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Coherent Solid-State Phase Transitions with Atomic Diffusion: A Thermomechanical Treatment

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Using the framework of modern continuum thermomechanics, we develop sharp- and diffuse-interface theories for coherent solid-state phase transitions. These theories account for atomic diffusion and for deformation. Of essential importance in our formulation of the sharp-interface theory are a system of "configurational forces" and an associated "configurational force balance." These forces, which are distinct from standard Newtonian forces, describe the intrinsic material structure of a body. The configurational balance, when restricted to the interface, leads to a generalization of the classical Gibbs–Thomson relation, a generalization that accounts for the orientation dependence of the interfacial energy density and also for a broad spectrum of dissipative transition kinetics. Our diffuse-interface theory involves nonstandard "microforces" and an associated "microforce balance." These forces arise naturally from an interpretation of the atomic densities as macroscopic parameters that describe atomistic kinematics distinct from the motion of material particles. When supplemented by thermodynamically consistent constitutive relations, the microforce balance yields a generalization of the Cahn–Hilliard relation giving the chemical potentials as variational derivatives of the total free energy with respect to the atomic densities. A formal asymptotic analysis (thickness of the transition layer approaching zero) demonstrates the correspondence between versions of our theories specialized to the case of a single mobile species for situations in which the time scale for interface propagation is small compared to that for bulk diffusion. While the configurational force balance is redundant in the diffuse-interface theory, when integrated over the transition layer, the limit of this balance is the interfacial configurational force balance (i.e., generalized Gibbs–Thomson relation) of the sharp-interface theory.

KEY WORDS: Phase transitions; solid-state diffusion; elasticity; generalized Gibbs–Thomson relation; Cahn–Hilliard theory.

Dedicated to John Cahn, whose work with Francis Larché and John Hilliard formed a basis for much of what is presented here.

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1. INTRODUCTION

Based on the approach of Gibbs (1878), materials scientists such as Cahn, Eshelby, Frank, Herring, Larché, Mullins, and Sekerka have developed continuum theories for phase transitions in which the interface between phases is modeled as a surface.[3] Of essential importance in these theories is an interface condition derived variationally as a consequence of an assumption of local equilibrium; in contrast to all other bulk equations and interface conditions, this condition, which results from arbitrary variations of the interface, cannot be identified with one of the standard balances for mass, force, or energy.

In parallel with the work of the materials scientists, mechanicians such as Coleman, Ericksen, Toupin, Truesdell, and Noll constructed a framework for general nonlinear theories of continua,[4] a framework based on three principal ingredients:

(*i*) balance laws (for mass, momentum, energy, etc.),

(*ii*) an imbalance that represents the second law of thermodynamics,

(*iii*) constitutive equations.

Here, a careful distinction is maintained between the basic laws embodied within (*i*) and (*ii*), which govern a broad spectrum of materials, and the relations (*iii*) that define particular elements within that spectrum. The basic laws are stated in integral form; when localized, the balances yield partial differential equations and jump conditions, whereas the imbalance results in differential and jump inequalities whose chief use is to restrict constitutive equations. The framework determined by (*i*)–(*iii*) has been used with great success in developing general theories for large classes of materials under a wide range of operating conditions. Standard examples include solids and fluids whose behavior may be elastic, plastic, viscous, or viscoelastic. More esoteric examples include granular materials, liquid crystals, and superconductors.

These simultaneous advances in materials science and in continuum mechanics have for the most part, proceeded independently, with little interaction, although workers in mechanics have recently become aware of the wealth of interesting conceptual problems that arise when materials science is discussed at a macroscopic level. The resulting studies, while firmly grounded in the framework (*i*)–(*iii*), involve issues that are completely nonstandard in continuum mechanics. To begin with, a basic tenet

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[3] Selected contributions include Cahn (1980), Cahn and Larché (1980, 1983), Eshelby (1956, 1970), Frank (1958), Herring (1951, 1953), Larché and Cahn (1973, 1978a, 1978b, 1982, 1983), Mullins (1956, 1960, 1982, 1984), and Mullins and Sekerka (1963, 1964, 1985).

[4] See Truesdell and Toupin (1960) and Truesdell and Noll (1965) and the references therein.

of continuum mechanics has been that basic laws should be formulated for given collections of material points; but evolving defect structures, such as phase interfaces, are composed of different material points at different times and, as such, possess no intrinsic material identity. Further, continuum mechanical laws involving energy require generalization to accomodate expenditures of power resulting from the evolution of the defect structures, and this in turn requires the introduction of forces that are, in some sense, work-conjugate to the motion of these structures. Such "configurational forces" have a physical nature far different from that of classical Newtonian forces (standard forces): configurational forces do not enter the standard momentum balance laws, nor do they affect the manner in which standard forces perform work. Further, a conceptual unification occurs when a force balance, distinct from the standard balance law for linear momentum, is postulated for configurational forces. This configurational force balance, while applicable to dynamical theories in the presence of dissipation, is, in fact, compatible with equilibrium theories derived variationally, as conditions resulting from arbitrary variations of the interface are consistent with its localization to the interface.

That additional configurational forces may be needed to describe phenomena associated with the material itself is clear from the work of Eshelby (1951, 1956, 1970, 1975) and is at least intimated by Gibbs (1878). Gibbs's discussion is paraphrased by Cahn (1980), as follows: "solid surfaces can have their physical area changed in two ways, either by creating or destroying surface without changing surface structure and properties per unit area, or by an elastic strain ... along the surface keeping the number of surface lattice sites constant ..." The creation of surface involves *configurational* forces, while stretching the surface involves *standard* forces.

To quote Herring (1951) on crystalline materials: "the principal cause of surface tension is the fact that surface atoms are bound by fewer neighbors than internal atoms; surface tension is therefore mainly a measure of the change in the number of atoms in the surface layer." We interpret this as an indication that surface tension in crystalline materials is primarily *configurational*.

The conceptual framework developed by continuum mechanicians seems almost entirely unknown to materials scientists, and the recent extension of continuum mechanics to the study of evolving defect structures seems not well known to the general continuum mechanics community; this paper, mostly a review, is intended to help remedy this situation.

Here, we discuss the interaction of deformation and composition. Following Larché and Cahn (1985), we associate with each point of the body microstructure defined by a lattice or network through which various (substitutional and interstitial) species of mobile atoms, characterized by their densities, diffuse. We use the framework described by (*i*)–(*iii*) to develop a thermodynamically consistent, dynamical theory appropriate to a single phase material, a treatment that we later extend to account for phase transitions. The underlying balances are balance of mass, balance of standard forces, and balance of configurational forces; the second law is the assertion that the energy of each evolving subregion of the body increase at a rate not greater than the rate at which the standard and configurational forces perform work on the subregion; interfacial free energy is taken into account; the force systems include forces, such as surface tension, relevant to the mechanics of the interface; the constitutive equations for the interface account for orientational dependence as well as rate dependence.

An alternative description of solid-state diffusional phase transitions is based on a rediscovery, by the materials scientists Cahn and Hilliard,[5] of an idea advanced by Fuchs (1888), Rayleigh (1892), and van der Waals (1893),[6] who, in their studies of liquid-vapor transitions, treated the phase interface not as a surface, but, rather, as a thin layer across which the density varies continuously but suffers a large gradient. The standard derivation of this theory begins with the provision of a constitutive equation that determines the free-energy density as a function of the atomic densities, their gradients, and the strain. Constitutive dependence upon density gradients renders problematic the standard assumption that the chemical potential of a given atomic species be determined by the derivative of the free energy with respect to the density of that species. To overcome this difficulty, Cahn (1961) suggested that the chemical potentials be determined by computing variational derivatives, with respect to the atomic densities, of the total free energy of the system. The atomic fluxes are then stipulated to be proportional to the gradients of the chemical potentials and the final governing equations consist of the atomic balances and the standard force balance, the latter arising by conventional variational arguments.

Here, we apply the framework (*i*)–(*iii*) to develop a thermodynamically consistent, dynamical, diffuse-interface theory of Cahn–Hilliard type. The features that most distinguish our approach arise in connection with our treatment of the atomic densities. Specifically, we interpret the atomic densities as macroscopic parameters that describe atomistic kinematics distinct from the motion of material particles. To account for the associated power expenditures, we introduce microforces. Further, we require that the microforces affiliated with each atomic species comply with an additional microforce balance. As an important consequence of our formulation, we

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[5] See Cahn (1959, 1961, 1962) and Cahn and Hilliard (1958, 1959, 1971).

[6] See Rowlison (1988) for a discussion of the early history of the role of density gradients in describing capillary phenomena.

find that the microforce balances yield expressions for the chemical potentials, expressions that generalize the variational definition advanced by Cahn (1961).

The notion that the microstructural fields should obey a supplemental balance is not novel. Oseen (1933) provided a theory for the motion of liquid crystals that included a vector field describing the average orientation of the liquid crystalline molecules, a generalized force associated with the time-rate of that field, and a balance distinct from the standard momentum balances and involving that force. Later, this approach to liquid crystals was refined and extended by Ericksen (1960, 1961, 1991) and Leslie (1968). Following Ericksen's approach, Goodman and Cowin (1972) developed a theory for flowing granular materials that, to account for variations in grain distribution, incorporates a scalar volume distribution function and generalized forces that act over changes in that function and are constrained by an additional balance. These and other applications involving microstructural variables, microforces, and microbalances are discussed by Capriz (1989), Capriz and Podio-Guidugli (1983), and Fried (1996). An alternate approach in which the microforce balance is a consequence of the *principle of virtual power*,[7] has been used by Fremond (1987, 1992) to construct theories for adherence and damage.

