(\vartheta)\big)\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n} - \big(\bar{\sigma}_0(\vartheta) - \bar{\sigma}_0'(\vartheta) - \bar{\sigma}_0''(\vartheta)\big)\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)K \\ - \big(\bar{\sigma}_0(\vartheta)\mathbf{n} + \bar{\sigma}_0'(\vartheta)\mathbf{t}\big)\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} + bV. \end{aligned}\tag{26.46}$$

Finally, if $\bar{\sigma}_0 =$ constant and $k = 0$, then (26.44) and (26.46) specializes to yield

$$\mathbf{Tn} = \bar{\sigma}_0K\mathbf{n}, \tag{26.47}$$

and

$$\mathcal{F} = \Psi - \left\{\psi_0(\vartheta) + \psi_0''(\vartheta) + \bar{\sigma}_0\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n} - \mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\right\}K - \bar{\sigma}_0\mathbf{n}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} + bV. \tag{26.48}$$

As discussed in §17.5, the local stability of the evolution equation (17.32) for a grain boundary is determined by the sign of the coefficient of the curvature — the interfacial stiffness. In (26.48), the coefficient of the curvature is the sum of the interfacial stiffness and the term $\bar{\sigma}_0(e_{nn} - e_{tt})$, with $e_{nn} = \mathbf{n}\cdot\partial\mathbf{u}/\partial n$ and $e_{tt} = \mathbf{t}\cdot\partial\mathbf{u}/\partial t$. Thus, notwithstanding the term $\bar{\sigma}_0\mathbf{n}\cdot\partial^2\mathbf{u}/\partial s^2$, it appears that a tensile normal strain (for which $e_{nn} > 0$) and a compressive tangential strain (for which $-e_{tt} > 0$) should be stabilizing.

(c) Equations neglecting standard surface stress

Here the interface remains traction-free and the atomic balance becomes

$$\rho^\alpha V = \frac{\partial}{\partial s}\bigg(\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial \mu^\beta}{\partial s}\bigg) + \boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha, \tag{26.49}$$

the normal configurational force balance has the form

$$\sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha = \Psi - \bigg(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\bigg)K + bV, \tag{26.50}$$

and, for a substitutional alloy, the configurational chemistry relations become

$$\mu^\alpha = \sum_{\beta=1}^{N} c^\beta \mu^{\alpha\beta} + \Omega\bigg\{\Psi - \bigg(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\bigg)K + bV\bigg\}. \tag{26.51}$$

Finally, restricting attention to mechanically simple materials, we find that (26.50) and (26.51), respectively, reduce to

$$\sum_{\alpha=1}^{N} \rho^\alpha(\mu^\alpha - \mu_0^\alpha) = \tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \bigg(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\bigg)K + bV \tag{26.52}$$

and

$$\mu^\alpha - \mu_0^\alpha = \sum_{\beta=1}^{N} c^\beta\, \mathbf{N}^{\beta\alpha}\cdot\mathbf{T} + \Omega\bigg\{\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \bigg(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\bigg)K + bV\bigg\}. \tag{26.53}$$

Granted cubic symmetry, so that $\mathbf{N}^{\alpha\beta} = \eta^{\alpha\beta}\mathbf{1}$ (cf. 9.68)), and assuming that $b \equiv 0$, (26.53) reduces to the following result of Spencer, Voorhees and Tersoff (2001, eqts. (2.10), (2.11)):[79]

$$\mu^\alpha - \mu_0^\alpha = \sum_{\beta=1}^{N} c^\beta\, \eta^{\beta\alpha}\,\mathrm{tr}\,\mathbf{T} + \Omega\bigg\{\tfrac{1}{2}\mathbf{T}\cdot\mathbb{K}[\mathbf{T}] - \bigg(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\bigg)K\bigg\}.$$

26.3 Addendum: Importance of the kinetic term $g = -bV$

In each of the cases discussed in the last two subsections, the normal configurational force balance contains the kinetic term bV resulting from the constitutive equation $g = -bV$ for g, a *dissipative force associated with the attachment of vapor atoms to the solid surface.* The dissipation associated with g,[80] measured per unit length of the interfacial curve, is bV^2; *without this term the attachment process is nondissipative.*

Interface conditions that play the role of the normal configurational force balance are typically derived using an assumption of local equilibrium or using a chemical potential derived as a variational derivative of the total free-energy with respect to variations in the configuration of the interface; thus the possibility of having a dynamical interface condition involving V are ruled out from the start by the use of such variational paradigms, which, by their very nature, *cannot involve the normal velocity* V.

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[79] Note that our $\eta^{\beta\alpha}$ is Ω times their modulus $\eta^{\beta\alpha}$.

[80] Cf. (25.10) and the remark following (23.9).

To assess the importance of the kinetic term, consider a single atomic species and neglect bulk diffusion, so that $\boldsymbol{\jmath} \equiv \mathbf{0}$ and the atomic volume $\Omega = 1/\rho$ is constant. Assume further that the mobility L for surface diffusion and the kinetic modulus b are constant, so that the atomic balance (26.49) and the normal configurational force balance (26.50) take the form

$$V = \Omega L \frac{\partial^2 \mu}{\partial s^2} + r, \qquad \mu = \Omega\biggl\{\Psi - \biggl(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\biggr)K + bV\biggr\}. \tag{26.54}$$

The field

$$\mu^{\rm eq} = \Omega\biggl\{\Psi - \biggl(\psi + \frac{\partial^2 \psi}{\partial \vartheta^2}\biggr)K\biggr\}$$

represents the *equilibrium chemical potential* (the chemical potential when $V = 0$); using this field we may write the normal configurational force balance in the form $\mu = \mu^{\rm eq} + \Omega bV$. This relation and the atomic balance $(26.54)_1$ yield the evolution equation

$$V - \lambda^2 \frac{\partial^2 V}{\partial s^2} = \Omega L \frac{\partial^2 \mu^{\rm eq}}{\partial s^2} + r \tag{26.55}$$

with

$$\lambda = \Omega\sqrt{bL} \tag{26.56}$$

a *material length-scale*; *the kinetic term $g = -bV$ is therefore important at length scales of order* λ and smaller.[81] Thus, whether or not the kinetic term is important depends on the magnitude of the product bL; consequently, when the Fickean mobility L is sufficiently large, the term $g = -bV$ may be important even when the modulus b is small.

27 Interfacial couples. Allowance for an energetic dependence on curvature

The notorious instability of strained solid-vapor interfaces results in a wide variety of surface patterns and morphologies, an example being the faceted islands (Figure 18) observed by Tersoff, Spencer, Rastelli and von Känel (2003). Such instabilities are reflected by the underlying evolution equations[82] and by the resulting difficulty of performing reliable simulations, which motivates the need for physically-based regularized theories.[83] Regularizations that account for an energetic dependence on curvature (DiCarlo, Gurtin and Podio-Guidugli, 1992) but neglect surface stress and adatom densities, are used Tersoff, Spencer, Rastelli and von Känel (2003) to describe the initial stages of island formation and by Seigel, Miksis and Voorhees (2003) to study the formation of wrinklings on a void surface.[84] To arrive at a theory that allows for an energetic dependence

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[81] This conclusion arose from conservations with Peter Voorhees.

[82] Asaro and Tiller (1972), Grinfeld (1986), and Srolovitz(1989) showed that a planar layer under stress may be unstable. Subsequent studies of related instabilities include Freund and Jonsdottir (1993), Grilhe (1993), Gao (1994), Freund (1995), Spencer and Meiron (1994), Yang and Srolovitz (1994), Suo and Wang (1997), Wang and Suo (1997), Xia, Bower, Suo and Shih (1997), Léonard and Desai (1998), Gao and Nix (1999), Shchukin and Bimberg (1999), Phan, Kaplan, Gray, Adalsteinsson, Sethian, Barvosa-Carter, and Aziz (2001), Danescu (2001), Spencer, Voorhees, and Tersoff (2001), and Xiang and E (2002).

[83] Our perspective here is identical to that in §18. As opposed to a pragmatical approach in which supplemental terms involving higher-order derivatives are added to stabilize an equation, we seek regularizations that reflect a consideration of relevant physical mechanisms.

[84] As discussed above, the inclusion of adatoms may provide at least a partial regularization as doing so can, with appropriate constitutive assumptions, lead to parabolic evolution equations for the adatom densities. However, constraining the curvature of the interface via an energetic dependence on curvature should provide a more effective regularization.

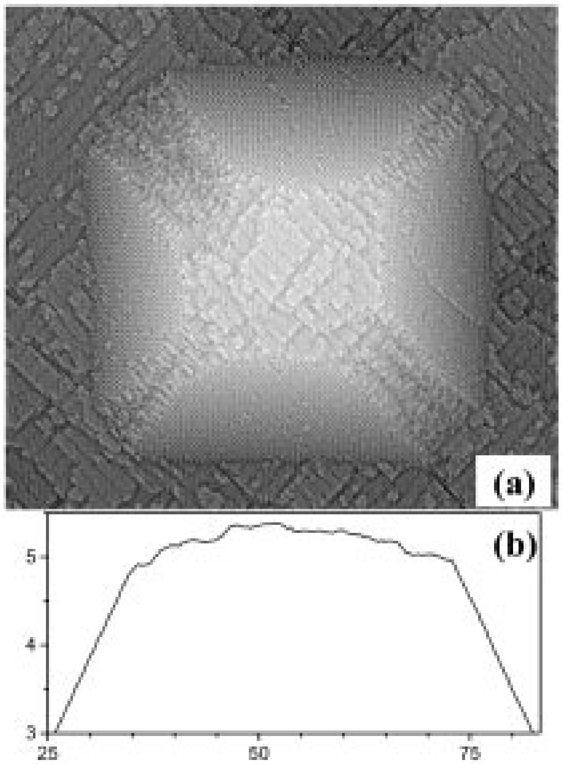

Figure 18: (a) STM image (108×108 nm^2) of a faceted island obtained by depositing $\mathrm{Si}_{0.6}\mathrm{Ge}_{0.4}$ on Si(001). (b) Cross-section of the region near the top of the island, from an average of 30 line scans taken from left to right close to the middle of the island. Scale in nm. (Images courtesy of Tersoff, Spencer, Rastelli and von Känel.)

on curvature, one may follow the steps taken in our extension of the classical theory of grain boundaries to allow for the study of facets and wrinklings (cf. §18). Specifically, we may introduce an interfacial couple stress and an interfacial internal couple together with an configurational torque balance. Taking into account the torques exerted by the configurational force system, the configurational torque balance for an interfacial pillbox $\mathcal{C}$ is (cf. (18.1))

$$\big[M + (\mathbf{x}-\mathbf{0})\times\mathbf{c}\big]_a^b + \int\limits_{\mathcal{C}} m\,ds + \int\limits_{\mathcal{C}} \big[(\mathbf{x}-\mathbf{0})\times(\mathbf{g}-\mathbf{C}\mathbf{n})\big]\,ds = 0. \qquad (27.1)$$

The foregoing considerations leave intact the basic balances considered in our previous treatment of strained solid-vapor interfaces. Thus, using the configurational force balance and proceeding as in the derivation of (18.3), we obtain the local statement

$$\frac{\partial^2 M}{\partial s^2} + \frac{\partial m}{\partial s} - \sigma K - g + \mathbf{n}\cdot\mathbf{C}\mathbf{n} = 0 \qquad (27.2)$$

of configurational torque balance.

In the presence of interfacial couples, the net power expended on an interfacial pillbox $\mathcal{C}$ must account for the action of the couple stress M at the endpoints of $\mathcal{C}$ and this leads to a free-energy imbalance of the form

$$\frac{d}{dt}\int\limits_{\mathcal{C}} \psi\, ds \le \left[M\frac{d\vartheta}{dt}\right]_a^b + \left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \mathbf{Cn}\cdot\mathbf{v}\, ds + \left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \mathbf{Tn}\cdot\overset{\square}{\mathbf{u}}\, ds$$
$$+ \sum_{\alpha=1}^{N}\left[\mu^\alpha(-h^\alpha+\delta^\alpha W)\right]_a^b + \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}} \mu^\alpha(\boldsymbol{\jmath}^\alpha\cdot\mathbf{n} - \rho^\alpha V + r^\alpha)\, ds. \quad (27.3)$$

Arguing as in §18.3 and §23.2, we find that, when interfacial configurational torques are taken into consideration, the interfacial Eshelby relation (23.6) must be modified to read

$$\sigma = \psi - \sum_{\alpha=1}^{N}\delta^\alpha\mu^\alpha - \bar{\sigma}\varepsilon - MK \quad (27.4)$$

and the interfacial dissipation inequality is of the form

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} + \bar{m}\overset{\square}{\vartheta} - M\overset{\square}{K} - \sum_{\alpha=1}^{N}\left(\mu^\alpha\overset{\square}{\delta}{}^\alpha - h^\alpha\frac{\partial\mu^\alpha}{\partial s}\right) + gV \le 0, \quad (27.5)$$

with

$$\bar{m} = m + \bar{\sigma}\gamma, \quad (27.6)$$

the *reduced internal configurational couple.*

Using the bulk Eshelby relation (12.15) and the identity

$$\frac{\partial m}{\partial s} = \frac{\partial\bar{m}}{\partial s} - \bar{\sigma}\,\frac{\partial\gamma}{\partial s} - \frac{\partial\bar{\sigma}}{\partial s}\gamma = \frac{\partial\bar{m}}{\partial s} - \gamma\mathbf{n}\cdot\mathbf{Tt} - \bar{\sigma}\,\frac{\partial\gamma}{\partial s}, \quad (27.7)$$

which follows from (27.6) and $\partial\bar{\sigma}/\partial s = \mathbf{t}\cdot\mathbf{Tn}$ (cf. (20.6)), we find that the balance (27.2) can be expressed in the form

$$\sum_{\alpha=1}^{N}(\rho^\alpha - \delta^\alpha K)\mu^\alpha = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}$$
$$- (\psi - \bar{\sigma}\varepsilon - MK)K - \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{m}}{\partial s} + \frac{\partial^2 M}{\partial s^2} - g. \quad (27.8)$$

For unconstrained materials, (27.8) supersedes the configurational balance (26.2). For substitutional alloys, (27.8) is replaced by

$$\mu^\alpha = \sum_{\beta=1}^{N} c_{\mathrm{ef}}^{\beta}\mu^{\alpha\beta} + \Omega_{\mathrm{ef}}\Big\{\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}$$
$$- (\psi - \bar{\sigma}\varepsilon - MK)K - \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{m}}{\partial s} + \frac{\partial^2 M}{\partial s^2} - g\Big\}. \quad (27.9)$$

which generalize the configurational-chemistry relations (26.3).

Guided by (27.5), we consider constitutive equations giving

$$\psi,\ \bar{\sigma},\ \bar{m},\ M,\ \vec{\mu}\ \text{ as functions of }\ (\varepsilon,\vartheta,K,\vec{\delta}\,)$$

in conjunction with constitutive equations for h^α and g of the form (25.1) with coefficients now possibly dependent on $(\varepsilon, \vartheta, K, \vec{\delta}\,)$. Appealing to the discussion of §17.8, we then find that the free energy determines the standard interfacial stress, reduced configurational couple, couple stress, and chemical potentials through the relations

$$\left.\begin{aligned} \bar{\sigma} &= \frac{\partial\hat{\psi}(\varepsilon, \vartheta, K, \vec{\delta}\,)}{\partial\varepsilon}, \\ \bar{m} &= -\frac{\partial\hat{\psi}(\varepsilon, \vartheta, K, \vec{\delta}\,)}{\partial\vartheta}, \\ M &= \frac{\partial\hat{\psi}(\varepsilon, \vartheta, K, \vec{\delta}\,)}{\partial K}, \\ \mu^\alpha &= \frac{\partial\hat{\psi}(\varepsilon, \vartheta, K, \vec{\delta}\,)}{\partial\delta^\alpha}. \end{aligned}\right\} \tag{27.10}$$

Further, for simplicity, hereafter we work only with the uncoupled relations (26.5) for h^α and g.

When interfacial couples and adatom densities are taken into account, the general relations are therefore (26.1), (26.11), and (27.8) for an unconstrained material, (26.13) and (27.9) for a substitutional alloy, along with the constitutive relations (26.5) and (27.10).