With this diffuse-interface theory there are no free boundaries and, hence, no interface conditions. There is, however, interfacial structure—as characterized by the constitutive dependencies on gradients and rates of the atomic densities. To illustrate the manner by which such structure arises, we consider a formal asymptotic analysis and show that, as the thickness of the transition layer tends to zero, the theory approaches a particular version of the sharp-interface theory developed earlier in the paper. This analysis provides a recipe that determines the constitutive equations of the diffuse-interface theory in terms of those of the sharp-interface theory in a manner that guarantees asymptotic consonance.

2. SOLID STATE DIFFUSION WITH DEFORMATION

2.1. Substitutional and Interstitial Atoms. Balance Law for Atoms

We consider a homogeneous crystalline body $\mathscr{B}$ that occupies a region of $\mathbb{R}^3$. Following Larché and Cahn (1985), we associate with each point $\mathbf{x}$ of $\mathscr{B}$ microstructure defined by a lattice (or network) through which atoms diffuse.

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[7] See Germain (1973) and Antman and Osborn (1979) for discussions of this principle.

We consider $\mathfrak{A}+1$ species of atoms, labelled $\alpha = 0, 1, 2, \ldots, \mathfrak{S}, \mathfrak{S}+1, \ldots, \mathfrak{A}$, and let $\nu^{\alpha}(\mathbf{x}, t)$ denote the **atomic density** of species α, measured in atoms per unit volume. We allow for two classes of atomic species: **substitutional species**, labelled $\alpha \in \{0, 1, 2, \ldots, \mathfrak{S}\}$, and **interstitial species**, labelled $\alpha \in \{\mathfrak{S}+1, \mathfrak{S}+2, \ldots, \mathfrak{A}\}$. When vacancies are to be considered we reserve one of the substitutional labels $\mathfrak{v}$ for vacancies, so that $\nu^{\mathfrak{v}}$ represents the **vacancy density**. Then, whether or not vacancies are being considered, the substitutional densities must be consistent with the **lattice constraint**

$$\sum_{\text{sub}} \nu^{\alpha} = \nu_{\text{sites}}, \qquad \text{where} \qquad \sum_{\text{sub}} \nu^{\alpha} = \sum_{\alpha=0}^{\mathfrak{S}} \nu^{\alpha} \tag{2.1}$$

with ν_{sites} the density of **substitutional sites**.

Let $\mathcal{P}$ be a part (bounded, regular subregion) of $\mathcal{B}$. Changes in the number of atoms of α in $\mathcal{P}$ are most generally brought about by diffusion across the boundary $\partial\mathcal{P}$. This diffusion is characterized by an **atomic flux** (vector) $\mathbf{h}^{\alpha}(\mathbf{x}, t)$, measured in atoms per unit area, per unit time. It is convenient to allow also for a (scalar) **supply** $\mathsf{h}^{\alpha}(\mathbf{x}, t)$ of α-atoms directly to the interior points of $\mathcal{P}$; $\mathsf{h}^{\alpha}(\mathbf{x}, t)$ is measured in atoms per unit volume, per unit time. The **balance law for atoms** may then be stated precisely as

$$\overset{\bullet}{\overline{\int_{\mathcal{P}} \nu^{\alpha}\, dv}} = -\int_{\partial\mathcal{P}} \mathbf{h}^{\alpha} \cdot \mathbf{n}\, da + \int_{\mathcal{P}} \mathsf{h}^{\alpha}\, dv \tag{2.2}$$

for all species α, where $\mathbf{n}$ denotes the outward unit normal to $\partial\mathcal{P}$, while

$$\left(\overset{\bullet}{\overline{\int_{\mathcal{P}} \nu^{\alpha}\, dv}}\right)(t) = \frac{d}{dt}\int_{\mathcal{P}} \nu^{\alpha}(\mathbf{x}, t)\, dv(\mathbf{x}) \tag{2.3}$$

Since $\mathcal{P}$ is arbitrary, we are led to the local balance law

$$\dot{\nu}^{\alpha} = -\operatorname{div} \mathbf{h}^{\alpha} + \mathsf{h}^{\alpha} \tag{2.4}$$

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

$$\sum_{\text{sub}} \dot{\nu}^{\alpha} = \sum_{\text{sub}} (-\operatorname{div} \mathbf{h}^{\alpha} + \mathsf{h}^{\alpha}) = 0 \tag{2.5}$$

A basic assumption of the theory is that the fluxes obey the **strong constraint**

$$\sum_{\text{sub}} \mathbf{h}^{\alpha} = 0 \tag{2.6}$$

so that, necessarily,

$$\sum_{\text{sub}} \mathsf{h}^{\alpha} = 0 \tag{2.7}$$

The strong constraint ensures that the substitutional transport of atoms and vacancies involve neither a net flux across any surface nor a net supply to any region; it ensures satisfaction of (2.5) and hence implies that solutions ν^{α} of the atomic balance conserve lattice points.

The strong constraint is discussed by Ågren (1982) and Cahn and Larché (1983). It is a consequence of the requirement that diffusion, as represented by the substitutional fluxes, arises, microscopically, from exchanges of atoms or exchanges of atoms with vacancies.

2.2. Mechanics. Small Deformations. Balance of Forces and Moments. Power

We work within the framework of "infinitesimal deformations" as described by a displacement field $\mathbf{u}(\mathbf{x}, t)$. We use the following terminology: the symmetric part

$$\mathbf{E} = \tfrac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\top}) \tag{2.8}$$

of the **displacement gradient** $\nabla\mathbf{u}$ is the infinitesimal **strain**; the skew part

$$\mathbf{W} = \tfrac{1}{2}(\nabla\mathbf{u} - \nabla\mathbf{u}^{\top}) \tag{2.9}$$

is the infinitesimal **rotation**. We will make use of the decomposition

$$\nabla\mathbf{u} = \mathbf{E} + \mathbf{W} \tag{2.10}$$

of the displacement gradient into a strain plus a rotation.

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 $\mathscr{B}$ a system of forces consisting of a stress (tensor) $\mathbf{S}(\mathbf{x}, t)$ and a body force (vector) $\mathbf{b}(\mathbf{x}, t)$. Given any part $\mathscr{P}$, $\mathbf{Sn}$ represents the surface traction (force per unit area) exerted on $\mathscr{P}$ across $\partial\mathscr{P}$, while $\mathbf{b}$ represents the force, per unit volume, exerted directly on the points of $\mathscr{P}$ by agencies exterior to $\mathscr{B}$, for example by gravitational attraction.

The balance laws for forces and moments take the form

$$\int_{\partial\mathscr{P}} \mathbf{Sn}\, da + \int_{\mathscr{P}} \mathbf{b}\, dv = \mathbf{0}, \qquad \int_{\partial\mathscr{P}} \mathbf{x} \times \mathbf{Sn}\, da + \int_{\mathscr{P}} \mathbf{x} \times \mathbf{b}\, dv = \mathbf{0} \tag{2.11}$$

for every part $\mathscr{P}$. As in the derivation of (2.4), we are led to local force and moment balances

$$\operatorname{div} \mathbf{S} + \mathbf{b} = \mathbf{0}, \qquad \mathbf{S} = \mathbf{S}^{\top} \tag{2.12}$$

Given any part $\mathscr{P}$,

$$\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} \mathbf{Sn} \cdot \dot{\mathbf{u}}\, da + \int_{\mathscr{P}} \mathbf{b} \cdot \dot{\mathbf{u}}\, dv \tag{2.13}$$

represents the power expended by the tractions and body forces acting on $\mathscr{P}$. Using the moment balance $(2.12)_2$, which implies that $\mathbf{S} \cdot \nabla\dot{\mathbf{u}} = \mathbf{S} \cdot (\dot{\mathbf{E}} + \dot{\mathbf{W}}) = \mathbf{S} \cdot \dot{\mathbf{E}}$, and the force balance $(2.12)_1$, we find that

$$\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} \mathbf{Sn} \cdot \dot{\mathbf{u}}\, da + \int_{\mathscr{P}} \mathbf{b} \cdot \dot{\mathbf{u}}\, dv = \int_{\mathscr{P}} \mathbf{S} \cdot \dot{\mathbf{E}}\, dv \tag{2.14}$$

2.3. Energetics

The theory is based on an energy imbalance that represents the second law of thermodynamics in situations for which all effects—other than those associated with deformation and the transport of atoms—are neglected. To discuss this imbalance, we introduce two additional concepts: an energy density and, for each atomic species, a chemical potential.

We use the term energy in a generic sense. The thermodynamic potential (free-energy density, etc.) actually involved depends on which thermodynamic theory this purely mechanical theory is meant to approximate. The current theory is independent of such considerations.

2.3.1. Energy Density. Chemical Potential.

The **energy density** $\Psi(\mathbf{x}, t)$ represents the energy, per unit volume, of the atomic structure (atoms and lattice); its integral

$$\int_{\mathscr{P}} \Psi\, dv \tag{2.15}$$

gives the energy of a part $\mathscr{P}$.

The **chemical potential** $\bar{\mu}^{\mathfrak{a}}(\mathbf{x}, t)$ of species $\mathfrak{a}$ represents the energy the body would gain per unit time by adding one atom per unit time of species $\mathfrak{a}$ at $\mathbf{x}$. Thus

$$\sum_{\mathfrak{a}=0}^{\mathfrak{A}} \left(-\int_{\partial\mathcal{P}} \bar{\mu}^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} \cdot \mathbf{n}\, da + \int_{\mathcal{P}} \bar{\mu}^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}}\, dv \right) \tag{2.16}$$

gives the net rate at which energy is being added to $\mathcal{P}$: the first term represents the energy entering $\mathcal{P}$ across $\partial\mathcal{P}$, while the second represents energy supplied directly to the interior of $\mathcal{P}$.

Granted the strong constraint, for any scalar μ^*,

$$\sum_{\text{sub}} \bar{\mu}^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} = \sum_{\text{sub}} (\bar{\mu}^{\mathfrak{a}} - \mu^*)\, \mathbf{h}^{\mathfrak{a}}, \qquad \sum_{\text{sub}} \bar{\mu}^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}} = \sum_{\text{sub}} (\bar{\mu}^{\mathfrak{a}} - \mu^*)\, \mathsf{h}^{\mathfrak{a}} \tag{2.17}$$

the energy transported by substitutional species is therefore invariant under the subtraction of a *species-independent* scalar μ^* from each of the substitutional chemical potentials. Most importantly, μ^* may depend on both $\mathbf{x}$ and t. Thus the choice of reference potential with respect to which the substitutional chemical potentials are reckoned is arbitrary. In particular, taking $\mu^* = \bar{\mu}^0$, say,

$$\sum_{\text{sub}} \bar{\mu}^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} = \sum_{\text{sub}} (\bar{\mu}^{\mathfrak{a}} - \bar{\mu}^0)\, \mathbf{h}^{\mathfrak{a}}, \qquad \sum_{\text{sub}} \bar{\mu}^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}} = \sum_{\text{sub}} (\bar{\mu}^{\mathfrak{a}} - \bar{\mu}^0)\, \mathsf{h}^{\mathfrak{a}} \tag{2.18}$$

so that the species $\mathfrak{a} = 0$ may be accounted for by simply replacing each substitutional potential $\bar{\mu}^{\mathfrak{a}}$ by $\bar{\mu}^{\mathfrak{a}} - \bar{\mu}^0$.

2.3.2. Energy Imbalance (Second Law).

We base the theory on the **energy imbalance**

$$\dot{\overline{\int_{\mathcal{P}} \Psi\, dv}} \leqslant \sum_{\mathfrak{a}=0}^{\mathfrak{A}} \left(-\int_{\partial\mathcal{P}} \bar{\mu}^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} \cdot \mathbf{n}\, da + \int_{\mathcal{P}} \bar{\mu}^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}}\, dv \right) + \mathcal{W}(\mathcal{P}) \tag{2.19}$$

which asserts that the energy of $\mathcal{P}$ not increase at a rate faster than the rate at which power is expended on $\mathcal{P}$ plus the rate at which energy is added to $\mathcal{P}$ via mass transport.

By (2.17), the energy imbalance is invariant under transformations of the form $\bar{\mu}^{\mathfrak{a}}(\mathbf{x}, t) \mapsto \bar{\mu}^{\mathfrak{a}}(\mathbf{x}, t) - \mu^*(\mathbf{x}, t)$ with μ^* independent of $\mathfrak{a}$. Further, because of the lattice constraint (2.1), we may omit the atomic balance for the substitutional species $\mathfrak{a} = 0$, say, and simply define $\nu^0 = \nu_{\text{sites}} - (\nu^1 + \nu^2 + \ldots + \nu^{\mathfrak{S}})$. Thus and by (2.18), using a change in reference for the substitutional chemical potentials in which $\mu^* = \bar{\mu}^0$ we may, without loss in generality:

(i) omit the balance law for atoms of species $\mathfrak{a} = 0$; and

(ii) omit mention of species $\mathfrak{a} = 0$ in the imbalance (2.19) provided we interpret the substitutional chemical potentials as differences $\bar{\mu}^{\mathfrak{a}} - \bar{\mu}^0$.

We therefore write

$$\mu^{\mathfrak{a}} = \begin{cases} \bar{\mu}^{\mathfrak{a}} - \bar{\mu}^0 & \text{for } \mathfrak{a} \text{ substitutional} \\ \bar{\mu}^{\mathfrak{a}} & \text{for } \mathfrak{a} \text{ interstitial} \end{cases} \tag{2.20}$$

so that, by (2.18),

$$\sum_{\mathfrak{a}=0}^{\mathfrak{A}} \bar{\mu}^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} = \sum_{\mathfrak{a}=1}^{\mathfrak{A}} \mu^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}}, \qquad \sum_{\mathfrak{a}=0}^{\mathfrak{A}} \bar{\mu}^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}} = \sum_{\mathfrak{a}=1}^{\mathfrak{A}} \mu^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}} \tag{2.21}$$

To avoid repeated summations, we adopt the convention that summation with respect to repeated superscripts over the integers $\{1, 2, \ldots, \mathfrak{A}\}$ is implied: if $A^{\mathfrak{a}}$, $B^{\mathfrak{a}}$, and $C^{\mathfrak{ab}}$ are defined for $\mathfrak{a}, \mathfrak{b} = 1, 2, \ldots, \mathfrak{A}$, then, for example,

$$A^{\mathfrak{a}} B^{\mathfrak{a}} = \sum_{\mathfrak{a}=1}^{\mathfrak{A}} A^{\mathfrak{a}} B^{\mathfrak{a}}, \qquad C^{\mathfrak{ab}} B^{\mathfrak{b}} = \sum_{\mathfrak{b}=1}^{\mathfrak{A}} C^{\mathfrak{ab}} B^{\mathfrak{b}} \tag{2.22}$$

In view of (2.21), we may write the energy imbalance more succinctly as

$$\dot{\overline{\int_{\mathscr{P}} \Psi \, dv}} \leqslant -\int_{\partial \mathscr{P}} \mu^{\mathfrak{a}} \mathbf{h}^{\mathfrak{a}} \cdot \mathbf{n} \, da + \int_{\mathscr{P}} \mu^{\mathfrak{a}} \mathsf{h}^{\mathfrak{a}} \, dv + \mathscr{W}(\mathscr{P}) \tag{2.23}$$

and, using the identity (2.14) for $\mathscr{W}(\mathscr{P})$, we arrive at the **dissipation inequality**

$$\dot{\Psi} - \mu^{\mathfrak{a}} \dot{v}^{\mathfrak{a}} - \mathbf{S} \cdot \dot{\mathbf{E}} + \mathbf{h}^{\mathfrak{a}} \cdot \nabla \mu^{\mathfrak{a}} \leqslant 0 \tag{2.24}$$

An equivalent form of this inequality, based on the **grand canonical potential**

$$\omega = \Psi - \mu^{\mathfrak{a}} v^{\mathfrak{a}} \tag{2.25}$$

has the form

$$\dot{\omega} + v^{\mathfrak{a}} \dot{\mu}^{\mathfrak{a}} - \mathbf{S} \cdot \dot{\mathbf{E}} + \mathbf{h}^{\mathfrak{a}} \cdot \nabla \mu^{\mathfrak{a}} \leqslant 0 \tag{2.26}$$

2.3.3. Lyapunov Relations.

We assume throughout this subsection that the external fields $\mathbf{b}$ and $\mathbf{h}^\alpha$ vanish. Then (2.2), (2.13), and (2.23) yield

$$\dot{\overline{\int_{\mathcal{P}} \Psi\, dv}} \leqslant -\int_{\partial\mathcal{P}} \mu^\alpha \mathbf{h}^\alpha \cdot \mathbf{n}\, da + \int_{\partial\mathcal{P}} \mathbf{S}\mathbf{n} \cdot \dot{\mathbf{u}}\, da, \qquad \dot{\overline{\int_{\mathcal{P}} \nu^\alpha\, dv}} = -\int_{\partial\mathcal{P}} \mathbf{h}^\alpha \cdot \mathbf{n}\, da \tag{2.27}$$

Consider the following types of boundaries:

$$\left.\begin{array}{llll} \textbf{impermeable}: & \mathbf{h}^\alpha \cdot \mathbf{n} = 0 & \text{on } \partial\mathcal{B} & \text{for all } \alpha \\ \textbf{isochemical} & \mu^\alpha = U^\alpha & \text{on } \partial\mathcal{B} & \text{for all } \alpha \quad (U^\alpha \text{ constant}) \\ \textbf{dead-loaded}: & \mathbf{S}\mathbf{n} = \mathbf{S}_0\mathbf{n} & \text{on } \partial\mathcal{B} & (\mathbf{S}_0 = \mathbf{S}_0^\top \text{ constant}) \\ \textbf{fixed}: & \dot{\mathbf{u}} = \mathbf{0} & \text{on } \partial\mathcal{B} & \end{array}\right\} \tag{2.28}$$

A direct consequence of (2.27) is that, for a *fixed* and *impermeable* boundary,

$$\dot{\overline{\int_{\mathcal{P}} \Psi\, dv}} \leqslant 0, \qquad \dot{\overline{\int_{\mathcal{P}} \nu^\alpha\, dv}} = 0 \tag{2.29}$$

and *the total energy decreases*, while *the total number of atoms of each species is conserved.*

Consider next a *dead-loaded* and *isochemical* boundary. Then

$$\int_{\partial\mathcal{P}} \mu^\alpha \mathbf{h}^\alpha \cdot \mathbf{n}\, da = U^\alpha \int_{\partial\mathcal{P}} \mathbf{h}^\alpha \cdot \mathbf{n}\, da, \qquad \int_{\partial\mathcal{P}} \mathbf{S}\mathbf{n} \cdot \dot{\mathbf{u}}\, da = \int_{\partial\mathcal{P}} \mathbf{S}_0 \cdot \dot{\mathbf{E}}\, da \tag{2.30}$$

therefore multiplying the second relation in (2.27) by U^α and subtracting it from the first, we are led to the inequality

$$\dot{\overline{\int_{\mathcal{P}} (\Psi - U^\alpha \nu^\alpha - \mathbf{S}_0 \cdot \mathbf{E})\, dv}} \leqslant 0 \tag{2.31}$$

The term $-U^\alpha \dot{\nu}^\alpha$ may be viewed as a decrease in energy per unit volume per unit time, that results upon removing atoms of chemical potential U^α at a rate $\dot{\nu}^\alpha$. The inequality (2.31) can be written in an alternative form involving the grand canonical potential ω defined in (2.25):

$$\dot{\overline{\int_{\mathcal{P}} (\omega + (\mu^\alpha - U^\alpha)\, \nu^\alpha - \mathbf{S}_0 \cdot \mathbf{E})\, dv}} \leqslant 0 \tag{2.32}$$

The Lyapunov relations (2.29), (2.31), and (2.32) are a consequence of the underlying thermodynamic structure; they are independent of constitutive equations. Such global relations furnish a tool for determining a-priori estimates for solutions of initial/boundary-value problems and provide a formal justification, within a dynamical setting, of the standard variational principles used to characterize equilibrium.