If we neglect adatom densities and, following our treatment of grain boundaries, assume that the free energy has the form[85]

$$\psi(\varepsilon, \vartheta) + \tfrac{1}{2}\lambda K^2, \tag{27.11}$$

with $\lambda > 0$ constant, it then follows from $(27.10)_{1\text{–}3}$ that

$$\bar{\sigma} = \frac{\partial\hat{\psi}(\varepsilon, \vartheta)}{\partial\varepsilon}, \qquad \bar{m} = -\frac{\partial\hat{\psi}(\varepsilon, \vartheta)}{\partial\vartheta}, \qquad M = \lambda K. \tag{27.12}$$

In this case, the basic interfacial balances are

$$\left.\begin{aligned} \mathbf{Tn} &= \frac{\partial\psi}{\partial\varepsilon}K\mathbf{n} + \left(\frac{\partial^2\psi}{\partial\varepsilon^2}\frac{\partial\varepsilon}{\partial s} + \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}K\right)\mathbf{t}, \\ \rho^\alpha V &= \frac{\partial}{\partial s}\left(\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\right) + \boldsymbol{\jmath}^\alpha \cdot \mathbf{n} + r^\alpha, \end{aligned}\right\} \tag{27.13}$$

the normal configurational force balance[86]

$$\begin{aligned} \sum_{\alpha=1}^{N}\rho^\alpha\mu^\alpha &= \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt} \\ &\quad - \left(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\right)K - \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\frac{\partial\varepsilon}{\partial s} - \frac{\partial\psi}{\partial\varepsilon}\frac{\partial\gamma}{\partial s} + bV + \lambda\left(\frac{\partial^2 K}{\partial s^2} + \tfrac{1}{2}K^3\right) \end{aligned} \tag{27.14}$$

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[85] Cf. DiCarlo, Gurtin, and Podio-Guidugli (1992), Stewart and Goldenfeld (1992), Liu and Metiu (1993), and Golovin, Davis and Nepomnyashchy (1998, 1999).

[86] Cf. Gurtin and Jabbour (2002), who consider a single atomic species in three space-dimensions, neglecting surface stress.

for unconstrained materials, and the configurational chemistry relations

$$\mu^\alpha = \sum_{\beta=1}^{N} c^\beta \mu^{\alpha\beta} + \Omega \biggl\{ \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt} \\ - \biggl(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\biggr)K - \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\frac{\partial\varepsilon}{\partial s} - \frac{\partial\psi}{\partial\varepsilon}\frac{\partial\gamma}{\partial s} + bV + \lambda\biggl(\frac{\partial^2 K}{\partial s^2} + \tfrac{1}{2}K^3\biggr)\biggr\} \tag{27.15}$$

for substitutional alloys. When the interface is the graph of a function $y = h(x,t)$, the term $\lambda\partial^2 K/\partial s^2$ in (27.14) and (27.15) would have the form $A\partial^4 h/\partial x^4$, with $A > 0$ a function of $\partial h/\partial x$, $\partial^2 h/\partial x^2$, and $\partial^3 h/\partial x^3$ (cf. §17.5). Therefore (considering the remaining fields as fixed), (27.14) and (27.15) would represent *elliptic* partial differential equations and as such should have a *regularizing* effect on the evolution of the interface.

28 Allowance for evaporation-condensation

To model processes in which evaporation-condensation is of importance, we now follow the approach taken in our treatment of grain-vapor interfaces (cf. §19) and endow the vapor with a chemical potential μ_v^α for each atomic species α. In addition, we reinterpret the role of the supplies r^α in the theory: we view r^α as the rate at which α-atoms of chemical potential μ_v^α are supplied from the vapor to the solid at the interface. Thus, while this change in perspective leaves unaltered the atomic balances (22.3), it is necessary to modify the free-energy imbalance (23.4) for a pillbox $\mathcal{C}$ to account for the net rate $\int_{\mathcal{C}} \mu_v^\alpha r^\alpha\, ds$ at which energy is added to $\mathcal{C}$ by evaporation-condensation; granted this net rate is accounted for, the free-energy imbalance for an interfacial pillbox $\mathcal{C} = \mathcal{C}(t)$ reads (cf. (19.15))

$$\frac{d}{dt}\int_{\mathcal{C}} \psi\, ds \le \biggl[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\biggr]_a^b - \int_{\mathcal{C}} \mathbf{Cn}\cdot\mathbf{v}\, ds + \biggl[\mathbf{T}\cdot\frac{d\mathbf{u}}{dt}\biggr]_a^b - \int_{\mathcal{C}} \mathbf{Tn}\cdot\overset{\square}{\mathbf{u}}\, ds \\ + \sum_{\alpha=1}^{N} \bigl[\mu^\alpha(-h^\alpha + \delta^\alpha W)\bigr]_a^b + \sum_{\alpha=1}^{N} \int_{\mathcal{C}} \Bigl(\mu^\alpha(\boldsymbol{\jmath}^\alpha\cdot\mathbf{n} - \rho^\alpha V) + \mu_v^\alpha r^\alpha\Bigr)\, ds. \tag{28.1}$$

Arguing as in §23.2, we find that our consideration of evaporation-condensation leaves the interfacial Eshelby relation (23.6) unchanged and results in an interfacial dissipation inequality of the form (cf. (19.18))

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N}\biggl(\mu^\alpha\overset{\square}{\delta}{}^\alpha - h^\alpha\frac{\partial\mu^\alpha}{\partial s} - (\mu^\alpha - \mu_v^\alpha)r^\alpha\biggr) + gV \le 0. \tag{28.2}$$

The inequality (28.2) differs from that, (23.9), valid in the absence of evaporation-condensation only by the presence of the term $(\mu^\alpha - \mu_v^\alpha)r^\alpha$. Thus the state relations (25.2) determining $\bar{\sigma}$, $\bar{\tau}$, and μ^α remain valid, leaving the residual dissipation inequality

$$\sum_{\alpha=1}^{N}\biggl(h^\alpha\frac{\partial\mu^\alpha}{\partial s} + (\mu^\alpha - \mu_v^\alpha)r^\alpha\biggr) + gV \le 0. \tag{28.3}$$

Granted essentially linear dissipative response, (28.3) leads to constitutive equations for

h^α, r^α and g of the general form (cf. (19.21))

$$\left.\begin{aligned} h^\alpha &= -\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s} - \sum_{\beta=1}^{N}\bar{\ell}^{\alpha\beta}(\mu^\beta-\mu_v^\beta) - \ell^\alpha V,\\ r^\alpha &= -\sum_{\beta=1}^{N} K^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s} - \sum_{\beta=1}^{N}\bar{k}^{\alpha\beta}(\mu^\beta-\mu_v^\beta) - k^\alpha V,\\ g &= -\sum_{\alpha=1}^{N} B^{\alpha}\frac{\partial\mu^\alpha}{\partial s} - \sum_{\alpha=1}^{N}\bar{b}^{\alpha}(\mu^\alpha-\mu_v^\alpha) - bV, \end{aligned}\right\} \tag{28.4}$$

where the coefficients that define the linear relations (28.4) may depend on $(\varepsilon,\vartheta,\vec{\delta}\,)$ and the relevant coefficient matrix is positive semi-definite.

If the equations (28.4) are *uncoupled*, so that

$$h^\alpha = -\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}, \qquad r^\alpha = -\sum_{\beta=1}^{N}\bar{k}^{\alpha\beta}(\mu^\beta-\mu_v^\beta), \qquad g=-bV, \tag{28.5}$$

then the basic equations of the theory remain exactly as described in §§26.1,26.2, but now the atomic supplies r^α are not arbitrarily prescribable, but are instead given by $(28.5)_2$.

A somewhat more robust version of (28.4) results upon assuming that diffusion along the surface is described by classical Fickean relations for h^α of the form

$$h^\alpha = -\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}, \tag{28.6}$$

while the solid-vapor interaction is described by coupled relations for r^α and g of the form (Fried and Gurtin, 2002)

$$\left.\begin{aligned} r^\alpha &= -\sum_{\beta=1}^{N}\bar{k}^{\alpha\beta}(\mu^\beta-\mu_v^\beta) - k^\alpha V,\\ g &= -\sum_{\alpha=1}^{N}\bar{b}^{\alpha}(\mu^\alpha-\mu_v^\alpha) - bV. \end{aligned}\right\} \tag{28.7}$$

Under this assumption the resulting equations, while complicated, are easily obtained from (26.1)–(26.3), (26.4), (28.6), and (28.7). For example, if we neglect adatom densities and surface stress, then the resulting equations for a substitutional alloy without vacancies are $\mathbf{Tn}=\mathbf{0}$,

$$(\rho^\alpha+k^\alpha)V = \frac{\partial}{\partial s}\bigg(\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\bigg) + \boldsymbol{\jmath}^\alpha\cdot\mathbf{n} - \sum_{\beta=1}^{N}\bar{k}^{\alpha\beta}(\mu^\beta-\mu_v^\beta).$$

and

$$\bigg(1+\sum_{\beta=1}^{N}\bar{b}^\beta\bigg)\mu^\alpha = \sum_{\beta=1}^{N}(c^\beta+\bar{b}^\beta)\mu^{\alpha\beta} + \Omega\bigg\{\Psi - \bigg(\psi+\frac{\partial^2\psi}{\partial\vartheta^2}\bigg)K - \sum_{\alpha=1}^{N}\bar{b}^\alpha\mu_v^\alpha + bV\bigg\}. \tag{28.8}$$

For the fully coupled theory based on (28.4), the resulting equations follow from (26.1)–(26.3), (26.4), and (28.4).

F COHERENT PHASE INTERFACES

We now consider a class of theories for a coherent phase interface. That bulk deformation and stress have a pronounced effect on the shape of coherent precipitates is well understood.[87] In addition, as argued by Cahn (1989), interfacial stress may be of importance. Hence, in addition to allowing for a multiplicity of atomic species, we account for stress in the bulk phases and on the interface. However, we *neglect interfacial atomic densities.*

29 Forces. Power

29.1 Configurational forces

For a coherent interface separating two solid phases, the configurational forces acting on a pillbox are identical to those arising in our discussion of grain boundaries. Thus, the configurational force balance (17.6) and its local consequences remain valid. In particular, we have the *normal configurational force balance*

$$\sigma K + \frac{\partial \tau}{\partial s} + \mathbf{n} \cdot [\![\mathbf{C}]\!]\mathbf{n} + g = 0. \tag{29.1}$$

29.2 Standard forces

Let $\mathcal{C} = \mathcal{C}(t)$ be an arbitrary interfacial pillbox. In addition to the standard forces $-\mathbf{s}_a$ and $\mathbf{s}_b$ exerted at $\mathbf{x}_a$ and $\mathbf{x}_b$ by the portion of $\mathcal{S}$ exterior to $\mathcal{C}$, the solid in the (+)-phase exerts a traction $\mathbf{T}^+\mathbf{n}$ on $\mathcal{C}^+$ and the solid in the (−)-phase exerts a traction $-\mathbf{T}^-\mathbf{n}$ on $\mathcal{C}^-$; the net traction exerted at each point of $\mathcal{C}$ by the bulk phases is then $\mathbf{T}^+\mathbf{n} - \mathbf{T}^-\mathbf{n} = [\![\mathbf{T}]\!]\mathbf{n}$ (Figure 19). The standard torque acting on a pillbox is determined analogously.

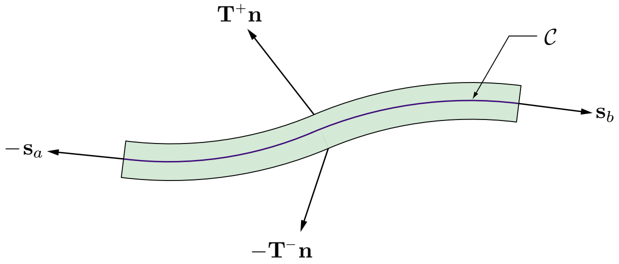

Figure 19: Standard forces on an interfacial pillbox $\mathcal{C}$ for a coherent interface $\mathcal{S}$. Balance of standard torques guarantees the tangency of $\mathbf{s}$.

In view of the preceding discussion, the *standard force and torque balances for* $\mathcal{C}$ take

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[87] Cf. the reviews of Johnson and Voorhees (1992) and Voorhees (1992) and the references therein.

the form

$$\left.\begin{aligned} \mathbf{s}\Big|_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{T} \rrbracket \mathbf{n}\, ds &= \mathbf{0}, \\ \big[(\mathbf{x}-\mathbf{0})\times\mathbf{s}\big]_a^b + \int\limits_{\mathcal{C}} (\mathbf{x}-\mathbf{0})\times \llbracket \mathbf{T} \rrbracket \mathbf{n}\, ds &= \mathbf{0}; \end{aligned}\right\} \tag{29.2}$$

since $\mathcal{C}$ is arbitrary, these yield the interfacial balances

$$\frac{\partial \mathbf{s}}{\partial s} + \llbracket \mathbf{T} \rrbracket \mathbf{n} = \mathbf{0}, \qquad \mathbf{t}\times\mathbf{s} = \mathbf{0} \tag{29.3}$$

Thus, as in the case of a solid-vapor interface, the stress vector $\mathbf{s}$ is *tangent to the interface*; hence

$$\mathbf{s} = \bar{\sigma}\mathbf{t}, \tag{29.4}$$

with $\bar{\sigma}$ the *standard scalar interfacial stress.* Since $\partial\mathbf{t}/\partial s = K\mathbf{n}$, we can rewrite the interface condition $(29.3)_1$ as

$$\bar{\sigma}K\mathbf{n} + \frac{\partial \bar{\sigma}}{\partial s}\mathbf{t} + \llbracket \mathbf{T} \rrbracket \mathbf{n} = \mathbf{0}, \tag{29.5}$$

or equivalently, as

$$\mathbf{n}\cdot \llbracket \mathbf{T} \rrbracket \mathbf{n} = -\bar{\sigma}K, \qquad \mathbf{t}\cdot \llbracket \mathbf{T} \rrbracket \mathbf{n} = -\frac{\partial \bar{\sigma}}{\partial s}. \tag{29.6}$$

The first of (29.6) represents a counterpart, for a coherent interface, of the classical Laplace–Young relation for a liquid-vapor interface.

29.3 Power

Consider a migrating pillbox $\mathcal{C} = \mathcal{C}(t)$. Arguing as for a solid-vapor interface (§21.1), we view: (i) the endpoint velocities $d\mathbf{x}_a/dt$ and $d\mathbf{x}_b/dt$ as the power-conjugate velocities for $\mathbf{c}$; (ii) the motion velocities $d\mathbf{u}_a/dt$ and $d\mathbf{u}_b/dt$ following $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$ as the power-conjugate velocities for $\mathbf{s}$; (iii) the normal velocity $\mathbf{v}$ of $\mathcal{C}$ as the power-conjugate velocity for the configurational tractions $\mathbf{C}^+\mathbf{n}$ and $-\mathbf{C}^-\mathbf{n}$ acting on $\mathcal{C}^+$ and $\mathcal{C}^-$; and (iv) the motion velocity $\overset{\square}{\mathbf{u}}$ following $\mathcal{S}(t)$ as the power-conjugate velocity for the standard tractions $\mathbf{T}^+\mathbf{n}$ and $-\mathbf{T}^-\mathbf{n}$ acting on $\mathcal{C}^+$ and $\mathcal{C}^-$. The (net) *external power expended* on $\mathcal{C}(t)$ is therefore presumed to have the form

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} \big(\llbracket \mathbf{C} \rrbracket \mathbf{n}\cdot\mathbf{v} + \llbracket \mathbf{T} \rrbracket \mathbf{n}\cdot\overset{\square}{\mathbf{u}}\big)\, ds. \tag{29.7}$$

Using the identity $\partial V/\partial s = \overset{\square}{\vartheta}$ and the normal configurational force balance (29.1), it follows that (cf. (17.13) and (17.15))

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b = \big[\sigma W + \tau V\big]_a^b = \big[\sigma W\big]_a^b + \int\limits_{\mathcal{C}} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g + \mathbf{n}\cdot\llbracket \mathbf{C} \rrbracket \mathbf{n})V\big]\, ds; \tag{29.8}$$

thus, since $\mathbf{v} = V\mathbf{n}$,

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{C} \rrbracket \mathbf{n}\cdot\mathbf{v}\, ds = \big[\sigma W\big]_a^b + \int\limits_{\mathcal{C}} \big[\tau\overset{\square}{\vartheta} - (\sigma K + g)V\big]\, ds. \tag{29.9}$$

Further, by (21.7), which continues to hold here, and the standard force balance $(29.3)_1$,

$$\left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b+\int\limits_{\mathcal{C}}[\![\mathbf{T}]\!]\mathbf{n}\cdot\overset{\scriptscriptstyle\square}{\mathbf{u}}\,ds=\big[\bar{\sigma}\varepsilon W\big]_a^b+\int\limits_{\mathcal{C}}\big[\bar{\sigma}(\overset{\scriptscriptstyle\square}{\varepsilon}-\gamma\overset{\scriptscriptstyle\square}{\vartheta})-\bar{\sigma}\varepsilon KV\big]\,ds. \tag{29.10}$$

Combining (29.9) and (21.8) then yields the *power balance*

$$\begin{aligned}\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}+\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b&+\int\limits_{\mathcal{C}}\big([\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}+[\![\mathbf{T}]\!]\mathbf{n}\cdot\overset{\scriptscriptstyle\square}{\mathbf{u}}\big)\,ds\\&=\big[(\sigma+\bar{\sigma}\varepsilon)W\big]_a^b+\int\limits_{\mathcal{C}}\big[\bar{\sigma}\overset{\scriptscriptstyle\square}{\varepsilon}+\bar{\tau}\overset{\scriptscriptstyle\square}{\vartheta}-\big((\sigma+\bar{\sigma}\varepsilon)K+g\big)V\big]\,ds,\end{aligned} \tag{29.11}$$

in which the internal power-expenditures are identical to those arising for a strained solid-vapor interface and discussed after (21.10).