2.4. Constitutive theory with atomic densities as independent variables

We view the balance law for atoms, the force and moment balances, and the energy imbalance as basic laws, common to large classes of materials; we keep such laws distinct from specific constitutive equations, which differentiate between particular materials. In this section we will discuss general constitutive equations in which the atomic densities appear as independent variables; in the next section we will consider a conjugate theory in which this role is played by the chemical potentials.

2.4.1. Standard Treatment for a Single Independent Atomic Species. To help motivate the general framework within which we develop constitutive equations we begin with critical discussion of the standard treatment for a material described by a single independent atomic species, neglecting deformation and stress.

The simplest constitutive equation for mass transport is the isotropic Fick's law

$$\mathbf{h} = -M(\nu)\,\nabla\mu \tag{2.33}$$

with $M(\nu)$, the **mobility**, assumed to be strictly positive to ensure that mass flows down a chemical-potential gradient. To (2.33) one classically adjoins "equations of state"

$$\Psi = \hat{\Psi}(\nu), \qquad \mu = \hat{\mu}(\nu) \tag{2.34}$$

subject to the restriction

$$\hat{\mu}(\nu) = \frac{d\hat{\Psi}}{d\nu}(\nu) = \hat{\Psi}'(\nu) \tag{2.35}$$

generally derived from variational or thermostatic arguments. Since $\nabla\mu = \kappa(\nu)\,\nabla\nu$ with $\kappa(\nu) = \hat{\mu}'(\nu) = \hat{\Psi}''(\nu)$, the definition $D(\nu) = \kappa(\nu)\,M(\nu)$ allows us to write (2.33) as

$$\mathbf{h} = -D(\nu)\,\nabla\nu \tag{2.36}$$

with $D(v)$ the **diffusivity**. The balance law (2.4) for atoms and the constitutive equation (2.36) together yield the partial differential equation

$$\dot{v} = \mathrm{div}(D(v)\nabla v) + \mathsf{h} \tag{2.37}$$

This "derivation," while simple and straightforward, does not provide a general framework for the formulation of dynamical constitutive relations. The crucial dependence in the relation (2.36) for the flux $\mathbf{h}$ is a dependence on the density gradient ∇v. But if the flux is allowed to depend on the density gradient, then might not such a dependence be important for the energy and chemical potential. In fact, Truesdell, in discussing the general formulation of constitutive theories, introduces the following guidline:[8] "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." As Truesdell and Noll assert: "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."

As a second criticism, the "state relation" (2.35) is generally derived from considerations of equilibrium, but the theory itself, as represented by the partial differential equation (2.37), is used in situations away from equilibrium. We take a different approach: we do not introduce an a-priori notion of equilibrium; instead we use the second law, which in this purely mechanical theory is represented by the energy imbalance, to obtain constitutive restrictions such as (2.35). The final results, when restricted to a single independent species, are not much different than those presented above; however, the underlying theoretical structure provides a self-consistent framework within which more general theories are readily developed.

2.4.2. General Constitutive Theory. Thermodynamic Restrictions. We return to the theory with $\mathfrak{A}$ independent species of atoms (cf. the paragraph containing (2.20)), and consider a general class of constitutive equations giving the energy, the chemical potentials, the atomic fluxes, and the stress at any point $(\mathbf{x}, t)$ when the atomic densities and their gradient as well as the first and second displacement gradients are known at $(\mathbf{x}, t)$,[9]

$$(\Psi, \boldsymbol{\mu}, \mathbf{h}, \mathbf{S}) = \hat{F}(\mathbf{v}, \nabla\mathbf{v}, \nabla\mathbf{u}, \nabla\nabla\mathbf{u}) \tag{2.38}$$

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[8] Cf. Truesdell and Noll (1965, §96).

[9] The expected dependences of $\boldsymbol{\mu}$ on $(\mathbf{v}, \mathbf{E})$ and $\mathbf{h}$ on $(\mathbf{v}, \nabla\boldsymbol{\mu})$ yields a dependence of $\mathbf{h}$ on $(\mathbf{v}, \mathbf{E}, \nabla\mathbf{v}, \nabla\mathbf{E})$; for that reason, we include $\nabla\nabla\mathbf{u}$ in the right-hand side of (2.38).

where, for example $\mathbf{v} = (v^1, v^2, \ldots, v^{\mathfrak{A}})$. We denote the individual response functions by $\hat{\Psi}$, $\hat{\boldsymbol{\mu}}$, $\hat{\mathbf{h}}$, and $\hat{\mathbf{S}}$, so that, e.g.,

$$\Psi = \hat{\Psi}(\mathbf{v}, \nabla\mathbf{v}, \nabla\mathbf{u}, \nabla\nabla\mathbf{u}) \tag{2.39}$$

and assume that these response functions are smooth, with $\hat{\mathbf{S}} = \hat{\mathbf{S}}^{\top}$ to ensure compatibility with the moment balance $(2.12)_2$.

We assume that the response of the body is unaffected by superposed (infinitesimal) rigid displacements. Such displacements have the form $\mathbf{u}_0 + \mathbf{W}_0\mathbf{x}$ with $\mathbf{u}_0$ a vector and $\mathbf{W}_0$ a skew tensor, and therefore, under a superposed rigid displacement, $\nabla\mathbf{u}$ transforms to $\nabla\mathbf{u} + \mathbf{W}_0$, but $\nabla\nabla\mathbf{u}$ remains unchanged. Thus, suppressing the arguments $\mathbf{v}$ and $\nabla\mathbf{v}$, $\hat{F}(\nabla\mathbf{u}, \nabla\nabla\mathbf{u}) = \hat{F}(\nabla\mathbf{u} + \mathbf{W}_0, \nabla\nabla\mathbf{u})$ for all skew $\mathbf{W}_0$, and this yields $\hat{F}(\nabla\mathbf{u}, \nabla\nabla\mathbf{u}) = \hat{F}(\mathbf{E}, \nabla\nabla\mathbf{u})$. Thus, letting

$$\mathbf{G} = \nabla\nabla\mathbf{u} \qquad \left(G_{ijk} = \frac{\partial^2 u_i}{\partial x_j\, \partial x_k}\right) \tag{2.40}$$

we can rewrite (2.38) as

$$(\Psi, \boldsymbol{\mu}, \mathbf{h}, \mathbf{S}) = \hat{F}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}, \mathbf{G}) \tag{2.41}$$

We do not prescribe constitutive equations for the supplies h^{α} and the body force $\mathbf{b}$, but allow these fields to be assigned arbitrarily in any manner consistent with the balance (2.4) for atoms and the balance $(2.12)_1$ for forces.

Given fields $\mathbf{v}(\mathbf{x}, t)$ and $\mathbf{u}(\mathbf{x}, t)$, the constitutive equations embodied in (2.41) may be used to compute fields $\Psi(\mathbf{x}, t)$, $\boldsymbol{\mu}(\mathbf{x}, t)$, $\mathbf{h}(\mathbf{x}, t)$ and $\mathbf{S}(\mathbf{x}, t)$; the balance laws (2.4) and $(2.12)_1$ then determine the supplies $\mathsf{h}^{\alpha}(\mathbf{x}, t)$ and the body force $\mathbf{b}(\mathbf{x}, t)$ needed to support this constitutive process. The second law in the form of the dissipation inequality (2.24) remains to be satisfied in all constitutive processes, a requirement we will use to restrict constitutive equations.

This method of restricting constitutive equations is due to Coleman and Noll (1963) and is based on the belief that the second law should hold in all conceivable processes, irrespective of the difficulties involved in producing such processes in the laboratory. The application of the Coleman–Noll procedure requires external fields that ensure satisfaction of the underlying balance laws in all processes. This may seem artificial, but it is no more so than theories based on virtual work or minimum "energy," as these require arbitrary variations of the fields, even though such variations are generally inconsistent with the resulting balance laws. The Coleman–Noll procedure has the same goal as variational approaches: to ensure a properly invariant theory consistent with basic physical laws under the widest possible set of circumstances. In essence the Coleman–Noll procedure extends to dynamics variational approaches that have been highly successful in describing equilibrium.

We therefore assume that *the dissipation inequality is satisfied in all constitutive processes*, or equivalently, writing $\mathbf{z} = (\boldsymbol{\nu}, \mathbf{p}, \mathbf{E}, \mathbf{G})$, $\mathbf{p} = \nabla\boldsymbol{\nu}$, and using the constitutive equations (2.41), that

$$\left(\frac{\partial\hat{\Psi}}{\partial\nu^{\mathfrak{a}}}(\mathbf{z}) - \hat{\mu}^{\mathfrak{a}}(\mathbf{z})\right)\dot{\nu}^{\mathfrak{a}} + \left(\frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{z})\right)\cdot\dot{\mathbf{p}}^{\mathfrak{a}} + \left(\frac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\mathbf{z}) - \hat{\mathbf{S}}(\mathbf{z})\right)\cdot\dot{\mathbf{E}}$$
$$+\left(\frac{\partial\hat{\Psi}}{\partial\mathbf{G}}(\mathbf{z})\right)\cdot\dot{\mathbf{G}} + \hat{\mathbf{h}}^{\mathfrak{a}}(\mathbf{z})\cdot\nabla\mu^{\mathfrak{a}} \leqslant 0 \tag{2.42}$$

with $(\partial\hat{\Psi}/\partial\mathbf{E})_{ij} = \partial\hat{\Psi}/\partial E_{ij}$ and $(\partial\hat{\Psi}/\partial\mathbf{G})_{ijk} = \partial\hat{\Psi}/\partial G_{ijk}$. Here $\nabla\mu^{\mathfrak{a}}$ is considered, via the constitutive relation for $\mu^{\mathfrak{a}}$ and the chain-rule, a function of $(\boldsymbol{\nu}, \nabla\boldsymbol{\nu}, \nabla\nabla\boldsymbol{\nu}, \mathbf{E}, \mathbf{G}, \nabla\mathbf{G})$.

We can always find fields $\boldsymbol{\nu}$ and $\mathbf{u}$ such that $\boldsymbol{\nu}, \dot{\boldsymbol{\nu}}, \mathbf{p} = \nabla\boldsymbol{\nu}$, $\dot{\mathbf{p}} = \nabla\dot{\boldsymbol{\nu}}$, $\nabla\mathbf{p} = \nabla\nabla\boldsymbol{\nu}$, $\mathbf{u}$, $\nabla\mathbf{u}$, $\dot{\mathbf{u}}$ (and, hence, $\mathbf{E}$, $\dot{\mathbf{E}}$), $\mathbf{G} = \nabla\nabla\mathbf{u}$, $\nabla\mathbf{G} = \nabla\nabla\nabla\mathbf{u}$, and $\dot{\mathbf{G}} = \nabla\nabla\dot{\mathbf{u}}$ have arbitrarily prescribed values at some $(\mathbf{x}, t)$. Writing

$$\frac{\partial\hat{\Psi}}{\partial\boldsymbol{\nu}}(\mathbf{z}) = \left(\frac{\partial\hat{\Psi}}{\partial\nu^1}(\mathbf{z}), \frac{\partial\hat{\Psi}}{\partial\nu^2}(\mathbf{z}),\ldots, \frac{\partial\hat{\Psi}}{\partial\nu^{\mathfrak{A}}}(\mathbf{z})\right) \tag{2.43}$$

we conclude that, since $\dot{\nu}^{\mathfrak{a}}$, $\dot{\mathbf{p}}^{\mathfrak{a}}$, $\dot{\mathbf{E}}$, and $\dot{\mathbf{G}}$ appear linearly in (2.42), their "coefficients" must vanish. This yields the following **constitutive restrictions**:

(*i*) *the energy, the chemical potentials, and the stress must be independent of the density gradients as well as the second displacement gradient, with*

$$\hat{\boldsymbol{\mu}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial\hat{\Psi}}{\partial\boldsymbol{\nu}}(\boldsymbol{\nu}, \mathbf{E}), \qquad \hat{\mathbf{S}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\boldsymbol{\nu}, \mathbf{E}) \tag{2.44}$$

(*ii*) the constitutive equations for $\mathbf{h}$ and $\boldsymbol{\mu}$ must be consistent with the **flux inequality**

$$\hat{\mathbf{h}}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{p}, \mathbf{E}, \mathbf{G})\cdot\nabla\mu^{\mathfrak{a}} \leqslant 0 \tag{2.45}$$

These restrictions are also sufficient for the validity of the dissipation inequality.

2.4.3. Consequences of the Thermodynamic Restrictions.

Immediate consequences of (2.44) are the **Maxwell relation**

$$\frac{\partial\hat{\mathbf{S}}}{\partial\boldsymbol{\nu}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial\hat{\boldsymbol{\mu}}}{\partial\mathbf{E}}(\boldsymbol{\nu}, \mathbf{E}) \tag{2.46}$$

(which uses obvious analogs of (2.43)) and the **Gibbs relations**

$$\dot{\Psi} = \mu^{\mathfrak{a}}\dot{\nu}^{\mathfrak{a}} + \mathbf{S}\cdot\dot{\mathbf{E}}, \qquad \dot{\omega} = -\nu^{\mathfrak{a}}\dot{\mu}^{\mathfrak{a}} + \mathbf{S}\cdot\dot{\mathbf{E}} \tag{2.47}$$

with ω the grand canonical potential as introduced in (2.25). Two identities that we will find useful are the **gradient Gibbs-relations**

$$\nabla\Psi = \mu^{\mathfrak{a}}\,\nabla\nu^{\mathfrak{a}} + \mathbf{S} : \nabla\mathbf{E}, \qquad \nabla\omega = -\nu^{\mathfrak{a}}\,\nabla\mu^{\mathfrak{a}} + \mathbf{S} : \nabla\mathbf{E} \tag{2.48}$$

where $(\nabla\mathbf{E})_{ijk} = \partial E_{ij}/\partial x_k = \frac{1}{2}(G_{ijk} + G_{jik})$, and where, for $\mathbf{F}$ a second-order tensor with components F_{ij} and $\mathbf{R}$ a third-order tensor with components R_{ijk}, $\mathbf{F} : \mathbf{R}$ is the vector with k-th component

$$(\mathbf{F} : \mathbf{R})_k = \sum_{i,\,j} F_{ij} R_{ijk} \tag{2.49}$$

Let

$$\left.\begin{aligned}
\kappa^{\mathfrak{ab}}(\boldsymbol{\nu}, \mathbf{E}) &= \frac{\partial\hat{\mu}^{\mathfrak{a}}}{\partial\nu^{\mathfrak{b}}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial^2\hat{\Psi}}{\partial\nu^{\mathfrak{b}}\,\partial\nu^{\mathfrak{a}}}(\boldsymbol{\nu}, \mathbf{E}) \\
\mathscr{C}(\boldsymbol{\nu}, \mathbf{E}) &= \frac{\partial\hat{\mathbf{S}}}{\partial\mathbf{E}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial^2\hat{\Psi}}{\partial\mathbf{E}^2}(\boldsymbol{\nu}, \mathbf{E}) \\
\mathbf{A}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{E}) &= \frac{\partial\hat{\mathbf{S}}}{\partial\nu^{\mathfrak{a}}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial\hat{\mu}^{\mathfrak{a}}}{\partial\mathbf{E}}(\boldsymbol{\nu}, \mathbf{E}) = \frac{\partial^2\hat{\Psi}}{\partial\mathbf{E}\,\partial\nu^{\mathfrak{a}}}(\boldsymbol{\nu}, \mathbf{E})
\end{aligned}\right\} \tag{2.50}$$

We will refer to $\kappa^{\mathfrak{ab}}(\boldsymbol{\nu}, \mathbf{E}) = \kappa^{\mathfrak{ba}}(\boldsymbol{\nu}, \mathbf{E})$ as the **chemistry-composition modulus** for the species $\mathfrak{a}$ and $\mathfrak{b}$, to $\mathscr{C}(\boldsymbol{\nu}, \mathbf{E})$ as the **elasticity tensor**, and to $\mathbf{A}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{E})$ as the **stress-composition** (or chemistry-strain) **tensor** for $\mathfrak{a}$. $\mathscr{C}(\boldsymbol{\nu}, \mathbf{E})$ is a symmetric linear transformation of symmetric tensors into symmetric tensors; the moduli $\mathbf{A}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{E})$ are symmetric tensors, and we will term these **nontrivial** if, given any $(\boldsymbol{\nu}, \mathbf{E})$ and any $\mathfrak{a}$, $\mathbf{A}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{E}) \neq \mathbf{0}$. By the chain-rule and (2.40),

$$\nabla\mu^{\mathfrak{a}} = \kappa^{\mathfrak{ab}}(\boldsymbol{\nu}, \mathbf{E})\,\nabla\nu^{\mathfrak{b}} + \mathbf{A}^{\mathfrak{a}}(\boldsymbol{\nu}, \mathbf{E}) : \nabla\mathbf{E} \tag{2.51}$$

We will refer to the constitutive equation for the atomic flux as **quasi-linear** if, for each pair $(\boldsymbol{\nu}, \mathbf{E})$, the function $\hat{\mathbf{h}}(\boldsymbol{\nu}, \nabla\boldsymbol{\nu}, \mathbf{E}, \mathbf{G}, \nabla\mathbf{G})$ is linear in the arguments $\nabla\boldsymbol{\nu}$ and $\mathbf{G}$. An important example of a quasi-linear constitutive relation for the atomic flux is (the generalized) **Fick's law**

$$\mathbf{h}^{\mathfrak{a}} = -M^{\mathfrak{ab}}(\boldsymbol{\nu}, \mathbf{E})\,\nabla\mu^{\mathfrak{b}} \tag{2.52}$$

with the matrix of mobility tensors $\mathbf{M}^{\alpha\mathrm{b}}(\mathbf{v}, \mathbf{E})$ positive semi-definite to ensure consistency with the flux inequality. Here the dependence of the atomic flux on the arguments $\nabla\mathbf{v}$ and $\mathbf{G}$ is through (2.51):

$$\mathbf{h}^{\alpha} = -\mathbf{M}^{\alpha\mathrm{b}}(\kappa^{\mathrm{bc}}(\mathbf{v}, \mathbf{E})\, \nabla v^{\mathrm{c}} + \mathbf{A}^{\mathrm{b}}(\mathbf{v}, \mathbf{E}) : \nabla\mathbf{E}) \tag{2.53}$$

The second law places no restriction on the general constitutive equation for the atomic flux other than the flux inequality, but this inequality has the following important consequence: *if the stress-composition moduli are nontrivial, then the most general quasi-linear constitutive equation of the form* $\mathbf{h} = \hat{\mathbf{h}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}, \mathbf{G})$ *is Fick's law*. This result is established in Appendix A; it remains valid if the requirement that the stress-composition moduli be nontrivial is replaced by the assumption that the matrix of chemistry-composition moduli be invertible; or, more generally, if the mapping $(\nabla\mathbf{v}, \nabla\mathbf{E}) \mapsto \boldsymbol{\mu}$ defined by (2.51) is onto.