30 Atomic transport

Let $\mathcal{C}=\mathcal{C}(t)$ be an arbitrary interfacial pillbox. In addition to the diffusive fluxes h_a^α and $-h_b^\alpha$ of α-atoms across $\mathbf{x}_a$ and $\mathbf{x}_b$, diffusion in the $(+)$-phase results in a flow $-\boldsymbol{\jmath}^{\alpha+}\cdot\mathbf{n}$ across $\mathcal{C}^+$ and diffusion in the $(-)$-phase results in a flow $\boldsymbol{\jmath}^{\alpha-}\cdot\mathbf{n}$ across $\mathcal{C}^-$, so that the net diffusional flow of α-atoms to each point of $\mathcal{C}$ from the bulk phases is $-\boldsymbol{\jmath}^{\alpha+}\cdot\mathbf{n}+\boldsymbol{\jmath}^{\alpha-}\cdot\mathbf{n}=-[\![\boldsymbol{\jmath}^{\alpha}]\!]\cdot\mathbf{n}$ (Figure 20). Hence, the net rate at which α-atoms are added to $\mathcal{C}$ by diffusive transport is

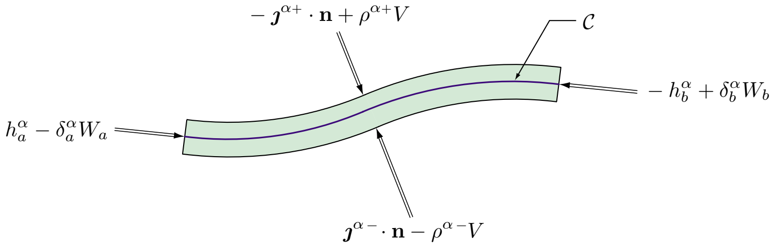

Figure 20: Transport of α-atoms into an interfacial pillbox $\mathcal{C}$.

$$-h^\alpha\big|_a^b-\int\limits_{\mathcal{C}}[\![\boldsymbol{\jmath}^{\alpha}]\!]\cdot\mathbf{n}\,ds. \tag{30.1}$$

There is no flow of interfacial atoms due to accretion, because we have neglected their densities. But accretion does result in flows $\rho^{\alpha+}V$ and $-\rho^{\alpha-}V$ of α-atoms across $\mathcal{C}^+$ and $\mathcal{C}^-$, so that the net accretive flow of α-atoms to each point of $\mathcal{C}$ is $\rho^{\alpha+}V-\rho^{\alpha-}V=[\![\rho^\alpha]\!]V$ (Figure 20). Hence, the net rate at which α-atoms are added to $\mathcal{C}$ by accretive transport is

$$\int\limits_{\mathcal{C}}[\![\rho^\alpha]\!]V\,ds. \tag{30.2}$$

In view of (30.1) and (30.2), the *atomic balance* for $\mathcal{C}$ takes the form

$$h^\alpha\Big|_a^b + \int\limits_{\mathcal{C}(t)} (\,[\![\boldsymbol{\jmath}^\alpha]\!]\cdot\mathbf{n} - [\![\rho^\alpha]\!]V\,)\,ds = 0 \tag{30.3}$$

for each species α, and this yields the local balance

$$[\![\rho^\alpha]\!]V = \frac{\partial h^\alpha}{\partial s} + [\![\boldsymbol{\jmath}^\alpha]\!]\cdot\mathbf{n}. \tag{30.4}$$

31 Free-energy imbalance

Basic to the theory is the assumption that the chemical potentials μ^α are continuous across the interface:

$$[\![\mu^\alpha]\!] = 0. \tag{31.1}$$

This requirement, often referred to as an *assumption of local chemical equilibrium*, allows us to consider the bulk fields μ^α, when evaluated on $\mathcal{S}$, as appropriate *interfacial* chemical-potentials.

Restrict attention to a single atomic species α. As in the case of a solid-vapor interface, the energy flow into a migrating pillbox $\mathcal{C}$ due to atomic transport includes contributions associated with diffusion and accretion. In addition to the diffusive energy fluxes $\mu^\alpha_a h^\alpha_a$ and $-\mu^\alpha_b h^\alpha_b$ associated with the flow of α-atoms across $\mathbf{x}_a$ and $\mathbf{x}_b$, the diffusion of α-atoms in the $(+)$-phase results in an energy flow $-\mu^\alpha\boldsymbol{\jmath}^{\alpha+}\cdot\mathbf{n}$ across $\mathcal{C}^+$ while diffusion of α-atoms in the $(-)$-phase results in an energy flow $\mu^\alpha\boldsymbol{\jmath}^{\alpha-}\cdot\mathbf{n}$ across $\mathcal{C}^-$, so that the diffusive energy flow of α-atoms to each point of $\mathcal{C}$ from the bulk material is $-\mu^\alpha[\![\boldsymbol{\jmath}^\alpha]\!]\cdot\mathbf{n}$. Hence, the net rate at which energy is added to $\mathcal{C}$ by diffusive transport is

$$-\sum_{\alpha=1}^{N}\big[\mu^\alpha h^\alpha\big]_a^b - \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}} \mu^\alpha[\![\boldsymbol{\jmath}^\alpha]\!]\cdot\mathbf{n}\,ds. \tag{31.2}$$

The motion of the interface results in accretive energy flows $\mu^\alpha\rho^{\alpha+}V$ and $-\mu^\alpha\rho^{\alpha-}V$ of α-atoms from the solid across $\mathcal{C}^+$ and $\mathcal{C}^-$, so that the net accretive energy flow of α-atoms to each point of $\mathcal{C}$ from the bulk material is $\mu^\alpha[\![\rho^\alpha]\!]V$. Hence, the net rate at which energy is added to $\mathcal{C}$ by the accretive transport of atoms is

$$\sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}} \mu^\alpha[\![\rho^\alpha]\!]V\,ds. \tag{31.3}$$

Letting ψ denote the free energy of the interface and bearing in mind (21.1), (31.2), and (31.3), the *free-energy imbalance* for an arbitrary interfacial pillbox $\mathcal{C}$ takes the form

$$\begin{aligned}\underbrace{\frac{d}{dt}\int\limits_{\mathcal{C}}\psi\,ds}_{\text{free energy}} \;\le\; &\underbrace{\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b + \int\limits_{\mathcal{C}}[\![\mathbf{C}]\!]\mathbf{n}\cdot\mathbf{v}\,ds}_{\substack{\text{power expended}\\ \text{by configurational forces}}} + \underbrace{\left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b + \int\limits_{\mathcal{C}}[\![\mathbf{T}]\!]\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\,ds}_{\substack{\text{power expended}\\ \text{by standard forces}}}\\ &\underbrace{-\sum_{\alpha=1}^{N}\big[\mu^\alpha h^\alpha\big]_a^b + \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}}\mu^\alpha(-[\![\boldsymbol{\jmath}^\alpha]\!]\cdot\mathbf{n} + [\![\rho^\alpha]\!]V)\,ds}_{\text{energy flow by atomic transport}}.\end{aligned} \tag{31.4}$$

31.1 Dissipation inequality for unconstrained materials

In view of (29.11) and (30.3), the free-energy imbalance (31.4) for $\mathcal{C}$ becomes

$$\int\limits_{\mathcal{C}} (\overset{\square}{\psi} - \psi K V)\, ds + \overbrace{\big[(\psi - \bar{\sigma}\varepsilon - \sigma)W\big]_a^b}^{(\#)}$$

$$\leq \int\limits_{\mathcal{C}} \big[\bar{\sigma}\overset{\square}{\varepsilon} + \bar{\tau}\overset{\square}{\vartheta} - (\sigma + \bar{\sigma}\varepsilon)KV - gV\big]\, ds - \sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha \frac{\partial h^\alpha}{\partial s}\, ds. \qquad (31.5)$$

Since $\mathcal{C}$ is arbitrary, so also are the tangential velocities W_a and W_b of the endpoints of $\mathcal{C}$; thus, since the only term in (31.5) dependent on these velocities is (#), we have the superficial Eshelby relation

$$\sigma = \psi - \bar{\sigma}\varepsilon, \qquad (31.6)$$

which differs from the Eshelby relation (23.6) for a strained solid-vapor interface only because of our present neglect of interfacial atomic densities.

By (31.6) and

$$\sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b = \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \Big(\mu^\alpha \frac{\partial h^\alpha}{\partial s} + h^\alpha \frac{\partial \mu^\alpha}{\partial s}\Big)\, ds, \qquad (31.7)$$

(31.5) becomes

$$\int\limits_{\mathcal{C}} \Big(\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} + \sum_{\alpha=1}^{N} h^\alpha \frac{\partial \mu^\alpha}{\partial s} + gV\Big)\, ds \leq 0; \qquad (31.8)$$

since $\mathcal{C}$ is arbitrary, this yields the *interfacial dissipation inequality*

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} + \sum_{\alpha=1}^{N} h^\alpha \frac{\partial \mu^\alpha}{\partial s} + gV \leq 0. \qquad (31.9)$$

31.2 Interfacial flux constraint and free-energy imbalance for substitutional alloys

Our treatment of substitutional alloys in bulk was based on the substitutional flux constraint

$$\sum_{\alpha=1}^{N} \boldsymbol{\jmath}^\alpha = \mathbf{0} \qquad (31.10)$$

discussed by Ågren (1982) and Cahn and Larché (1983), who argue that (31.10) is a consequence of the requirement that diffusion, as represented by atomic fluxes, arises from exchanges of atoms or exchanges of atoms with vacancies. A consequence of coherency is that (cf. (15.6))

$$[\![\nabla \mathbf{u}]\!]\mathbf{t} = \mathbf{0},$$

so that, roughly speaking, infinitesimal pieces of the lattices on the two sides of the interface fit together.[88] The argument of Ågren and Cahn and Larché should therefore

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[88] Cf. the discussion of Cermelli and Gurtin (1994a) following their eqt. (3.7).

apply at the interface, and noting that, by continuity, the substitutional flux constraint (31.10) is satisfied *at the interface*, it would seem reasonable to require that

$$\sum_{\alpha=1}^{N} h^\alpha = 0, \tag{31.11}$$

and this we shall do. We refer to (31.11) as the *substitutional flux constraint for the interface*. By the lattice constraint and the substitutional flux constraint in bulk,

$$\sum_{\alpha=1}^{N} \llbracket \rho^\alpha \rrbracket = 0, \qquad \sum_{\alpha=1}^{N} \llbracket \boldsymbol{\jmath}^\alpha \rrbracket = \mathbf{0}; \tag{31.12}$$

therefore (30.4) when summed over all species is satisfied identically.

The interfacial flux constraint allows us to establish a counterpart of the theorem on relative chemical potentials (§5.2), and the proof is not much different. We first show that the free-energy imbalance (31.4) is invariant under all transformations of the form

$$\mu^\alpha(\mathbf{x},t) \to \mu^\alpha(\mathbf{x},t) + \lambda(\mathbf{x},t) \qquad \text{for all species } \alpha, \tag{31.13}$$

with $\lambda(\mathbf{x},t)$ independent of α. Given any such field $\lambda(\mathbf{x},t)$, (31.11) and (31.12) imply that

$$\sum_{\alpha=1}^{N} (\mu^\alpha + \lambda) h^\alpha = \sum_{\alpha=1}^{N} \mu^\alpha h^\alpha,$$

$$\sum_{\alpha=1}^{N} (\mu^\alpha + \lambda) \llbracket \rho^\alpha \rrbracket = \sum_{\alpha=1}^{N} \mu^\alpha \llbracket \rho^\alpha \rrbracket, \qquad \sum_{\alpha=1}^{N} (\mu^\alpha + \lambda) \llbracket \boldsymbol{\jmath}^\alpha \rrbracket = \sum_{\alpha=1}^{N} \mu^\alpha \llbracket \boldsymbol{\jmath}^\alpha \rrbracket,$$

and hence, by (31.4),

$$\begin{aligned} \frac{d}{dt} \int\limits_{\mathcal{C}} \psi \, ds \le \left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt} \right]_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{C} \rrbracket \mathbf{n} \cdot \mathbf{v} \, ds + \left[\mathbf{s} \cdot \frac{d\mathbf{u}}{dt} \right]_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{T} \rrbracket \mathbf{n} \cdot \overset{\square}{\mathbf{u}} \, ds \\ - \sum_{\alpha=1}^{N} \big[(\mu^\alpha + \lambda) h^\alpha \big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} (\mu^\alpha + \lambda)(-\llbracket \boldsymbol{\jmath}^\alpha \rrbracket \cdot \mathbf{n} + \llbracket \rho^\alpha \rrbracket V) \, ds; \end{aligned} \tag{31.14}$$

thus, since the field λ is arbitrary, the free-energy imbalance (31.4) is invariant under all transformations of the form (31.13).[89] Choosing a species ζ arbitrarily and taking $\lambda = -\mu^\zeta$ in (31.14), so that $\mu^\alpha + \lambda$ reduces to the relative chemical potential $\mu^{\alpha\zeta}$, we arrive at the *free-energy imbalance for substitutional alloys*:

$$\begin{aligned} \frac{d}{dt} \int\limits_{\mathcal{C}} \psi \, ds \le \left[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt} \right]_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{C} \rrbracket \mathbf{n} \cdot \mathbf{v} \, ds + \left[\mathbf{s} \cdot \frac{d\mathbf{u}}{dt} \right]_a^b + \int\limits_{\mathcal{C}} \llbracket \mathbf{T} \rrbracket \mathbf{n} \cdot \overset{\square}{\mathbf{u}} \, ds \\ - \sum_{\alpha=1}^{N} \big[\mu^{\alpha\zeta} h^\alpha \big]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^{\alpha\zeta}(-\llbracket \boldsymbol{\jmath}^\alpha \rrbracket \cdot \mathbf{n} + \llbracket \rho^\alpha \rrbracket V) \, ds. \end{aligned} \tag{31.15}$$

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[89] Conversely, granted the (bulk) substitutional flux constraint, invariance of (31.4) under all transformations of the form (31.13) yields the substitutional flux constraint for the interface. The proof is identical to that of the remark containing (5.13).

Steps identical to those used to establish the interfacial dissipation inequality (31.9) for unconstrained materials, but with the chemical potentials μ^α replaced by the relative chemical potentials $\mu^{\alpha\zeta}$, yield the *interfacial dissipation inequality*

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\varepsilon} - \bar{\tau}\overset{\square}{\vartheta} + \sum_{\alpha=1}^{N} h^\alpha \frac{\partial \mu^{\alpha\zeta}}{\partial s} + gV \le 0. \tag{31.16}$$

32 Global theorems

Following Gurtin and Voorhees (1993), we now generalize the global theorems presented in §6 for a two-phase body that contains a single closed interface $\mathcal{S}$ disjoint from $\partial\mathcal{B}$ and across which the conditions (15.4) and (31.1) of coherency and local chemical equilibrium are met.

Consider first an unconstrained material. As in §6, the global conservation and decay relations are based upon expressions of the atomic balance and the free-energy imbalance for the body itself. To obtain these statements, we utilize the control-volume equivalency theorem of Appendix B to state the atomic balance and free-energy imbalance for a general migrating control-volume $\mathcal{R}$ containing a portion $\mathcal{C} = \mathcal{S} \cap \mathcal{R}$ of the interface, giving

$$\frac{d}{dt}\int\limits_{\mathcal{R}} \rho^\alpha \, da = -\int\limits_{\partial\mathcal{R}} (\boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} - \rho^\alpha V_{\partial\mathcal{R}}) \, ds - \big[h^\alpha\big]_a^b, \tag{32.1}$$

and (cf. (B1))

$$\begin{aligned} \frac{d}{dt}\Bigg\{\int\limits_{\mathcal{R}} \Psi \, da + \int\limits_{\mathcal{C}} \psi \, ds\Bigg\} \le \int\limits_{\partial\mathcal{R}} (\mathbf{C}\boldsymbol{\nu} \cdot \mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu} \cdot \overset{\circ}{\mathbf{u}}) \, ds + \bigg[\mathbf{c} \cdot \frac{d\mathbf{x}}{dt} + \mathbf{s} \cdot \frac{d\mathbf{u}}{dt}\bigg]_a^b \\ + \sum_{\alpha=1}^{N} \int\limits_{\partial\mathcal{R}} \mu^\alpha(-\boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} + \rho^\alpha V_{\partial\mathcal{R}}) \, ds - \sum_{\alpha=1}^{N} \big[\mu^\alpha h^\alpha\big]_a^b. \end{aligned} \tag{32.2}$$

Thus, choosing $\mathcal{R} = \mathcal{B}$ and bearing in mind that $\mathcal{S}$ is closed and disjoint from $\partial\mathcal{B}$, we find that (32.1) and (32.2) specialize to yield

$$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, da = -\sum_{\alpha=1}^{N} \int\limits_{\partial\mathcal{B}} \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} \, ds \tag{32.3}$$

and

$$\frac{d}{dt}\Bigg\{\int\limits_{\mathcal{B}} \Psi \, da + \int\limits_{\mathcal{S}} \psi \, ds\Bigg\} \le \int\limits_{\partial\mathcal{B}} \mathbf{T}\boldsymbol{\nu} \cdot \dot{\mathbf{u}} \, ds - \int\limits_{\partial\mathcal{B}} \mu^\alpha \boldsymbol{\jmath}^\alpha \cdot \boldsymbol{\nu} \, ds. \tag{32.4}$$

For a substitutional alloy, (32.4) remains valid, but with the chemical potentials μ^α replaced by the relative chemical potentials $\mu^{\alpha\zeta}$.

By (32.3) and (32.4) with $\dot{\mathbf{u}} = \mathbf{0}$ and $\boldsymbol{\jmath}^\alpha \cdot \mathbf{n} = 0$ on $\partial\mathcal{B}$, we have the

> GLOBAL THEOREM FOR AN ISOLATED TWO-PHASE BODY Consider a two-phase body $\mathcal{B}$ containing a single closed interface $\mathcal{S}$ which is disjoint from $\partial\mathcal{B}$. If the body is isolated, that is if $\partial\mathcal{B}$ is fixed and impermeable, then the total

number of atoms of each species remains fixed, while the total free-energy is nonincreasing:

$$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, da = 0, \quad \alpha = 1, 2, \dots, N,$$

$$\frac{d}{dt}\Bigg\{\int\limits_{\mathcal{B}} \Psi \, da + \int\limits_{\mathcal{S}} \psi \, ds\Bigg\} \le 0.$$

Global Theorem for a Two-Phase Body Assume that a portion of $\partial\mathcal{B}$ is fixed and the remainder is subject to dead loads.

(a) If $\partial\mathcal{B}$ is impermeable, then

$$\frac{d}{dt}\int\limits_{\mathcal{B}} \rho^\alpha \, da = 0, \quad \alpha = 1, 2, \dots, N,$$

$$\frac{d}{dt}\Bigg\{\int\limits_{\mathcal{B}} (\Psi - \mathbf{T}_* \cdot \mathbf{E}) \, da + \int\limits_{\mathcal{S}} \psi \, ds\Bigg\} \le 0.$$

(b) If a portion $\mathcal{E}$ of $\partial\mathcal{B}$ is impermeable and the remainder, $\partial\mathcal{B}\backslash\mathcal{E}$, in chemical equilibrium, then

$$\frac{d}{dt}\Bigg\{\int\limits_{\mathcal{B}} \Bigg(\Psi - \mathbf{T}_* \cdot \mathbf{E} - \sum_{\alpha=1}^{N} \mu_*^\alpha \rho^\alpha\Bigg) \, da + \int\limits_{\mathcal{S}} \psi \, ds\Bigg\} \le 0$$

if the material is unconstrained, while

$$\frac{d}{dt}\Bigg\{\int\limits_{\mathcal{B}} \Bigg(\Psi - \mathbf{T}_* \cdot \mathbf{E} - \sum_{\alpha=1}^{N} \mu_*^{\alpha\zeta} \rho^\alpha\Bigg) \, da + \int\limits_{\mathcal{S}} \psi \, ds\Bigg\} \le 0$$

if the material is a substitutional alloy.

Assertion (a) of this theorem follows on using (6.3) and the boundary condition $\jmath^\alpha \cdot \mathbf{n} = 0$ in (32.3) and (32.4); similarly, assertion (b) follows on using (6.3)–(6.5) in (32.4).

33 Normal configurational force balance revisited

33.1 General relation

Since we account for deformation and atomic transport, the bulk configurational stress $\mathbf{C}$ is determined by the full Eshelby relation (12.15), namely

$$\mathbf{C} = \Bigg(\Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha\Bigg)\mathbf{1} - (\nabla\mathbf{u})^{\top}\mathbf{T},$$

while the interfacial configurational tension σ is determined by the interfacial Eshelby relation (23.6). Thus, we may write the normal configurational force balance (29.1) in the form

$$\sum_{\alpha=1}^{N} [\![\rho^\alpha]\!]\mu^\alpha = [\![\Psi - \mathbf{Tn} \cdot (\nabla\mathbf{u})\mathbf{n}]\!] + (\psi - \bar{\sigma}\varepsilon)K + \frac{\partial\tau}{\partial s} + g, \tag{33.1}$$

which, like the statement (24.1) arising in our treatment of strained solid-vapor interfaces, equates terms associated with atomic transport to terms that are purely mechanical. Thus, trivially, for

$$\mathcal{G} \overset{\text{def}}{=} [\![\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n}]\!] + (\psi - \bar{\sigma}\varepsilon)K + \frac{\partial\tau}{\partial s} + g, \tag{33.2}$$

we may write the normal configurational force balance succinctly as

$$\sum_{\alpha=1}^{N} [\![\rho^\alpha]\!]\mu^\alpha = \mathcal{G}. \tag{33.3}$$

When $g = 0$, $\mathcal{G}$ represents the variational derivative of the total free energy with respect to variations of the position of the interface. If, in addition to taking $g = 0$, we neglect interfacial structure, so that $\psi = 0$, $\sigma = 0$, $\tau = 0$, and $\bar{\sigma} = 0$, then $\mathcal{G}$ reduces to the *interfacial driving traction* $[\![\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n}]\!]$. The requirement that the driving traction vanish is the classical Maxwell equation for the equilibrium of a coherent interface.[90]

33.2 Substitutional alloys

For a substitutional alloy, the lattice constraint (5.1) and the identity $\mu^\beta = \mu^\alpha - \mu^{\alpha\beta}$ reduce (33.1) to

$$\sum_{\beta=1}^{N} [\![\rho^\beta]\!]\mu^{\beta\alpha} = \mathcal{G}, \tag{33.4}$$

which, for each species α, involves the chemical potentials relative to all other species β. Hence, in contrast to the situation at a strained interface separating a substitutional alloy from vapor, *it is not possible to determine the individual chemical potentials on a coherent interface in a substitutional alloy.*

Because of (33.4), the remaining results are essentially the same for substitutional alloys as they are for unconstrained materials. For that reason, we limit the ensuing discussion to unconstrained materials with the proviso that:

> *for substitutional alloys the chemical potentials μ^α be interpreted as chemical potentials $\mu^{\alpha\zeta}$ relative to a fixed choice of species ζ.*

33.3 Alternative forms for $\mathcal{G}$

$\mathcal{G}$ admits a variety of equivalent representations. Here, we obtain counterparts of relations obtained in §24.1 for a strained solid-vapor interface. The first of these follows on noting that, by the equation $\tau = \bar{\sigma}\gamma + \bar{\tau}$ used to define $\bar{\tau}$ (cf. (21.10)) and the tangential component $\partial\bar{\sigma}/\partial s = -\mathbf{t}\cdot[\![\mathbf{T}]\!]\mathbf{n} = -\mathbf{n}\cdot[\![\mathbf{T}]\!]\mathbf{t}$ of the standard interfacial force balance (cf. (29.6)),

$$\frac{\partial\tau}{\partial s} = \frac{\partial\bar{\sigma}}{\partial s}\gamma + \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{\tau}}{\partial s} = -\gamma\mathbf{n}\cdot[\![\mathbf{T}]\!]\mathbf{t} + \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{\tau}}{\partial s}, \tag{33.5}$$

which yields the identity

$$\mathcal{G} = [\![\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}]\!] + (\psi - \bar{\sigma}\varepsilon)K + \bar{\sigma}\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar{\tau}}{\partial s} + g. \tag{33.6}$$

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[90] Cf. Eshelby (1970), Robin (1974), Larché and Cahn (1978), Grinfeld (1981), James (1981), and Gurtin, (1983).

Next, we consider the term $[\![\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}]\!] - \varepsilon\bar\sigma K$ on the right side of (33.6) and note that, by the symmetry of $\mathbf{T}$, the representation $\mathbf{1} = \mathbf{t}\otimes\mathbf{t} + \mathbf{n}\otimes\mathbf{n}$, the relations $\mathbf{e} = (\nabla\mathbf{u})^{\pm}\mathbf{t} = \varepsilon\mathbf{t} + \gamma\mathbf{n}$, and the normal component $\bar\sigma K = -\mathbf{n}\cdot[\![\mathbf{T}]\!]\mathbf{n}$ of the standard interfacial force balance (cf. (29.6))

$$[\![\mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} + \gamma\mathbf{n}\cdot\mathbf{Tt}]\!] - \varepsilon\bar\sigma K = [\![\mathbf{T}\cdot\mathbf{E}]\!] - \varepsilon\,\mathrm{tr}\,[\![\mathbf{T}]\!]; \tag{33.7}$$

this allows us to rewrite (33.6) yielding the identity

$$\mathcal{G} = [\![\Psi - \mathbf{T}\cdot\mathbf{E}]\!] + \varepsilon\,\mathrm{tr}\,[\![\mathbf{T}]\!] + \psi K + \bar\sigma\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar\tau}{\partial s} + g. \tag{33.8}$$

In view of the definition $\Phi = \Psi - \mathbf{T}\cdot\mathbf{E}$ (cf. (7.15)) of the free enthalpy, (33.8) is equivalent to

$$\mathcal{G} = [\![\Phi]\!] + \varepsilon\,\mathrm{tr}\,[\![\mathbf{T}]\!] + \psi K + \bar\sigma\,\frac{\partial\gamma}{\partial s} + \frac{\partial\bar\tau}{\partial s} + g. \tag{33.9}$$

Finally, *if surface stress is neglected*, so that $\bar\sigma = 0$, $[\![\mathbf{T}]\!]\mathbf{n} = \mathbf{0}$, and $\bar\tau = \tau$, then, since $\mathbf{T} = \mathbf{T}^{\top}$, $\mathbf{1} = \mathbf{n}\otimes\mathbf{n} + \mathbf{t}\otimes\mathbf{t}$, and $[\![\nabla\mathbf{u}]\!]\mathbf{t} = \mathbf{0}$,[91]

$$\begin{aligned}
[\![\mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n}]\!] &= \langle\!\langle\mathbf{T}\rangle\!\rangle\mathbf{n}\cdot[\![\nabla\mathbf{u}]\!]\mathbf{n} + [\![\mathbf{T}]\!]\mathbf{n}\cdot\langle\!\langle\nabla\mathbf{u}\rangle\!\rangle\mathbf{n}\\
&= \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\nabla\mathbf{u}]\!]\mathbf{n}\otimes\mathbf{n}\\
&= \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\nabla\mathbf{u}]\!](\mathbf{1} - \mathbf{t}\otimes\mathbf{t})\\
&= \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\nabla\mathbf{u}]\!] - \langle\!\langle\mathbf{T}\rangle\!\rangle\mathbf{t}\cdot[\![\nabla\mathbf{u}]\!]\mathbf{t}\\
&= \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\mathbf{E}]\!];
\end{aligned} \tag{33.10}$$

thus, in this case,

$$\mathcal{G} = [\![\Psi]\!] - \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\mathbf{E}]\!] - \psi K + \frac{\partial\tau}{\partial s} + g. \tag{33.11}$$

34 Constitutive equations for the interface

Our approach to the constitutive theory is guided by the interfacial dissipation inequality (31.16), which is almost identical to the inequality (23.9) that arises in the theory for strained solid-vapor interfaces. Thus, reasoning as in §25, we arrive at constitutive equations

$$\left.\begin{aligned}
\bar\sigma &= \frac{\partial\hat\psi(\varepsilon,\vartheta)}{\partial\varepsilon},\\
\bar\tau &= \frac{\partial\hat\psi(\varepsilon,\vartheta)}{\partial\vartheta},
\end{aligned}\right\} \tag{34.1}$$

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[91] Equation (4.15) of Gurtin and Voorhees (1993) erroneously asserts that $[\![\mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n}]\!] = [\![\mathbf{T}\cdot\mathbf{E}]\!]$ (†), which differs from (33.10). Because of this, results ensuing from (†), such as their (8.3), are incorrect.

determining the standard scalar interfacial stress and the reduced shear in conjunction with constitutive equations[92]

$$\left.\begin{aligned} h^\alpha &= -L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}, \\ g &= -bV, \end{aligned}\right\} \tag{34.2}$$

for the interfacial atomic fluxes and the normal internal force. Here the matrix with coefficients $L^{\alpha\beta}$ is positive semi-definite, while $b \geq 0$; these moduli may be dependent upon (ε, ϑ).