2.4.4. Theory in Which the Chemical Potential, Stress, and Atomic Flux Are Constitutively Linear (Single Independent Species).

Consistent with the assumption of infinitesimal deformations, we might require that

$$\Psi = \hat{\Psi}(v, \mathbf{E}) = f(v) + \mathbf{E} \cdot (\mathbf{A}(v) + \tfrac{1}{2}\bar{\mathscr{C}}\mathbf{E}) \tag{2.54}$$

with constant elasticity tensor $\bar{\mathscr{C}}$.[10] Further, with a view to dicussing problems in which the density v remains close to a base value v_0, we might assume that

$$f(v) = \mu_0(v - v_0) + \tfrac{1}{2}\bar{\kappa}(v - v_0)^2, \qquad \mathbf{A}(v) = (v - v_0)\,\bar{\mathbf{A}} \tag{2.55}$$

with μ_0, $\bar{\kappa}$, and $\bar{\mathbf{A}}$ constant; the chemical potential and the stress are then each linear in v and $\mathbf{E}$:

$$\mu = \mu_0 + \bar{\kappa}(v - v_0) + \bar{\mathbf{A}} \cdot \mathbf{E}, \qquad \mathbf{S} = (v - v_0)\,\bar{\mathbf{A}} + \bar{\mathscr{C}}\mathbf{E} \tag{2.56}$$

further, granted the additional requirement that the mobility $\mathbf{M}$ be constant, the atomic flux has the form

$$\mathbf{h} = -\mathbf{M}(\bar{\kappa}\,\nabla v + \bar{\mathbf{A}} : \nabla\mathbf{E}) \tag{2.57}$$

Despite its simplicity, such a description allows for a nontrivial interaction between composition and stress.[11]

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[10] Using the terminology of Larché and Cahn (1973), $\bar{\mathscr{C}}$ appearing in (2.54) corresponds to the "open system" elasticity tensor.

[11] Later, in Section 3.6, we will discuss a less general theory for phase transitions in which this interaction occurs only at the interface.

2.5. Constitutive Theory with Chemical Potentials as Independent Variables

2.5.1. Constitutive Theory. Thermodynamic Restrictions.

A second formulation of the constitutive theory, also important, treats the chemical potentials as independent variables:

$$(\Psi, \mathbf{v}, \mathbf{h}, \mathbf{S}) = \hat{\mathbf{F}}(\boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}, \mathbf{G}) \tag{2.58}$$

with $\hat{\Psi}$, $\hat{\mathbf{v}}$, $\hat{\mathbf{h}}$, and $\hat{\mathbf{S}}$ the individual response functions. The argument leading to (2.44) and (2.45), here based on the dissipation inequality in the form (2.26) with $\omega = \hat{\omega}(\boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}, \mathbf{G}) = \Psi - \mu^{\mathfrak{a}}\nu^{\mathfrak{a}}$, remains unchanged. The results are the following **constitutive restrictions**:

(*i*) $\hat{\omega}$, $\hat{\mathbf{v}}$, and $\hat{\mathbf{S}}$ must be independent of $\nabla\boldsymbol{\mu}$ and $\mathbf{G}$, with

$$\hat{\mathbf{v}}(\boldsymbol{\mu}, \mathbf{E}) = -\frac{\partial\hat{\omega}}{\partial\boldsymbol{\mu}}(\boldsymbol{\mu}, \mathbf{E}), \qquad \hat{\mathbf{S}}(\boldsymbol{\mu}, \mathbf{E}) = \frac{\partial\hat{\omega}}{\partial\mathbf{E}}(\boldsymbol{\mu}, \mathbf{E}) \tag{2.59}$$

(*ii*) $\hat{\mathbf{h}}$ must be consistent with the **flux inequality**

$$\hat{\mathbf{h}}^{\mathfrak{a}}(\boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}, \mathbf{G}) \cdot \nabla\mu^{\mathfrak{a}} \leqslant 0 \tag{2.60}$$

An important result, verified in Appendix A, is that Fick's law

$$\mathbf{h}^{\mathfrak{a}} = -\mathbf{M}^{\mathfrak{ab}}(\boldsymbol{\mu}, \mathbf{E})\, \nabla\mu^{\mathfrak{b}} \tag{2.61}$$

with the matrix of mobility tensors $\mathbf{M}^{\mathfrak{ab}}(\boldsymbol{\mu}, \mathbf{E})$ *positive semi-definite is the most general quasi-linear constitutive equation of the form* $\mathbf{h} = \check{\mathbf{h}}(\boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}, \mathbf{G})$ *consistent with the flux inequality*. Here quasi-linearity is the requirement that $\check{\mathbf{h}}(\boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}, \mathbf{G})$ be linear in $\nabla\boldsymbol{\mu}$ and $\mathbf{G}$ for each $(\boldsymbol{\mu}, \mathbf{E})$. It is important to note that *no extraneous assumptions such as the nontriviality of moduli are needed.*

Consider the two formulations: (**AD**) in which atomic densities are independent variables; and (**CP**) in which that role is played by the chemical potentials. In both cases, we assume compliance with the restrictions implied by the energy imbalance and we restrict attention to the appropriate version of Fick's law. Granted this, *the essential assumption yielding the equivalence of the two formulations is the invertibility of the relation between the chemical potentials and the atomic densities.* We leave the proof of this assertion to the reader.

The requirement that the relation between the chemical potentials and atomic densities be invertible is not always satisfied. This is the case when the response function $\hat{\Psi}$ is strictly convex, which is an assumption often imposed when discussing single-phase materials. Phase transitions are more complicated; here there are two standard models: (*i*) the material is described by two or more strictly convex energy-densities, one for each phase; (*ii*) the material is described by a single energy density, generally a "multi-well" potential. In case (*i*), it seems reasonable to consider the formulation (**CP**) for each phase, and this we shall do. For case (*ii*), the nonconvexity of the energy density renders the assumption of invertibility unwarranted; and, while the chemical potentials are generally single-valued functions of the atomic densities, the converse is not true. In this sense (**AD**) is more general than (**CP**).

2.6. Simple Theories. Single Independent Species

2.6.1. Theory in Which the Atomic Density, Stress, and Atomic Flux are Constitutively linear.

Mimicking the linear theory presented in Section 2.4.4, we might require that

$$\omega = \hat{\omega}(v, \mathbf{E}) = -v_0(\mu - \mu_0) - \tfrac{1}{2}\tilde{\kappa}(\mu - \mu_0)^2 + \mathbf{E} \cdot ((\mu - \mu_0)\,\tilde{\mathbf{A}} + \tfrac{1}{2}\tilde{\mathscr{C}}\mathbf{E}) \quad (2.62)$$

with μ_0 a base-value of the chemical potential and v_0, $\tilde{\kappa}$, $\tilde{\mathbf{A}}$, and $\tilde{\mathscr{C}}$ constant,[12] in which case the atomic density and the stress pre linear in both μ and $\mathbf{E}$:

$$v = v_0 + \tilde{\kappa}(\mu - \mu_0) - \tilde{\mathbf{A}} \cdot \mathbf{E}, \qquad \mathbf{S} = (\mu - \mu_0)\,\tilde{\mathbf{A}} + \tilde{\mathscr{C}}\mathbf{E} \quad (2.63)$$

Provided that

$$\tilde{\mathscr{C}} = \bar{\mathscr{C}} - \frac{1}{\bar{\kappa}}\,\bar{\mathbf{A}} \otimes \bar{\mathbf{A}}, \qquad \tilde{\mathbf{A}} = \frac{1}{\kappa}\,\bar{\mathbf{A}}, \qquad \tilde{\kappa}\bar{\kappa} = 1 \quad (2.64)$$

where for second order tensors **B** and **C** with components B_{ij} and C_{ij}, $\mathbf{A} \otimes \mathbf{B}$ is the fourth-order tensor with components

$$(\mathbf{B} \otimes \mathbf{C})_{ijkl} = B_{ij} C_{kl} \quad (2.65)$$

and that the mobility is constant, this theory is equivalent to that presented in Section 2.4.4.