35 General equations for the interface

The basic interfacial balances are the standard force-balance, the atomic balance, and the normal configurational force balance (cf. §29.2, §30)

$$\left.\begin{gathered} \llbracket\mathbf{T}\rrbracket\mathbf{n} = -\bar\sigma K\mathbf{n} - \frac{\partial\bar\sigma}{\partial s}\mathbf{t}, \qquad \llbracket\rho^\alpha\rrbracket V = \frac{\partial h^\alpha}{\partial s} + \llbracket\boldsymbol{\jmath}^\alpha\rrbracket\cdot\mathbf{n}, \\ \sum_{\alpha=1}^{N}\llbracket\rho^\alpha\rrbracket\mu^\alpha = \llbracket\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{t}\cdot\mathbf{Tn}\rrbracket + (\psi - \bar\sigma\varepsilon)K + \bar\sigma\frac{\partial\gamma}{\partial s} + \frac{\partial\bar\tau}{\partial s} + g. \end{gathered}\right\} \tag{35.1}$$

These interfacial balances are coupled to the interfacial constitutive relations (34.1) and (34.2). Thus, combining the interfacial balances and the constitutive relations and using the identity (26.6), which applies here also, we arrive at the standard force and atomic balances

$$\left.\begin{aligned} \llbracket\mathbf{T}\rrbracket\mathbf{n} &= -\frac{\partial\psi}{\partial\varepsilon}K\mathbf{n} - \left(\frac{\partial^2\psi}{\partial\varepsilon^2}\frac{\partial\varepsilon}{\partial s} + \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}K\right)\mathbf{t}, \\ \llbracket\boldsymbol{\jmath}^\alpha\rrbracket\cdot\mathbf{n} &= \frac{\partial}{\partial s}\left(\sum_{\beta=1}^{N}L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\right) + \llbracket\rho^\alpha\rrbracket V, \end{aligned}\right\} \tag{35.2}$$

and the normal configurational force balance

$$\begin{aligned} \sum_{\alpha=1}^{N}\llbracket\rho^\alpha\rrbracket\mu^\alpha = \llbracket\Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - \gamma\mathbf{n}\cdot\mathbf{Tt}\rrbracket& \\ + \left(\psi + \frac{\partial^2\psi}{\partial\vartheta^2} - \varepsilon\frac{\partial\psi}{\partial\varepsilon}\right)K + \frac{\partial^2\psi}{\partial\varepsilon\partial\vartheta}\frac{\partial\varepsilon}{\partial s} + \frac{\partial\psi}{\partial\varepsilon}\frac{\partial\gamma}{\partial s} - bV.& \end{aligned} \tag{35.3}$$

If we neglect surface stress, then $\psi = \psi(\vartheta)$ and the standard force-balance $(35.2)_1$ has the simple form

$$\llbracket\mathbf{T}\rrbracket\mathbf{n} = \mathbf{0} \tag{35.4}$$

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[92] For convenience, we neglect coupling from the outset; the corresponding coupled equations would have the form

$$h^\alpha = -\sum_{\beta=1}^{N}L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s} - \ell^\alpha V, \qquad g = -\sum_{\alpha=1}^{N}B^\alpha\frac{\partial\mu^\alpha}{\partial s} - bV.$$

asserting that the (standard) traction be continuous across the interface, the atomic balance $(35.2)_2$ reads

$$[\![\jmath^\alpha]\!]\cdot\mathbf{n} = \frac{\partial}{\partial s}\biggl(\sum_{\beta=1}^{N} L^{\alpha\beta}\frac{\partial\mu^\beta}{\partial s}\biggr) + [\![\rho^\alpha]\!]V, \tag{35.5}$$

and the normal configurational force balance (35.3) becomes

$$\sum_{\alpha=1}^{N}[\![\rho^\alpha]\!]\mu^\alpha = [\![\Psi]\!] - \langle\!\langle\mathbf{T}\rangle\!\rangle\cdot[\![\mathbf{E}]\!] + \biggl(\psi + \frac{\partial^2\psi}{\partial\vartheta^2}\biggr)K - bV. \tag{35.6}$$

The internal force $g = -bV$, a dissipative force associated with the rearrangement of atoms at the interface, and, thus, is of a physical nature akin to that encountered in our discussion of grain boundaries. Such a force is generally not included in discussions of migrating coherent interfaces, typically because the possibility of having such a force is precluded from the outset by an appeal to local equilibrium. The other sources of kinetics for such problems are bulk and interfacial diffusion; because the time-scales associative with such processes are typically very long, the force $g = -bV$ could possibly be relevant. We know of no investigations as to the relative importance of these disparate measures of kinetics.

APPENDICES

A Justification of the free-energy conditions (9.45) at zero stress. Gibbs relation

Consider a substitutional alloy without vacancies and, as before, let $\Psi_0(\vec{\rho})$ denote the free energy at zero stress. In addition, consider a second material identical to the substitutional alloy in question except that vacancies with density $\rho^{\rm v}$ are present, and let $\check{\Psi}_0(\vec{\rho},\rho^{\rm v})$ denote the corresponding free energy at zero stress. We now show that:

- if $\check{\Psi}_0(\vec{\rho},\rho^{\rm v}) \to \Psi_0(\vec{\rho})$ as $\rho^{\rm v}\to 0$, and
- if, as $\rho^{\rm v}\to 0$, the corresponding chemical potentials $\check{\mu}_0^{\alpha\rm v}(\vec{\rho},\rho^{\rm v})$ relative to vacancies have limiting values,

then, writing $\mu_0^\alpha(\vec{\rho})$ for the limiting values of $\check{\mu}_0^{\alpha\rm v}(\vec{\rho},\rho^{\rm v})$ as $\rho^{\rm v}$ approaches zero, *the free-energy conditions at zero stress are satisfied.*

We consider $\mu_0^\alpha(\vec{\rho})$ to be the species-α chemical-potential for $\Psi_0(\vec{\rho})$; $\mu_0^\alpha(\vec{\rho})$ should be interpreted as a chemical potential, relative to vacancies, in the limit of vanishing vacancies.

Note that μ_0^α is defined solely as a limiting value. This limiting value cannot be equal to $\partial\Psi_0/\partial\rho^\alpha$, which, in light of of the lattice constraint, *is not meaningful.* On the other hand, by (9.45), the difference $\mu_0^\alpha(\vec{\rho}) - \mu_0^\beta(\vec{\rho})$ represents, for $\Psi_0(\vec{\rho})$, the chemical potential of α relative to β.

To establish the foregoing assertions, we assume that

(i) $\check{\Psi}_0(\vec{\rho},\rho^{\rm v})$ is continuous with continuous Larché–Cahn derivatives on the set

$$\mathrm{D}_{\rm vac} \overset{\rm def}{=} \biggl\{(\vec{\rho},\rho^{\rm v})\ :\ \sum_{\alpha=1}^{N}\rho^\alpha = \rho^{\rm sites}+\rho^{\rm v},\quad \rho^\alpha>0\ (\alpha=1,2,\ldots,N),\quad \rho^{\rm v}\ge 0\biggr\} \tag{A1}$$

(so that the smoothness described above is up to $\rho^{\rm v} = 0$);

(ii) $\Psi_0(\vec{\rho})$ is the zero-vacancy limit of $\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})$,

$$\Psi_0(\vec{\rho}) = \check{\Psi}_0(\vec{\rho}, 0). \tag{A2}$$

By (i) and (ii), $\Psi_0(\vec{\rho})$ is continuous with continouous Larché–Cahn derivatives on the *constraint set*

$$\mathrm{D}_{\rm con} \overset{\rm def}{=} \left\{ \vec{\rho} \ : \ \sum_{\alpha=1}^{N} \rho^\alpha = \rho^{\rm sites}, \quad \rho^\alpha > 0 \ (\alpha = 1, 2, \dots, N) \right\}. \tag{A3}$$

Further, by (9.44) applied to $\check{\Psi}_0$,

$$\left.\begin{aligned} \check{\mu}_0^{\alpha{\rm v}}(\vec{\rho}, \rho^{\rm v}) &= \frac{\partial^{({\rm v})}\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})}{\partial \rho^\alpha}, \\ \check{\mu}_0^{\alpha\beta}(\vec{\rho}, \rho^{\rm v}) &= \frac{\partial^{(\beta)}\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})}{\partial \rho^\alpha}. \end{aligned}\right\} \tag{A4}$$

Moreover, $(5.6)_3$ yields

$$\check{\mu}_0^{\alpha\beta}(\vec{\rho}, \rho^{\rm v}) = \check{\mu}_0^{\alpha{\rm v}}(\vec{\rho}, \rho^{\rm v}) - \check{\mu}_0^{\beta{\rm v}}(\vec{\rho}, \rho^{\rm v}). \tag{A5}$$

By (i), the Larché–Cahn derivatives of $\check{\Psi}_0$ exist and are continuous *up to* $\rho^{\rm v} = 0$. The limit $\rho^{\rm v} \to 0$ therefore yields

$$\frac{\partial^{(\beta)}\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})}{\partial \rho^\alpha} \longrightarrow \frac{\partial^{(\beta)}\check{\Psi}_0(\vec{\rho}, 0)}{\partial \rho^\alpha} = \frac{\partial^{(\beta)}\Psi_0(\vec{\rho})}{\partial \rho^\alpha} \tag{A6}$$

and

$$\frac{\partial^{({\rm v})}\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})}{\partial \rho^\alpha} \longrightarrow \frac{\partial^{({\rm v})}\check{\Psi}_0(\vec{\rho}, 0)}{\partial \rho^\alpha} \overset{\rm def}{=} \mu_0^\alpha(\vec{\rho}). \tag{A7}$$

Thus, by (A4)–(A7),

$$\check{\mu}_0^{\alpha\beta}(\vec{\rho}, \rho^{\rm v}) \longrightarrow \mu_0^\alpha(\vec{\rho}) - \mu_0^\beta(\vec{\rho}), \tag{A8}$$

and by $(\mathrm{A4})_2$ and (A6),

$$\check{\mu}_0^{\alpha\beta}(\vec{\rho}, \rho^{\rm v}) = \frac{\partial^{(\beta)}\check{\Psi}_0(\vec{\rho})}{\partial \rho^\alpha} \longrightarrow \frac{\partial^{(\beta)}\Psi_0(\vec{\rho})}{\partial \rho^\alpha} = \mu^{\alpha\beta}(\vec{\rho});$$

therefore, appealing to (9.44),

$$\mu_0^{\alpha\beta}(\vec{\rho}) = \frac{\partial^{(\beta)}\Psi_0(\vec{\rho})}{\partial \rho^\alpha} = \mu_0^\alpha(\vec{\rho}) - \mu_0^\beta(\vec{\rho}), \tag{A9}$$

which is $(9.45)_2$.

We are now in a position to establish the Gibbs relation $(9.45)_1$. Let $\Psi_0^{({\rm v})}(\vec{\rho})$ denote $\check{\Psi}_0(\vec{\rho}, \rho^{\rm v})$ with $\rho^{\rm v}$ eliminated via the lattice constraint:

$$\Psi_0^{({\rm v})}(\vec{\rho}) = \check{\Psi}_0(\vec{\rho}, \rho^{\rm v})\Big|_{\rho^{\rm v} = \rho^{\rm sites} - \sum\limits_{\alpha=1}^{N} \rho^\alpha}.$$

The domain of $\Psi_0^{(\mathrm{v})}(\vec{\rho})$ is the set

$$\mathrm{D}^{(\mathrm{v})} \overset{\mathrm{def}}{=} \left\{ \vec{\rho} \,:\, \sum_{\alpha=1}^{N} \rho^{\alpha} \le \rho^{\mathrm{sites}}, \quad \rho^{\alpha} > 0 \ (\alpha = 1, 2, \dots, N) \right\}. \tag{A10}$$

and the boundary of $\mathrm{D}^{(\mathrm{v})}$ contains the constraint set $\mathrm{D}_{\mathrm{con}}$. By (9.8),

$$\frac{\partial \Psi_0^{(\mathrm{v})}(\vec{\rho})}{\partial \rho^{\alpha}} = \left. \frac{\partial^{(\mathrm{v})} \check{\Psi}_0(\vec{\rho}, \rho^{\mathrm{v}})}{\partial \rho^{\alpha}} \right|_{\rho^{\mathrm{v}} = \rho^{\mathrm{sites}} - \sum\limits_{\alpha=1}^{N} \rho^{\alpha}}$$

and, in view of (i), $\Psi_0^{(\mathrm{v})}(\vec{\rho})$ is continuously differentiable on $\mathrm{D}^{(\mathrm{v})}$, up to $\mathrm{D}_{\mathrm{con}}$. Define

$$\mu^{(\mathrm{v})\alpha}(\vec{\rho}) = \frac{\partial \Psi_0^{(\mathrm{v})}(\vec{\rho})}{\partial \rho^{\alpha}}. \tag{A11}$$

Then, by (A2) and (A7), since $\mathrm{D}_{\mathrm{con}}$ corresponds to $\rho^{\mathrm{v}} = 0$,

$$\Psi_0(\vec{\rho}) = \Psi_0^{(\mathrm{v})}(\vec{\rho}) \quad \text{and} \quad \mu_0^{\alpha}(\vec{\rho}) = \mu^{(\mathrm{v})\alpha}(\vec{\rho}) \quad \text{for all} \quad \vec{\rho} \in \mathrm{D}_{\mathrm{con}}. \tag{A12}$$

Finally, since $\Psi_0^{(\mathrm{v})}(\vec{\rho})$ and $\mu^{(\mathrm{v})\alpha}(\vec{\rho})$ are consistent with (A11) and are unencumbered by the lattice constraint in the interior of $\mathrm{D}_{\mathrm{con}}$, we may argue as in §8 to show that $\Psi_0^{(\mathrm{v})}(\vec{\rho}) = \rho^{\alpha} \mu^{(\mathrm{v})\alpha}(\vec{\rho})$. Thus, by (A12), passing to the limit $\rho^{\mathrm{v}} = 0$, we have the Gibbs relation $(9.45)_1$.

B Equivalent formulations of the basic laws. Control-volume equivalency theorem

In our development of the equations governing the bulk material, we formulated the basic laws — the configurational force, standard force, and atomic balances, and the imbalance for free energy — first for fixed parts $\mathcal{P}$ of the body and then, to account for the role of configurational forces, for migrating control volumes $\mathcal{R}(t)$. On the other hand, our discussion of interfaces is based almost exclusively on the use of interfacial pillboxes. Alternatively we could base this discussion on the use of migrating control volumes that *contain a portion of the interface.* The purpose of this section is to show that the two methods of formulating basic laws are equivalent. With this in mind, let $\mathcal{R}(t)$ denote *a migrating control volume* (in the sense of §11.2). We then refer to $\mathcal{R}(t)$:

- as a *migrating bulk control-volume* if $\mathcal{R}(t)$ lies solely in the bulk material;
- as a *migrating interfacial control-volume* if $\mathcal{R}(t)$ contains a portion of the interface in its interior;
- as a *general migrating control-volume* if $\mathcal{R}(t)$ is either a migrating bulk control-volume or a migrating interfacial control-volume.

CONTROL-VOLUME EQUIVALENCY THEOREM For each of the basic laws $\mathcal{L}$ under consideration, $\mathcal{L}$ is satisfied for all general migrating control-volumes if and only if:

(i) $\mathcal{L}$ is satisfied for all migrating bulk control-volumes:
(ii) $\mathcal{L}$ is satisfied for all interfacial pillboxes.

Since the family of all general migrating control-volumes includes the family of migrating bulk control-volumes, to establish the theorem it suffices to show that, granted $\mathcal{L}$ is satisfied for all migrating bulk control-volumes, $\mathcal{L}$ is satisfied for all migrating interfacial control-volumes if and only if $\mathcal{L}$ is satisfied for all interfacial pillboxes. The basic laws under consideration are the balance laws for configurational forces, standard forces, and atoms, and the imbalance for free energy. Here we shall establish equivalence for

$$\mathcal{L} = \{\text{free-energy imbalance}\},$$

but not for the three balance laws, as their proof is similar and not as difficult.