2.6.2. Theory with Constant Atomic Density and with Stress and Atomic Flux Constitutively Linear.

An important

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[12] Using the terminology of Larché and Cahn (1973), $\tilde{\mathscr{C}}$ appearing in (2.62) corresponds to the "closed system" elasticity tensor.

specialization of the theory presented in Section 2.6.1 occurs on requiring that both $\tilde{\kappa}$ and $\tilde{\mathbf{A}}$ vanish,

$$\omega = \hat{\omega}(\mu, \mathbf{E}) = -v_0(\mu - \mu_0) + \tfrac{1}{2}\mathbf{E} \cdot \tilde{\mathscr{C}}\mathbf{E} \tag{2.66}$$

in which case the atomic density is constant and the stress is independent of μ:

$$v = v_0, \qquad \mathbf{S} = \tilde{\mathscr{C}}\mathbf{E} \tag{2.67}$$

Granted a constant mobility $\mathbf{M}$, the governing equations are then

$$\operatorname{div}(\mathbf{M}\,\nabla\mu) = 0, \qquad \operatorname{div}(\tilde{\mathscr{C}}\mathbf{E}) = \mathbf{0}, \qquad \mathbf{E} = \tfrac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\top}) \tag{2.68}$$

These equations, in which time appears only as a parameter and coupling between diffusion and deformation is absent, prove useful for describing bulk material response in phase transitions that proceed slowly in comparison to bulk diffusion. A detailed discussion of this application is provided in Section 3.6.

Under the present specialization, the relations (2.64) between the coefficients $\bar{\kappa}$, $\bar{\mathbf{A}}$, and $\bar{\mathscr{C}}$ of the theory presented in Section 2.4.4 and the coefficients $\tilde{\kappa}$, $\tilde{\mathbf{A}}$, and $\tilde{\mathscr{C}}$ of Section 2.6.1 fail. The theory discussed here therefore has no thermodynamically consistent counterpart wherein v and $\mathbf{E}$ appear as independent constitutive variables.

2.7. Basic Theory of Configurational Forces

Much is to be gained by a discussion of configurational forces within a context that neglects evolving material structures such as defects and phase interfaces, even though within that context such forces are extraneous to the solution of actual initial/boundary-value problems.

In classical continuum mechanics the response of a body to deformation is described by standard forces consistent with balance laws for linear and angular momentum. Configurational forces are less intuitive: they are related to the intrinsic coherency of a body's material structure and perform work in the addition and removal of material and in the evolution of structural defects. Following Gurtin and Struthers (1990) and Gurtin (1995, 1999), we view configurational forces as primitive objects consistent with their own force balance. Configurational forces defined via the calculus of variations as derivatives of an energy have been introduced earlier, e.g., in the classic work of Eshelby (1951) on lattice defects.[13] The role of

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[13] Cf. Maugin (1993) for a treatment of configurational forces within an Eshelbian framework.

configurational forces, however, seems more pervasive and fundamental than problems susceptible to a variational formulation can indicate.

2.7.1. Configurational Forces and Their Balance.

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

$$\int_{\partial\mathscr{P}} \mathbf{C}\mathbf{n}\, da + \int_{\mathscr{P}} \mathbf{f}\, dv = \mathbf{0} \tag{2.69}$$

for all parts $\mathscr{P}$, a requirement equivalent to the local force balance

$$\operatorname{div} \mathbf{C} + \mathbf{f} = \mathbf{0} \tag{2.70}$$

2.7.2. Migrating Control Volumes. Accretion.

To characterize the manner in which configurational forces perform work, a means of capturing the kinematics associated with the transfer of material is needed. We accomplish this using control volumes $\mathscr{P}(t)$ that migrate through $\mathscr{B}$ and thereby result in the transfer of material to $\mathscr{P}(t)$ across $\partial\mathscr{P}(t)$, a process we refer to as **accretion**.

Parts should not be confused with migrating control volumes $\mathscr{P}(t)$, which are not fixed subregions of $\mathscr{B}$, but instead *migrate* through $\mathscr{B}$. The phrase "transfer of material *to* $\mathscr{P}$" is meant in a general sense that allows also for the "transfer of material *from* $\mathscr{P}$," and similarly for the phrase "addition of material *to* $\mathscr{P}$."

Let $\mathscr{P} = \mathscr{P}(t)$ be a **migrating control volume** with $U_{\partial\mathscr{P}}$ the (scalar) **normal velocity** of $\partial\mathscr{P}$ in the direction of the outward unit normal $\mathbf{n}$. To describe the working associated with the evolution of $\mathscr{P}(t)$, we introduce a field $\mathbf{q}$ interpreted as the velocity with which an external agency adds material to $\partial\mathscr{P}$. Compatibility then requires that $\mathbf{q}$ have $U_{\partial\mathscr{P}}$ as its normal component,

$$\mathbf{q} \cdot \mathbf{n} = U_{\partial\mathscr{P}} \tag{2.71}$$

but $\mathbf{q}$ is otherwise arbitrary.

This discussion should motivate the following definition: an assignment, at each t, of a vector $\mathbf{q}(\mathbf{x}, t)$ to each position $\mathbf{x}$ on $\partial\mathscr{P}(t)$ is a velocity field for $\partial\mathscr{P}$ if $\mathbf{q}$ is a smooth field that satisfies $\mathbf{q} \cdot \mathbf{n} = U_{\partial\mathscr{P}}$.

One might ask: Why not use, as velocity field, the vectorial normal velocity $(U_{\partial\mathscr{P}})\,\mathbf{n}$, which is intrinsic? One reason for not doing this is that, granted smoothness, $\partial\mathscr{P}(t)$ may be parametrized locally in time by a function of the form $\mathbf{x} = \hat{\mathbf{x}}(\boldsymbol{\xi}, t)$, $\boldsymbol{\xi} = (\xi_1, \xi_2)$; the field $\mathbf{q}(\mathbf{x}, t) = \partial\hat{\mathbf{x}}(\boldsymbol{\xi}, t)/\partial t$ then represents a (generally non-normal) velocity field for $\partial\mathscr{P}(t)$.

Let $\mathscr{P}(t)$ be a migrating control volume. A velocity field $\mathbf{q}$ for $\partial\mathscr{P}$ may be viewed as a velocity field for particles evolving on the migrating surface $\partial\mathscr{P}$, with the trajectory $\boldsymbol{\zeta}(\tau)$ of the particle that passes through position $\mathbf{x}$ on $\partial\mathscr{P}(t)$ at time t the unique solution of

$$\frac{d\boldsymbol{\zeta}}{d\tau}(\tau) = \mathbf{q}(\boldsymbol{\zeta}(\tau), \tau), \qquad \boldsymbol{\zeta}(\tau) = \mathbf{x} \tag{2.72}$$

Given a field $\Phi(\mathbf{x}, t)$, its time-rate following the motion of $\partial\mathscr{P}$, as described by $\mathbf{q}$, is the derivative with respect to time along such trajectories:

$$\overset{\circ}{\Phi}(\mathbf{x}, t) = \frac{d\Phi}{d\tau}(\boldsymbol{\zeta}(\tau), \tau)\bigg|_{\tau = t} \tag{2.73}$$

By the chain-rule, $\overset{\circ}{\mathbf{u}}$, the corresponding motion velocity following $\partial\mathscr{P}$, satisfies

$$\overset{\circ}{\mathbf{u}} = \dot{\mathbf{u}} + (\nabla\mathbf{u})\,\mathbf{q} \tag{2.74}$$

2.7.3. Versions of the Basic Laws That Account for Accretion. A standard precept of continuum mechanics is that when writing basic laws for a control volume $\mathscr{P}$, all that is external to $\mathscr{P}$ may be accounted for by the action of forces on $\mathscr{P}$, fluxes across $\partial\mathscr{P}$, and supplies directly to $\mathscr{P}$. For a migrating control volume $\mathscr{P}(t)$, generalization of the atomic balance and the energy imbalance is necessary but by no means obvious. Standard treatments of such laws would augment the terms

$$\overline{\int_{\mathscr{P}(t)} \Psi\, dv}^{\boldsymbol{\cdot}}, \qquad \overline{\int_{\mathscr{P}(t)} \nu^{\alpha}\, dv}^{\boldsymbol{\cdot}} \tag{2.75}$$

with the explicit outflow terms

$$\int_{\partial\mathscr{P}(t)} \Psi U_{\partial\mathscr{P}}\, da, \qquad \int_{\partial\mathscr{P}(t)} \nu^{\alpha} U_{\partial\mathscr{P}}\, da \tag{2.76}$$

On the contrary, we view interactions with the material exterior to $\mathscr{P}(t)$ in terms of the working of configurational and standard forces and of the transfer of mass and energy through accretive and diffusive fluxes. For that reason our formulations of these laws do not explicitly include the outflow terms (2.76).