Thus consider a migrating interfacial control-volume $\mathcal{R}(t)$, and let $\mathcal{C}(t)$, with $\mathbf{x}_a(t)$ and $\mathbf{x}_b(t)$ the endpoints of $\mathcal{C}(t)$, denote the portion of the interface in $\mathcal{R}(t)$. For such a control volume the appropriate generalization of the free-energy imbalance (12.17) has the form

$$\begin{aligned}\underbrace{\frac{d}{dt}\left\{\int\limits_{\mathcal{R}(t)}\Psi\,da+\int\limits_{\mathcal{C}(t)}\psi\,ds\right\}}_{\text{net free energy of }\mathcal{R}} &\le \underbrace{\int\limits_{\partial\mathcal{R}(t)}(\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}}+\mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\,ds+\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}+\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b}_{\substack{\text{power expended on }\mathcal{R}\text{ across }\partial\mathcal{R}\text{ and}\\ \text{across the end points }\mathbf{x}_a\text{ and }\mathbf{x}_b\text{ of }\mathcal{C}}}\\ &\quad\underbrace{+\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^\alpha(-\boldsymbol{\jmath}^\alpha\cdot\boldsymbol{\nu}+\rho V_{\partial\mathcal{R}})\,ds+\sum_{\alpha=1}^{N}\big[\mu^\alpha\big(-h^\alpha+\delta^\alpha W\big)\big]_a^b}_{\substack{\text{energy flow into }\mathcal{R}\text{ by atomic transport across }\partial\mathcal{R}\\ \text{and across the endpoints }\mathbf{x}_a\text{ and }\mathbf{x}_b\text{ of }\mathcal{C}}}.\end{aligned}\tag{B1}$$

On the other hand, the free-energy imbalance for a interfacial pillbox $\mathcal{C}(t)$ has the form

$$\begin{aligned}\underbrace{\frac{d}{dt}\int\limits_{\mathcal{C}(t)}\psi\,ds}_{\substack{\text{free energy}\\ \text{of }\mathcal{C}}} &\le \underbrace{\int\limits_{\mathcal{C}(t)}(\llbracket\mathbf{C}\rrbracket\mathbf{n}\cdot\mathbf{v}+\llbracket\mathbf{T}\rrbracket\mathbf{n}\cdot\overset{\square}{\mathbf{u}})\,ds+\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}+\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b}_{\substack{\text{power expended on }\mathcal{C}\text{ by the bulk material across }\mathcal{C}^+\text{ and }\mathcal{C}^-\\ \text{and by the remainder of the interface across }\mathbf{x}_a\text{ and }\mathbf{x}_b}}\\ &\quad\underbrace{+\sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}(t)}\mu^\alpha\big(-\llbracket\boldsymbol{\jmath}^\alpha\rrbracket\cdot\mathbf{n}+\llbracket\rho^\alpha\rrbracket V\big)\,ds+\sum_{\alpha=1}^{N}\big[\mu^\alpha\big(-h^\alpha+\delta^\alpha W\big)\big]_a^b}_{\substack{\text{energy flow into }\mathcal{C}\text{ by atomic transport from the bulk material across}\\ \mathcal{C}^+\text{ and }\mathcal{C}^-\text{ and from the remainder of the interface across }\mathbf{x}_a\text{ and }\mathbf{x}_b}}.\end{aligned}\tag{B2}$$

In the imbalances (B1) and (B2) the bulk fields are as defined in Part A. The remaining fields consist of an interfacial free-energy ψ, vector fields $\mathbf{c}$ and $\mathbf{s}$ that represent configurational and standard stress within the interface, and scalar fields h and δ that represent the atomic flux and atomic density within the interface. The interface is assumed to be coherent and the (bulk) chemical potential μ, assumed continuous across the interface, represents the chemical potential of $\mathcal{S}$. For convenience, we restrict attention to a single species of atoms. The formulation of (B2) is discussed at length in Part E, and one may use that discussion and the bulk imbalance (12.17) to infer the imbalance (B1). But to follow our proof of equivalency it is not necessary that one understand in detail the formulation of (B1) and (B2).

Specifically, we will show that, *granted* (cf. (12.17))

$$\frac{d}{dt}\int\limits_{\mathcal{R}(t)}\Psi\,da \;\le\; \int\limits_{\partial\mathcal{R}(t)}(\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}}+\mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\,ds-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}(t)}\mu^{\alpha}\big(\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}-\rho^{\alpha}V_{\partial\mathcal{R}}\big)\,ds$$

for all migrating bulk control-volumes $\mathcal{R}(t)$, (B3)

the imbalance (B1) *is satisfied for all migrating interfacial control-volumes if and only if the imbalance* (B2) *is satisfied for all interfacial pillboxes.* To establish this assertion, let $\mathcal{R}(t)$ be an interfacial control volume and let $\mathcal{R}^+(t)$ and $\mathcal{R}^-(t)$ denote the bulk control volumes represented by the portions of $\mathcal{R}(t)$ that lie in the $(+)$ and $(-)$ phases, so that the portion of $\partial\mathcal{R}^+(t)$ that coincides with $\mathcal{C}(t)$ is viewed as lying in the $(+)$-phase at the interface, and similarly for $\partial\mathcal{R}^-(t)$. Dropping the argument t when convenient, let $\boldsymbol{\nu}_{\partial\mathcal{R}^\pm}$ denote the outward unit normal on $\partial\mathcal{R}^\pm$ (Figure 21). Then, by (B3) with $\mathcal{R}=\mathcal{R}^\pm$,

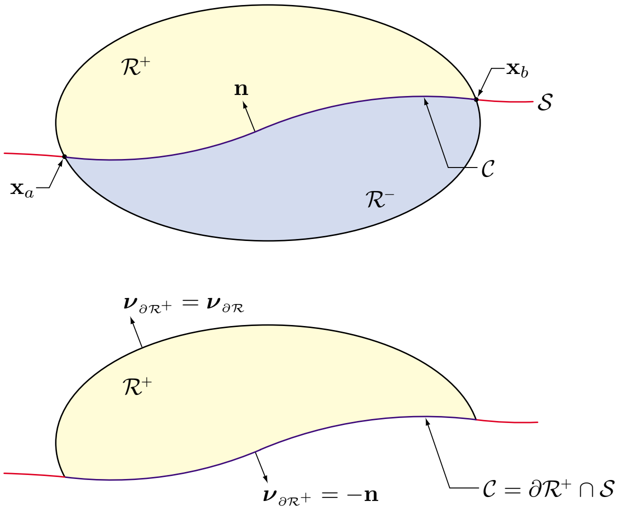

Figure 21: An interfacial control volume $\mathcal{R}$ and the bulk control volume $\mathcal{R}^+$. $\mathcal{C}$ is the portion of the interface that lies inside $\mathcal{R}$.

$$\frac{d}{dt}\int\limits_{\mathcal{R}^\pm}\Psi\,da \le \int\limits_{\partial\mathcal{R}^\pm}(\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}^\pm}+\mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\,ds-\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{P}^\pm}\mu^{\alpha}\big(\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu}-\rho^{\alpha}V_{\partial\mathcal{R}^\pm}\big)\,ds, \qquad \text{(B4)}$$

Moreover, on $\mathcal{C}$,

$$\left.\begin{aligned}\boldsymbol{\nu}_{\partial\mathcal{R}^+}&=-\mathbf{n}, & V_{\partial\mathcal{R}^+}&=-V, & \mathbf{v}_{\partial\mathcal{R}^+}&=\mathbf{v}=V\mathbf{n},\\ \boldsymbol{\nu}_{\partial\mathcal{R}^-}&=\mathbf{n}, & V_{\partial\mathcal{R}^-}&=V, & \mathbf{v}_{\partial\mathcal{R}^-}&=\mathbf{v}=V\mathbf{n},\end{aligned}\right\} \qquad \text{(B5)}$$

and

$$\mathring{\mathbf{u}}=\overset{\square}{\mathbf{u}} \quad \text{on both } \partial\mathcal{R}^{+}\cap\mathcal{C} \text{ and } \partial\mathcal{R}^{-}\cap\mathcal{C}. \qquad \text{(B6)}$$

Therefore, adding the two equations represented by (B4),

$$\begin{aligned}\frac{d}{dt}\int\limits_{\mathcal{R}} \Psi\, da \;&\leq \int\limits_{\partial\mathcal{R}} (\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\, ds + \int\limits_{\partial\mathcal{R}} \mu^{\alpha}(-\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu} + \rho^{\alpha}V_{\partial\mathcal{R}})\, ds \\ &\quad - \int\limits_{\mathcal{C}(t)} \big(\llbracket\mathbf{C}\rrbracket\mathbf{n}\cdot\mathbf{v} + \llbracket\mathbf{T}\rrbracket\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\big)\, ds - \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}(t)} \mu^{\alpha}\big(-\llbracket\boldsymbol{\jmath}^{\alpha}\rrbracket\cdot\mathbf{n} + \llbracket\rho^{\alpha}\rrbracket V\big)\, ds. \qquad \text{(B7)}\end{aligned}$$

Assume that the free-energy imbalance (B2) for a interfacial pillbox is satisfied. Then adding (B2) and (B7) we arrive at the free-energy imbalance (B1) for a migrating interfacial control-volume.

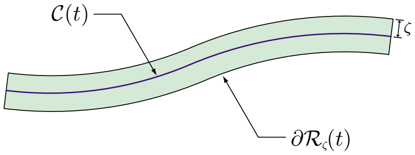

Figure 22: The migrating interfacial control volume $\mathcal{R}_{\zeta}$.

To prove the converse assertion, assume that (B1) holds for all migrating interfacial control-volumes. Choose an arbitrary evolving subcurve $\mathcal{C}(t)$ and let $\mathcal{R}_{\zeta}(t)$ denote the migrating interfacial control-volume defined by (Figure 22)

$$\mathcal{R}_{\zeta}(t) = \big\{\mathbf{x} : \mathbf{x} = \mathbf{z} \pm \zeta\mathbf{m}(\mathbf{z},t),\ \mathbf{z}\in\mathcal{C}(t),\ 0 \leq \zeta \ll 1\big\},$$

so that $\mathcal{R}_{\zeta} \to \mathcal{C}$ as $\zeta \to 0$. In this limit, using limiting relations for the upper and lower faces of the approximate pillbox $\mathcal{R}_{\zeta}$ analogous to the identities (B5)–(B6), we find that

$$\frac{d}{dt}\int\limits_{\mathcal{R}_{\zeta}} \Psi\, da \to 0,$$

$$\int\limits_{\partial\mathcal{R}_{\zeta}} (\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}_{\zeta}} + \mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\, ds \to \int\limits_{\mathcal{C}} (\llbracket\mathbf{C}\rrbracket\mathbf{n}\cdot\mathbf{v} + \llbracket\mathbf{T}\rrbracket\mathbf{n}\cdot\overset{\square}{\mathbf{u}})\, ds,$$

$$\sum_{\alpha=1}^{N}\int\limits_{\partial\mathcal{R}_{\zeta}} \mu^{\alpha}(-\boldsymbol{\jmath}^{\alpha}\cdot\boldsymbol{\nu} + \rho^{\alpha}V_{\partial\mathcal{R}_{\zeta}})\, ds \to \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}} \mu^{\alpha}\big(-\llbracket\boldsymbol{\jmath}^{\alpha}\rrbracket\cdot\mathbf{n} + \llbracket\rho^{\alpha}\rrbracket V\big)\, ds.$$

Thus passing to the limit $\zeta \to 0$ in (B1) (with $\mathcal{R} = \mathcal{R}_{\zeta}$), we are led to the free-energy imbalance (B2) for the interfacial pillbox $\mathcal{C}$.

This completes the proof of the portion of the Control-Volume Equivalency Theorem relevant to free-energy imbalances.

C Status of the theory as an approximation of the finite-deformation theory

The theory developed in the body of this study is restricted to small deformations. Here, we give an abbreviated account of the finite-deformation theory and of the formal analysis involved in the approximation of small deformations within that theory.

C.1 Theory for finite deformations

(a) Kinematics

We now use the symbol $\mathbf{x}$ to denote an arbitrary material point as labelled in a fixed *reference configuration.* The interface $\mathcal{S} = \mathcal{S}(t)$ and all pillboxes $\mathcal{C} = \mathcal{C}(t)$ are assumed to lie in the reference configuration.

In a theory of finite deformations the *deformation* $\mathbf{y}$ is related to the displacement through the relation

$$\mathbf{y}(\mathbf{x}, t) = \mathbf{x} + \mathbf{u}(\mathbf{x}, t);$$

$\mathbf{y}(\mathbf{x}, t)$ represents the point of space occupied by the material point $\mathbf{x}$ at time t. By (C4), the interfacial *deformation-derivative*

$$\mathbf{f} \overset{\text{def}}{=} \frac{\partial \mathbf{y}}{\partial s} \tag{C1}$$

is related to the interfacial surface-strain $\mathbf{e} = \partial \mathbf{u}/\partial s$ through

$$\mathbf{f} = \mathbf{t} + \mathbf{e}. \tag{C2}$$

Consistent with the small-deformation theory, we refer to

$$\varepsilon = \mathbf{t} \cdot \mathbf{e}, \qquad \gamma = \mathbf{n} \cdot \mathbf{e} \; (= \mathbf{n} \cdot \mathbf{f}) \tag{C3}$$

as the interfacial tensile and shear strains. The field

$$\lambda = |\,\mathbf{f}\,|$$

represents the interfacial *stretch*; clearly,

$$\lambda^2 = 1 + 2\varepsilon + |\mathbf{e}|^2. \tag{C4}$$

The vector field

$$\bar{\mathbf{t}} = \lambda^{-1}\mathbf{f} \tag{C5}$$

represents a (unit) *tangent to the deformed interface.* Trivially, $\mathbf{f} = \lambda\bar{\mathbf{t}}$; hence (C2) and the identity $\bar{\mathbf{t}} \cdot \bar{\mathbf{t}}^{\square} = 0$ imply that $\lambda^{\square} = \bar{\mathbf{t}} \cdot \mathbf{f}^{\square}$. Thus, since $\mathbf{t}^{\square} = \vartheta^{\square}\mathbf{n}$ (14.16), the stretch rate satisfies

$$\overset{\square}{\lambda} = \bar{\mathbf{t}} \cdot \overset{\square}{\mathbf{e}} + \overset{\square}{\vartheta}\bar{\mathbf{t}} \cdot \mathbf{n}. \tag{C6}$$

(b) Standard and configurational forces. Power

The treatment of configurational forces follows §19.1 and, as before, leads to the *normal configurational force balance* (20.1), viz.

$$\sigma K + \frac{\partial \tau}{\partial s} + g - \mathbf{n} \cdot \mathbf{C}\mathbf{n} = 0. \tag{C7}$$

The *standard force and torque balances for* a pillbox $\mathcal{C}$ take the form

$$\left.\begin{aligned} \mathbf{s}\big|_a^b - \int\limits_{\mathcal{C}} \mathbf{T}\mathbf{n}\, ds &= \mathbf{0}, \\ \big[(\mathbf{y} - \mathbf{0}) \times \mathbf{s}\big]_a^b - \int\limits_{\mathcal{C}} (\mathbf{y} - \mathbf{0}) \times \mathbf{T}\mathbf{n}\, ds &= \mathbf{0}; \end{aligned}\right\} \tag{C8}$$

comparing these balances to their small-deformation conterparts (20.2), we see that the force balance is unchanged, but the torque balance reflects the fact that we are working in the finite-deformation theory. The integral balances (C8) are equivalent to the local balances[93]

$$\frac{\partial \mathbf{s}}{\partial s} = \mathbf{T}\mathbf{n}, \qquad \bar{\mathbf{t}} \times \mathbf{s} = \mathbf{0}. \tag{C9}$$

The second of (C9) renders $\mathbf{s}$ tangent to the *deformed* interface; hence there is a scalar field $\bar{\sigma}$, the (scalar) standard surface stress, such that

$$\mathbf{s} = \bar{\sigma}\bar{\mathbf{t}}. \tag{C10}$$

Our discussion of *power* follows §21.1. The net external power expended on a pillbox $\mathcal{C}(t)$ has the form

$$\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \big(\mathbf{C}\mathbf{n}\cdot\mathbf{v} + \mathbf{T}\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\big)\,ds.$$

The configurational portion of this expenditure is given by (29.9). To determine the contribution of the standard forces, we use (15.17) and the identity $\partial\overset{\square}{\mathbf{u}}/\partial s = \overset{\square}{\mathbf{e}} - KV\mathbf{e}$ (15.12) to obtain

$$\begin{aligned}\left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b &= \big[\mathbf{s}\cdot\overset{\square}{\mathbf{u}} + (\mathbf{s}\cdot\mathbf{e})W\big]_a^b \\ &= \big[(\mathbf{s}\cdot\mathbf{e})W\big]_a^b + \int\limits_{\mathcal{C}}\left(\frac{\partial\mathbf{s}}{\partial s}\cdot\overset{\square}{\mathbf{u}} + \mathbf{s}\cdot\overset{\square}{\mathbf{e}} - (\mathbf{s}\cdot\mathbf{e})KV\right)ds\end{aligned}$$

(cf. (21.1)), and, using the standard force balance $(\mathrm{C9})_1$,

$$\left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \mathbf{T}\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\,ds = \big[(\mathbf{s}\cdot\mathbf{e})W\big]_a^b + \int\limits_{\mathcal{C}}\Big(\mathbf{s}\cdot\overset{\square}{\mathbf{e}} - (\mathbf{s}\cdot\mathbf{e})KV\Big)\,ds. \tag{C11}$$

Combining (29.9) and (C11) yields the *power balance*

$$\begin{aligned}&\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}} \big(\mathbf{C}\mathbf{n}\cdot\mathbf{v} + \mathbf{T}\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\big)\,ds \\ &\qquad = \big[(\sigma + \mathbf{s}\cdot\mathbf{e})W\big]_a^b + \int\limits_{\mathcal{C}} \big[\mathbf{s}\cdot\overset{\square}{\mathbf{e}} + \tau\overset{\square}{\vartheta} - \big((\sigma + \mathbf{s}\cdot\mathbf{e})K + g\big)V\big]\,ds.\end{aligned} \tag{C12}$$

(c) Free-energy imbalance

Our discussion of atomic transport is as in §22 and leads to the atomic balance (22.4).

The *free-energy imbalance* for an arbitrary interfacial pillbox $\mathcal{C} = \mathcal{C}(t)$ takes the form

$$\begin{aligned}\frac{d}{dt}\int\limits_{\mathcal{C}}\psi\,ds \le\ &\left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt}\right]_a^b - \int\limits_{\mathcal{C}}\mathbf{C}\mathbf{n}\cdot\mathbf{v}\,ds + \left[\mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b - \int\limits_{\mathcal{C}}\mathbf{T}\mathbf{n}\cdot\overset{\square}{\mathbf{u}}\,ds \\ &+ \sum_{\alpha=1}^{N}\big[\mu^\alpha(-h^\alpha + \delta^\alpha W)\big]_a^b + \sum_{\alpha=1}^{N}\int\limits_{\mathcal{C}}\mu^\alpha(\boldsymbol{\jmath}^\alpha\cdot\mathbf{n} - \rho^\alpha V + r^\alpha)\,ds\end{aligned}$$

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[93] Cf. Gurtin and Murdoch (1974), who derive three-dimensional force and moment balances in a finite-strain setting. See also Fried and Gurtin (2003).

(cf. (23.4)), and, in view of (C12), (22.4), and the integral transport theorem (14.29), yields the inequality

$$\int\limits_{\mathcal{C}} (\overset{\square}{\psi} - \psi K V)\, ds + \overbrace{\left[\left(\psi - \mathbf{s}\cdot\mathbf{e} - \sum_{\alpha=1}^{N} \mu^\alpha \delta^\alpha - \sigma\right) W\right]_a^b}^{(\#)}$$
$$\leq \int\limits_{\mathcal{C}} \left(\mathbf{s}\cdot\overset{\square}{\mathbf{e}} + \tau\overset{\square}{\vartheta} - \left(\sigma + \mathbf{s}\cdot\mathbf{e} + \sum_{\alpha=1}^{N}\mu^\alpha\delta^\alpha\right) K V - gV\right) ds$$
$$- \sum_{\alpha=1}^{N} \left[\mu^\alpha h^\alpha\right]_a^b + \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \mu^\alpha \left(\overset{\square}{\delta}{}^\alpha + \frac{\partial h^\alpha}{\partial s}\right) ds. \tag{C13}$$

Since $\mathcal{C}$ is arbitrary, so also are the tangential velocities W_a and W_b of the endpoints of $\mathcal{C}$; thus, since the only term in (C13) dependent on these velocities is the term (#), we have the *interfacial Eshelby relation*

$$\sigma = \psi - \mathbf{s}\cdot\mathbf{e} - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha, \tag{C14}$$

which should be compared with its counterpart (23.6) of the small-deformation theory.

Since

$$\sum_{\alpha=1}^{N} \left[\mu^\alpha h^\alpha\right]_a^b = \sum_{\alpha=1}^{N} \int\limits_{\mathcal{C}} \left(\mu^\alpha \frac{\partial h^\alpha}{\partial s} + h^\alpha \frac{\partial \mu^\alpha}{\partial s}\right) ds,$$

we may use (C14) to rewrite (C13) as

$$\int\limits_{\mathcal{C}} \left(\overset{\square}{\psi} - \mathbf{s}\cdot\overset{\square}{\mathbf{e}} - \tau\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N}\left(\mu^\alpha \overset{\square}{\delta}{}^\alpha - h^\alpha \frac{\partial \mu^\alpha}{\partial s}\right) + gV\right) ds \leq 0;$$

since $\mathcal{C}$ is arbitrary, this yields the *interfacial dissipation inequality*

$$\overset{\square}{\psi} - \mathbf{s}\cdot\overset{\square}{\mathbf{e}} - \tau\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N}\left(\mu^\alpha \overset{\square}{\delta}{}^\alpha - h^\alpha \frac{\partial \mu^\alpha}{\partial s}\right) + gV \leq 0. \tag{C15}$$

(d) Normal configurational force balance revisited

As before, we have the bulk Eshelby relation (12.15), but now the interfacial Eshelby relation has the form (C14); we may therefore write the normal configurational force balance and (for a substitutional alloy) the chemistry-composition relations in the respective forms (24.3) and (24.12), viz.

$$\sum_{\alpha=1}^{N} (\rho^\alpha - \delta^\alpha K)\mu^\alpha = \mathcal{F}, \qquad \mu^\alpha = \sum_{\beta=1}^{N} c_{\mathrm{ef}}^{\beta} \mu^{\alpha\beta} + \Omega_{\mathrm{ef}}\mathcal{F}, \tag{C16}$$

but with the mechanical force now given by (cf. (24.2))

$$\mathcal{F} = \Psi - \mathbf{Tn}\cdot(\nabla\mathbf{u})\mathbf{n} - (\psi - \mathbf{s}\cdot\mathbf{e})K - \frac{\partial \tau}{\partial s} - g. \tag{C17}$$

(e) Constitutive equations without regard to torque balance

Our discussion of constitutive equations closely follows §**??**. Guided by the interfacial dissipation inequality (C20), we consider constitutive equations giving

$$\psi,\ \mathbf{s},\ \tau,\ \vec{\mu}\ \text{ as functions of }\ (\mathbf{e}, \vartheta, \vec{\delta}\,) \tag{C18}$$

in conjunction with constititutive equations for h^α and g of the form (25.1), with coefficients possibly dependent on $(\mathbf{e}, \vartheta, \vec{\delta}\,)$, rather than $(\varepsilon, \vartheta, \vec{\delta}\,)$. (The discussion of constitutive equations for h^α and g, follows §25.)

Appealing to the discussion of §17.8, we find that

$$\left.\begin{aligned} \mathbf{s} &= \frac{\partial\tilde{\psi}(\mathbf{e}, \vartheta, \vec{\delta}\,)}{\partial\mathbf{e}}, \\ \tau &= \frac{\partial\tilde{\psi}(\mathbf{e}, \vartheta, \vec{\delta}\,)}{\partial\vartheta}, \\ \mu^\alpha &= \frac{\partial\tilde{\psi}(\mathbf{e}, \vartheta, \vec{\delta}\,)}{\partial\delta^\alpha}. \end{aligned}\right\} \tag{C19}$$

The difference between (C19) and the constitutive relations (25.2) of the small-deformation theory is reflected by the use of $\mathbf{s}$, τ, and $\mathbf{e}$ as constitutive variables in place of $\bar{\sigma}$, $\bar{\tau}$, and ε.

> **Remark** The theory as developed thus far is valid whether or not the local torque balance $\bar{\mathbf{t}} \times \mathbf{s} = \mathbf{0}$ is satisfied.

This observation is central to what follows. As we shall see, *the theory we develop as a small-deformation approximation of the finite-deformation theory satisfies the torque balance only approximately, but otherwise falls within the thermomechanical structure of the finite-deformation theory.* We refer to the finite-deformation theory based on the constitutive equations discussed above, but with the torque balance omitted, as the *finite-deformation theory without torque balance.*

(f) Constitutive equations consistent with torque balance

To establish consequences of the torque balance, we return to the dissipation inequality (C20), which, by virtue of (C6) and (C10), we may rewrite as

$$\overset{\square}{\psi} - \bar{\sigma}\overset{\square}{\lambda} - \bar{\tau}\overset{\square}{\vartheta} - \sum_{\alpha=1}^{N}\left(\mu^\alpha\overset{\square}{\delta}{}^\alpha - h^\alpha\frac{\partial\mu^\alpha}{\partial s}\right) + gV \le 0, \tag{C20}$$

where

$$\bar{\tau} = \tau - (\bar{\mathbf{t}} \cdot \mathbf{n})\bar{\sigma}$$

is the *reduced shear.*

Consider once again constitutive relations in the form (C18). By (C2) and (C5), a dependence on $(\mathbf{e}, \vartheta, \vec{\delta}\,)$ is equivalent to a dependence on $(\lambda, \bar{\mathbf{t}}, \vartheta, \vec{\delta}\,)$; thus, since $\mathbf{s} = \bar{\sigma}\bar{\mathbf{t}}$ is a consequence of the torque balance (cf. (C10)), (C18) is equivalent to relations giving

$$\psi,\ \bar{\sigma},\ \bar{\tau},\ \vec{\mu}\ \text{ as functions of }\ (\lambda, \bar{\mathbf{t}}, \vartheta, \vec{\delta}\,). \tag{C21}$$

Therefore, arguing as before, we conclude, as a consequence of the dissipation inequality, that *the free energy must be independent of the deformed tangent* $\bar{\mathbf{t}}$,

$$\psi = \hat{\psi}(\lambda, \vartheta, \vec{\delta}\,), \tag{C22}$$

and must generate $\bar{\sigma}$, $\bar{\tau}$, and $\vec{\mu}$ through the relations (Fried and Gurtin, 2003)

$$\left.\begin{aligned} \bar{\sigma} &= \frac{\partial\hat{\psi}(\lambda,\vartheta,\vec{\delta}\,)}{\partial\lambda}, \\ \bar{\tau} &= \frac{\partial\hat{\psi}(\lambda,\vartheta,\vec{\delta}\,)}{\partial\vartheta}, \\ \mu^\alpha &= \frac{\partial\hat{\psi}(\lambda,\vartheta,\vec{\delta}\,)}{\partial\delta^\alpha}. \end{aligned}\right\} \tag{C23}$$

The finite-deformation theory is discussed at great length by Fried and Gurtin (2003) and the reader is referred there for a thorough discussion of the basic equations as well as of the partial differential equations resulting from various simplifying assumptions.[94]

C.2 Theory for small deformations as an approximation of the finite-deformation theory

The chief differences between the small-deformation theory developed in the body of this study and the theory discussed in this section involves the constitutive interactions between stress, strain, and orientation. So as to not obscure these differences we simplify the theory by *neglecting adatoms.* The inclusion of adatoms involves only minor modifications.

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[94] The finite-deformation theory as described by Fried and Gurtin (2003) is based on a configurational stress of the form

$$\check{\mathbf{C}} = \Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha - \mathbf{F}^{\top}\mathbf{T},$$

with $\mathbf{F} = \mathbf{1} + \nabla\mathbf{u}$ the *deformation gradient*, but here — because $\mathbf{F}$ is not suitable for a discussion of small deformations — the configurational stress has the form

$$\mathbf{C} = \Psi - \sum_{\alpha=1}^{N} \rho^\alpha \mu^\alpha - (\nabla\mathbf{u})^{\top}\mathbf{T}.$$

However, the bulk theory itself is independent of which of the two configurational stress tensors one uses; to prove this one notes that $\check{\mathbf{C}} = \mathbf{C} - \mathbf{T}$ and hence

$$\int\limits_{\partial\mathcal{R}(t)} (\check{\mathbf{C}}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{y}})\,da = \int\limits_{\partial\mathcal{R}(t)} (\mathbf{C}\boldsymbol{\nu}\cdot\mathbf{v}_{\partial\mathcal{R}} + \mathbf{T}\boldsymbol{\nu}\cdot\mathring{\mathbf{u}})\,da$$

(cf. (11.9)), whereby the superficial power is invariant with respect to whether the theory is based on deformation or on displacement (Gurtin (2000, §13). Similarly, Fried and Gurtin (2003) show that the the appropriate form of the interfacial Eshelby relation in the deformation-gradient based formulation is

$$\check{\sigma} = \psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha - \mathbf{s}\cdot\mathbf{f},$$

while we here find that

$$\sigma = \psi - \sum_{\alpha=1}^{N} \delta^\alpha \mu^\alpha - \mathbf{s}\cdot\mathbf{e},$$

so that $\check{\sigma} = \sigma - \mathbf{t}\cdot\mathbf{s}$. Assuming that the internal configurational force $\mathbf{g}$ is the same for both formulations, the configurational shear transforms according to $\check{\tau} = \tau - \mathbf{n}\cdot\mathbf{s}$, so that $\check{\mathbf{c}} = \mathbf{c} - \mathbf{s}$ and again the theory itself is independent of which of the two expressions for the interfacial configurational tension is used, the relevant step here being to show that

$$\left[\check{\mathbf{c}}\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\frac{d\mathbf{y}}{dt}\right]_a^b = \left[(\mathbf{c}-\mathbf{s})\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\left(\frac{d\mathbf{x}}{dt} + \frac{d\mathbf{u}}{dt}\right)\right]_a^b = \left[\mathbf{c}\cdot\frac{d\mathbf{x}}{dt} + \mathbf{s}\cdot\frac{d\mathbf{u}}{dt}\right]_a^b.$$

(a) Small-strain estimates

We are interested in a theory appropriate to situations in which $\mathbf{e}$ is small; thus, using the symbol $\mathrm{o}(\mathbf{e})$ to denote terms that, in a precise sense, are smaller than $\mathbf{e}$ in the limit $\mathbf{e} \to \mathbf{0}$,[95] we have the estimate

$$\lambda = 1 + \varepsilon + \mathrm{o}(\mathbf{e}). \tag{C24}$$

By (C2) and (C24),

$$\bar{\mathbf{t}} = \mathbf{t} + \gamma \mathbf{n} + \mathrm{o}(\mathbf{e}). \tag{C25}$$

The estimates (C24) and (C25) are central to our discussion of small deformations.

(b) Constitutive relations appropriate to small deformations

In developing an approximate theory appropriate to small deformations, the relevant constitutive relation is that for the stress; since $\mathbf{s} = \bar{\sigma}\bar{\mathbf{t}}$, the first of (C23) yields the relation

$$\mathbf{s} = \bar{\sigma}(\lambda)\bar{\mathbf{t}}, \tag{C26}$$

where, for convenience, we have suppressed the argument ϑ and have written

$$\bar{\sigma}(\lambda) = \frac{\partial \hat{\psi}(\lambda)}{\partial \lambda}.$$

Granted smoothness, we may use (C24) to conclude that

$$\bar{\sigma}(\lambda) = \bar{\sigma}_0 + \left.\frac{\partial \bar{\sigma}}{\partial \lambda}\right|_0 \varepsilon + \mathrm{o}(\mathbf{e}),$$

where the subscript 0 denotes evaluation at $\lambda = 1$. Thus, by (C25) and (C26), we have the estimate

$$\mathbf{s} = \left(\bar{\sigma}_0 + \left.\frac{\partial \bar{\sigma}}{\partial \lambda}\right|_0 \varepsilon + \mathrm{o}(\mathbf{e})\right)\Big(\mathbf{t} + \mathbf{e} - \varepsilon \mathbf{t} + \mathrm{o}(\mathbf{e})\Big), \tag{C27}$$

and, introducing the *surface elasticity*

$$k = \left.\frac{\partial \bar{\sigma}}{\partial \lambda}\right|_0$$

and appealing to (C3), we have the equivalent estimates[96]

$$\begin{aligned} \mathbf{s} &= \bar{\sigma}_0 \mathbf{t} + (k - \bar{\sigma}_0)\varepsilon \mathbf{t} + \bar{\sigma}_0 \mathbf{e} + \mathrm{o}(\mathbf{e}), \\ &= (\bar{\sigma}_0 + k\varepsilon)\mathbf{t} + \bar{\sigma}_0 \gamma \mathbf{n} + \mathrm{o}(\mathbf{e}). \end{aligned} \tag{C28}$$

Consider now the second of these estimates with terms of $\mathrm{o}(\mathbf{e})$ neglected:

$$\mathbf{s} = (\bar{\sigma}_0 + k\varepsilon)\mathbf{t} + \underline{\bar{\sigma}_0 \gamma \mathbf{n}}. \tag{C29}$$

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[95] A function $f(\mathbf{z})$ is $\mathrm{o}(\mathbf{z}^n)$ if $|\mathbf{z}|^{-n} f(\mathbf{z}) \to 0$ as $\mathbf{z} \to \mathbf{0}$; $f(\mathbf{z})$ is $\mathrm{O}(\mathbf{z}^n)$ if $|\mathbf{z}|^{-n} f(\mathbf{z})$ is bounded as $\mathbf{z} \to \mathbf{0}$.

[96] These represent a two-dimensional version of (L) of the Addenda to Gurtin and Murdoch (1975).

(Without the underlined term the stress $\mathbf{s}$ is consistent with the torque balance $\mathbf{t}\times\mathbf{s}=\mathbf{0}$ $(29.3)_2$ of the theory as presented in the main body of the paper.) Writing

$$\left.\begin{aligned} w &= \bar{\sigma}_0\varepsilon + \tfrac{1}{2}k\varepsilon^2 + \tfrac{1}{2}\bar{\sigma}_0\gamma^2, \\ &= \bar{\sigma}_0(\mathbf{e}\cdot\mathbf{t}) + \tfrac{1}{2}k(\mathbf{e}\cdot\mathbf{t})^2 + \tfrac{1}{2}\bar{\sigma}_0(\mathbf{e}\cdot\mathbf{n})^2, \end{aligned}\right\} \tag{C30}$$

we see that $\mathbf{s}=\partial w/\partial\mathbf{e}$ and hence that $w=w(\mathbf{e})$ represents an interfacial *strain energy.*

Thus far the orientation ϑ has been irrelevant to our discussion. We now include orientational dependences and therefore write $\bar{\sigma}_0=\bar{\sigma}_0(\vartheta)$ and $k=k(\vartheta)$. Then, if $\tilde{\psi}(\mathbf{e},\vartheta)$ represents the resulting free energy, we must have

$$\tilde{\psi}(\mathbf{e},\vartheta)=\psi_0(\vartheta)+w(\mathbf{e},\vartheta), \qquad \mathbf{s}=\frac{\partial\tilde{\psi}(\mathbf{e},\vartheta)}{\partial\mathbf{e}}, \tag{C31}$$

with

$$w(\mathbf{e},\vartheta)=\bar{\sigma}_0(\vartheta)(\mathbf{e}\cdot\mathbf{t})+\tfrac{1}{2}k(\vartheta)(\mathbf{e}\cdot\mathbf{t})^2+\tfrac{1}{2}\bar{\sigma}_0(\vartheta)(\mathbf{e}\cdot\mathbf{n})^2, \tag{C32}$$

bearing in mind that

$$\mathbf{t}=\mathbf{t}(\vartheta), \qquad \mathbf{n}=\mathbf{n}(\vartheta).$$

For consistency with both (25.5) and $(\text{C19})_2$, we define the configurational shear through

$$\tau=\frac{\partial\tilde{\psi}(\mathbf{e},\vartheta)}{\partial\vartheta}. \tag{C33}$$

We supplement these constitutive relations by Fick's law (25.8) and the kinetic relation (25.9), allowing for anisotropy, viz

$$h^\alpha=-\sum_{\beta=1}^{N}L^{\alpha\beta}(\vartheta)\frac{\partial\mu^\beta}{\partial s}, \qquad g=-b(\vartheta)V. \tag{C34}$$

To ensure ensure satisfaction of the dissipation inequality (C20), we assume that $b(\vartheta)\geq 0$ and that the matrix with entries $L^{\alpha\beta}(\vartheta)$ is positive semi-definite. *The constitutive theory as defined by* (C31)–(C34) *is then a special case of the constitutive relations* (C19) *of the finite-deformation theory without torque balance.*

(c) Basic equations of the theory

Bearing in mind that we are neglecting adatom densities, the balances for standard forces and atoms, namely (C9) and (22.4), take the form

$$\left.\begin{aligned} \mathbf{Tn} &= \frac{\partial\mathbf{s}}{\partial s}, \\ \rho^\alpha V &= -\frac{\partial h^\alpha}{\partial s}+\boldsymbol{\jmath}^\alpha\cdot\mathbf{n}+r^\alpha, \end{aligned}\right\} \tag{C35}$$

while the normal configurational force balance and the configurational-chemistry relations (for substitutional alloys) take the respective forms

$$\sum_{\alpha=1}^{N}\rho^\alpha\mu^\alpha=\mathcal{F}, \qquad \mu^\alpha=\sum_{\beta=1}^{N}c^\beta\mu^{\alpha\beta}+\Omega\mathcal{F} \tag{C36}$$

(cf. (26.26)), with mechanical potential $\mathcal{F}$ given by (C17).

Since the constitutive relations (C31)–(C34) render the theory consistent with the dissipation inequality (C20), the balances (C35) and (C36) supplemented by (C31)–(C34) represents an *exact* system of equations within the framework of the finite-deformation theory without torque balance. The single basic relation not satisfied is the torque balance; as we shall see, this balance is satisfied to within and error of $\mathrm{o}(\mathbf{e})$.

The constitutive relations (C31)–(C33) have the specific form

$$\left.\begin{aligned}
&\psi = \psi_0(\vartheta) + \bar{\sigma}_0(\vartheta)\varepsilon + \tfrac{1}{2}k(\vartheta)\varepsilon^2 + \underline{\tfrac{1}{2}\bar{\sigma}_0(\vartheta)\gamma^2},\\
&\mathbf{s} = (\bar{\sigma}_0(\vartheta) + k(\vartheta)\varepsilon)\mathbf{t} + \underline{\bar{\sigma}_0(\vartheta)\gamma\mathbf{n}},\\
&\tau = \psi_0'(\vartheta) + \bar{\sigma}_0'(\vartheta)\varepsilon + \tfrac{1}{2}k'(\vartheta)\varepsilon^2 + \bar{\sigma}_0(\vartheta)\gamma + k(\vartheta)\varepsilon\gamma + \underline{\tfrac{1}{2}\bar{\sigma}_0'(\vartheta)\gamma^2 - \bar{\sigma}_0(\vartheta)\varepsilon\gamma},
\end{aligned}\right\} \tag{C37}$$

where the underlined terms in (C37) represent those terms emanating from the underlined term in (C29).

With the exception of the atomic balance, which with $(\mathrm{C34})_2$ has the form

$$\rho^\alpha V = \frac{\partial}{\partial s}\bigg(\sum_{\beta=1}^{N} L^{\alpha\beta}(\vartheta)\frac{\partial \mu^\beta}{\partial s}\bigg) + \boldsymbol{j}^\alpha\cdot\mathbf{n} + r^\alpha$$

(cf. $(26.32)_2$), the partial differential equations resulting from this general theory are excessively complicated and nothing is to be gained by writing them explicitly.

(d) Basic equations with isotropic strain energy

The ensuing calculations make repeated use of the kinematical relations (15.10) and (15.11).

Isotropy of the strain energy renders both $\bar{\sigma}$ and k *constant*; consequently, the normal and tangential components of the standard force balance have the respective forms

$$\left.\begin{aligned}
\mathbf{n}\cdot\mathbf{T}\mathbf{n} &= \bigg(\bar{\sigma}_0 + (k-\bar{\sigma}_0)\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)K + \bar{\sigma}_0\mathbf{n}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2},\\
\mathbf{t}\cdot\mathbf{T}\mathbf{n} &= \bigg((k-\bar{\sigma}_0)\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)K + k\mathbf{t}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2},
\end{aligned}\right\} \tag{C38}$$

and the mechanical potential becomes

$$\begin{aligned}
\mathcal{F} = \Psi - \mathbf{T}\mathbf{n}\cdot(\nabla\mathbf{u})\mathbf{n} - \bigg\{&\psi_0(\vartheta) + \psi_0''(\vartheta) - \tfrac{3}{2}k\bigg(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)^2 + k\bigg(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)^2\\
&- \bar{\sigma}_0\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s} + \bar{\sigma}_0\bigg[\bigg(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)^2 - \tfrac{3}{2}\bigg(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)^2\bigg]\bigg\}K\\
&- \bigg\{\bar{\sigma}_0\mathbf{n} + (k-\bar{\sigma}_0)\bigg[\bigg(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)\mathbf{n} + \bigg(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)\mathbf{t}\bigg]\bigg\}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} + b(\vartheta)V.
\end{aligned} \tag{C39}$$

In the theory developed in the main body of this paper, the underlined terms in (C37) are absent. These terms lead to the presence of additional terms

$$-\bar{\sigma}_0\bigg(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)K + \bar{\sigma}_0\mathbf{n}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2} \qquad \text{and} \qquad -\bar{\sigma}_0\bigg(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\bigg)K$$

in $(\mathrm{C38})_1$ and $(\mathrm{C38})_2$, respectively, and to the additional terms

$$\bar{\sigma}_0\left[\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)^2-\tfrac{3}{2}\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial n}\right)^2\right]K \qquad\text{and}\qquad \bar{\sigma}_0\left[\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{n}+\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{t}\right]\cdot\frac{\partial^2\mathbf{u}}{\partial s^2}$$

in (C39).

These equations simplify further when the *interface has negligible elasticity* in the sense that

$$k=0,$$

for then the standard force balance has the form

$$\left.\begin{aligned}\mathbf{n}\cdot\mathbf{T}\mathbf{n}&=\bar{\sigma}_0\left\{\left(1-\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)K+\mathbf{n}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2}\right\}\\ \mathbf{t}\cdot\mathbf{T}\mathbf{n}&=-\bar{\sigma}_0\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}K\end{aligned}\right\}\tag{C40}$$

and the mechanical potential reduces to

$$\begin{aligned}\mathcal{F}=\Psi-\Bigg\{&\psi_0(\vartheta)+\psi_0''(\vartheta)+\bar{\sigma}_0\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n}-\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)-\bar{\sigma}_0\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n}\right)\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\\ &-\bar{\sigma}_0\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial n}\right)+\bar{\sigma}_0\left[\left(\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)^2-\tfrac{3}{2}\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)^2\right]\Bigg\}K\\ &-\bar{\sigma}_0\left\{\left(1+\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial n}-\mathbf{t}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{n}-\left(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\right)\mathbf{t}\right\}\cdot\frac{\partial^2\mathbf{u}}{\partial s^2}+b(\vartheta)V.\end{aligned}\tag{C41}$$

(e) Comparison of small-deformation theories

The general finite-deformation theory discussed in §C.1 satisfies the *torque balance*

$$\big[(\mathbf{y}-\mathbf{0})\times\mathbf{s}\big]_a^b-\int\limits_{\mathcal{C}}(\mathbf{y}-\mathbf{0})\times\mathbf{T}\mathbf{n}\,ds=\mathbf{0}\tag{C42}$$

(cf. $(\mathrm{C8})_2$), which has the local form

$$\bar{\mathbf{t}}\times\mathbf{s}=\mathbf{0},\tag{C43}$$

but the theory developed in this section (§C.2) — which we refer to as *the first-order strain theory* — satisfies this torque balance only approximately. Specifically, the first-order strain theory is based on the stress-strain relation

$$\mathbf{s}=(\bar{\sigma}_0+k\varepsilon)\mathbf{t}+\bar{\sigma}_0\gamma\mathbf{n},\tag{C44}$$

so that, by (C2), (C3), and (C5),

$$|\bar{\mathbf{t}}\times\mathbf{s}|=\lambda^{-1}\big|(\mathbf{t}+\varepsilon\mathbf{t}+\gamma\mathbf{n})\times\big((\bar{\sigma}_0+k\varepsilon)\mathbf{t}+\sigma_0\gamma\mathbf{n}\big)\big|=\lambda^{-1}|\varepsilon\gamma(\bar{\sigma}_0-k)|,$$

giving the estimate

$$|\bar{\mathbf{t}}\times\mathbf{s}|=\mathrm{O}(\mathbf{e}^2).\tag{C45}$$

Thus, while the local torque balance (C43) is not satisfied exactly, it is satisfied to within an error of $\mathrm{O}(\mathbf{e}^2)$.

Consider, next, the theory developed in the main body of the paper, but with the specific free-energy defined by (26.34) and (26.35), a theory that we refer to as the *exact infinitesimal strain theory.* This theory is based on the *torque balance*

$$\big[(\mathbf{x}-\mathbf{0})\times\mathbf{s}\big]_a^b-\int\limits_{\mathcal{C}}(\mathbf{x}-\mathbf{0})\times\mathbf{Tn}\,ds=\mathbf{0} \tag{C46}$$

(cf. (20.2)), whose localization, $\mathbf{t}\times\mathbf{s}=\mathbf{0}$, yields $\mathbf{s}=\bar{\sigma}\mathbf{t}$ (20.4). Thus, in view of (20.4) and the constitutive relations (26.34), (26.35), and (25.2),

$$\mathbf{s}=(\bar{\sigma}_0+k\varepsilon)\mathbf{t}; \tag{C47}$$

hence the argument leading to (C45) yields

$$|\bar{\mathbf{t}}\times\mathbf{s}|=\lambda^{-1}|\gamma(\bar{\sigma}_0+k\varepsilon)|$$

and results in the estimate

$$|\bar{\mathbf{t}}\times\mathbf{s}|=\mathrm{O}(\mathbf{e}). \tag{C48}$$

The first-order strain theory therefore provides a better approximation to the torque balance (C43) *of the finite-deformation theory than does the exact infinitesimal strain theory.*

On the other hand, *the exact infinitesimal strain theory is compatible with the theory in bulk as developed in Part A, but the first-order strain theory is not.* Indeed, the torque balance (C46) of the exact infinitesimal strain theory is compatible with the *bulk* torque balance

$$\int\limits_{\partial\mathcal{P}}(\mathbf{x}-\mathbf{0})\times\mathbf{T}\boldsymbol{\nu}\,da=\mathbf{0} \tag{C49}$$

(cf. $(2.2)_2$), and hence the two balances may be combined to form a torque balance for a control volume that contains both bulk and interfacial material. But the stress $\mathbf{s}$ of the first-order strain theory does not satisfy the torque balance (C46), since $|\mathbf{t}\times\mathbf{s}|=|\bar{\sigma}_0\gamma|$. Further, the exact infinitesimal strain theory and the theory in bulk are consistent with the form of material frame-indifference appropriate to small deformations; namely invariance under transformations of the form $\nabla\mathbf{u}\mapsto\nabla\mathbf{u}+\mathbf{W}$, with $\mathbf{W}$ an arbitrary skew tensor. But the first-order strain theory does not have this invariance, since $\gamma\mapsto\gamma+\mathbf{n}\cdot\mathbf{Wt}$ under transformations of the form $\nabla\mathbf{u}\mapsto\nabla\mathbf{u}+\mathbf{W}$. In fact, in the first-order theory, an infinitesimal rigid rotation induces stress.

Pragmatically, one might expect that the exact infinitesimal strain theory might be suitable to situations in which $\bar{\sigma}_0$ is of the same order as $k\varepsilon$ (and ε is small), for then the term $\bar{\sigma}_0\gamma$ in the first-order strain theory should be negligible. On the other hand, for $\bar{\sigma}_0$ large we would expect the first-order strain theory to be more appropriate. In considering this issue one should bear in mind that, for $\bar{\sigma}_0$ large and k negligibly small, the tangential part of the standard force balance has the form

$$\mathbf{t}\cdot\mathbf{Tn}=-\bar{\sigma}_0\Big(\mathbf{n}\cdot\frac{\partial\mathbf{u}}{\partial s}\Big)K$$

(cf. $(\mathrm{C40})_2$) in the first-order strain theory, as compared to

$$\mathbf{t}\cdot\mathbf{Tn}=0$$

(cf. (26.47)) in the exact infinitesimal strain theory.

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1014	Brown, E. N., M. R. Kessler, N. R. Sottos, and S. R. White	*In situ* poly(urea-formaldehyde) microencapsulation of dicyclopentadiene—*Journal of Microencapsulation* (submitted)	Feb. 2003
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1018	Costello, G. A.	Mechanics of wire rope—Mordica Lecture, Interwire 2003, Wire Association International, Atlanta, Georgia, May 12, 2003	Mar. 2003
1019	Wang, J., N. R. Sottos, and R. L. Weaver	Thin film adhesion measurement by laser induced stress waves—*Journal of the Mechanics and Physics of Solids* (submitted)	Apr. 2003
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