We begin with our generalization of the atomic balance for a migrating control volume $\mathscr{P}(t)$. We introduce a scalar field H^{α} for each species α; $H^{\alpha}U_{\partial\mathscr{P}}$ represents a flux of α-atoms associated with the transfer of material across $\partial\mathscr{P}$ as it migrates. Both the **accretional flux** $H^{\alpha}\, U_{\partial\mathscr{P}}$ and the atomic flux $\mathbf{h}^{\alpha}\cdot\mathbf{n}$ are measured in atoms per unit area and time, but the two fluxes represent different phenomena: $H^{\alpha}U_{\partial\mathscr{P}}$ represents the flux of α-atoms associated solely with the gain of atomic sites due to accretion; $-\mathbf{h}^{\alpha}\cdot\mathbf{n}$ represents the flow of α-atoms relative to the material. In view of this discussion, we write the **balance law for atoms**, for a migrating control volume $\mathscr{P}(t)$, in the form

$$\overline{\int_{\mathscr{P}} \nu^{\alpha}\, dv}^{\,\boldsymbol{\cdot}} = -\int_{\partial\mathscr{P}} \mathbf{h}^{\alpha}\cdot\mathbf{n}\, da + \int_{\mathscr{P}} \mathsf{h}^{\alpha}\, dv + \int_{\partial\mathscr{P}} H^{\alpha}U_{\partial\mathscr{P}}\, da \tag{2.77}$$

We turn next to the generalization of the energy imbalance. As with the atomic fluxes $-\mathbf{h}^{\alpha}\cdot\mathbf{n}$, the accretional fluxes $H^{\alpha}U_{\partial\mathscr{P}}$ give rise to a net influx of energy, per unit area and time, of amount $\mu^{\alpha}H^{\alpha}u_{\partial\mathscr{P}}$. Thus

$$\mathscr{E}(\mathscr{P}) = -\int_{\partial\mathscr{P}} \mu^{\alpha}\mathbf{h}^{\alpha}\cdot\mathbf{n}\, da + \int_{\mathscr{P}} \mu^{\alpha}\mathsf{h}^{\alpha}\, dv + \int_{\partial\mathscr{P}} \mu^{\alpha}H^{\alpha}U_{\partial\mathscr{P}}\, da \tag{2.78}$$

represents the total energy carried into $\mathscr{P}(t)$ by diffusion, by direct supply, and by accretion.

Consider the standard and configurational forces associated with a migrating control volume $\mathscr{P}(t)$, with $\mathbf{q}$ a velocity field for $\partial\mathscr{P}$ and $\mathring{\mathbf{u}}$ the corresponding motion velocity following $\partial\mathscr{P}$. We view the traction $\mathbf{Cn}$ as a force that performs work in conjunction with the migration of $\partial\mathscr{P}$ and therefore choose $\mathbf{q}$ as an appropriate work-conjugate velocity for $\mathbf{Cn}$. Classically, the standard traction $\mathbf{Sn}$ on $\partial\mathscr{P}$ is work-conjugate to the motion velocity $\dot{\mathbf{u}}$, but $\partial\mathscr{P}$ when migrating has no intrinsic material description, as material is continually being added and removed, and it would seem appropriate to use as work-conjugate velocity for $\mathbf{Sn}$ the motion velocity $\mathring{\mathbf{u}}$ following $\partial\mathscr{P}$. Material is added to $\mathscr{P}(t)$ only along its boundary $\partial\mathscr{P}(t)$; there is no transfer of material to the interior of $\mathscr{P}$, nor is there any change in the material structure. For that reason the configurational body force $\mathbf{f}$ performs no work, while the power expended by the standard body force $\mathbf{b}$ has the form $\mathbf{b}\cdot\dot{\mathbf{u}}$. We therefore write the working of the standard and configurational force systems as

$$\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} \mathbf{Cn}\cdot\mathbf{q}\, da + \int_{\partial\mathscr{P}} \mathbf{Sn}\cdot\mathring{\mathbf{u}}\, da + \int_{\mathscr{P}} \mathbf{b}\cdot\dot{\mathbf{u}}\, dv \tag{2.79}$$

The **energy imbalance** for a migrating control volume $\mathscr{P}(t)$ therefore takes the form

$$\overline{\int_{\mathscr{P}} \Psi \, dv}^{\boldsymbol{\cdot}} \leqslant \mathscr{W}(\mathscr{P}) + \mathscr{E}(\mathscr{P}) \tag{2.80}$$

2.7.4. Consequences of Invariance under Changes in Velocity Field for $\partial\mathscr{P}$. The Eshelby Relation.

We require that the energy imbalance be invariant under changes in the choice of velocity field $\mathbf{q}$ describing the motion of $\partial\mathscr{P}(t)$. By (2.71),

$$\mathbf{q} = U_{\partial\mathscr{P}}\mathbf{n} + \boldsymbol{\ell} \tag{2.81}$$

with $\boldsymbol{\ell}(\mathbf{x}, t)$ an arbitrary tangential vector field on $\partial\mathscr{P}$, and, by (2.74), the working may be written in the form

$$\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} \mathbf{Sn} \cdot \mathring{\mathbf{u}} \, da + \int_{\mathscr{P}} \mathbf{b} \cdot \dot{\mathbf{u}} \, dv + \int_{\partial\mathscr{P}} \mathbf{n} \cdot \mathbf{Gn} U_{\partial\mathscr{P}} \, da + \int_{\partial\mathscr{P}} \mathbf{Gn} \cdot \boldsymbol{\ell} \, da \tag{2.82}$$

with $\mathbf{G} = \mathbf{C} + (\nabla\mathbf{u})^{\top}\mathbf{S}$. Since $\boldsymbol{\ell}$ appears linearly in (2.82), and not elsewhere in (2.80), the invariance of (2.80) under changes in velocity field is equivalent to the requirement that $\int_{\partial\mathscr{P}} \mathbf{Gn} \cdot \boldsymbol{\ell} \, da = 0$ for all $\mathscr{P}$ and all fields $\boldsymbol{\ell}$ tangential to $\partial\mathscr{P}$. Since both $\mathscr{P}$ and $\boldsymbol{\ell}$ are arbitrary, $\mathbf{Gn} \cdot \boldsymbol{\ell} = 0$ for all orthogonal vectors $\mathbf{n}$ and $\boldsymbol{\ell}$; thus $\mathbf{G} = \pi\mathbf{1}$ and

$$\mathbf{C} = \pi\mathbf{1} - (\nabla\mathbf{u})^{\top}\mathbf{S} \tag{2.83}$$

with π a *scalar field* (cf. Gurtin 1995). The working therefore has the intrinsic form

$$\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} \mathbf{Sn} \cdot \mathring{\mathbf{u}} \, da + \int_{\mathscr{P}} \mathbf{b} \cdot \dot{\mathbf{u}} \, dv + \int_{\partial\mathscr{P}} \pi U_{\partial\mathscr{P}} \, da \tag{2.84}$$

The scalar field π is a *bulk tension* that performs work when the volume of $\mathscr{P}$ is increased through the addition of material at its boundary.

A standard transport theorem asserts that, for $\mathscr{P}(t)$ a migrating control volume and $\Phi(\mathbf{x}, t)$ a smooth field,

$$\overline{\int_{\mathscr{P}} \Phi \, dv}^{\boldsymbol{\cdot}} = \int_{\mathscr{P}} \dot{\Phi} \, dv + \int_{\partial\mathscr{P}} \Phi U_{\partial\mathscr{P}} \, da \tag{2.85}$$

Thus, using (2.84) and the symmetry of **S**, (2.77) and (2.80) may be rewritten as

$$\left.\begin{aligned} &\int_{\mathscr{P}} \dot{\nu}^{\alpha}\,dv = -\int_{\partial\mathscr{P}} \mathbf{h}^{\alpha}\cdot\mathbf{n}\,da + \int_{\mathscr{P}} \mathsf{h}^{\alpha}\,dv + \int_{\partial\mathscr{P}} (H^{\alpha}-\nu^{\alpha})\,U_{\partial\mathscr{P}}\,da \\ &\int_{\mathscr{P}} \dot{\Psi}\,dv \leqslant \int_{\partial\mathscr{P}} (\mathbf{S}\dot{\mathbf{u}} - \mu^{\alpha}\mathbf{h}^{\alpha})\cdot\mathbf{n}\,da + \int_{\mathscr{P}} (\mathbf{b}\cdot\dot{\mathbf{u}} + \mu^{\alpha}\mathsf{h}^{\alpha})\,dv \\ &\qquad\qquad + \int_{\partial\mathscr{P}} (\mu^{\alpha}H^{\alpha} - \Psi + \pi)\,U_{\partial\mathscr{P}}\,da \end{aligned}\right\} \tag{2.86}$$

Given a time τ, it is possible to find a second migrating control volume $\mathscr{P}'(t)$ with $\mathscr{P}'(\tau)=\mathscr{P}(\tau)$, but with $U_{\partial\mathscr{P}'}$, the normal velocity of $\partial\mathscr{P}'$ at $t=\tau$, an *arbitrary scalar field* on $\partial\mathscr{P}'$; satisfaction of (2.86) for all such $U_{\partial\mathscr{P}'}$ implies

$$\pi = \omega, \qquad H^{\alpha} = \nu^{\alpha} \tag{2.87}$$

where we have used (2.25). The bulk tension π therefore coincides with the grand canonical potential $\omega = \Psi - \mu^{\alpha}\nu^{\alpha}$; but what is more important, (2.83) yields the **Eshelby relation**

$$\mathbf{C} = \omega\mathbf{1} - (\nabla\mathbf{u})^{\top}\,\mathbf{S} \tag{2.88}$$

The Eshelby relation, the configurational balance (2.70), and the notational agreement (2.49) yield the decomposition

$$\mathbf{f} = \mathbf{g} + \mathbf{e}, \qquad \begin{cases} \mathbf{g} = -\nabla\omega + \mathbf{S} : \nabla\nabla\mathbf{u} \\ \mathbf{e} = -(\nabla\mathbf{u})^{\top}\,\mathbf{b} \end{cases} \tag{2.89}$$

We will refer to **g** as an **internal** force, as it is affected by variations in the grand canonical potential and the displacement gradient; and to **e** as an **external** force as it is affected only by the external body force. Granted the constitutive equations introduced in Section 2.4, a consequence of the gradient Gibbs-relation (2.48) is a relation

$$\mathbf{g} = \nu^{\alpha}\,\nabla\mu^{\alpha} \tag{2.90}$$

showing that internal configurational forces arise in response to spatial variations in the chemical potentials.

A major difference between the standard and configurational force systems is the presence of *internal configurational forces* such as the body force **g**. These forces are connected with the material structure of the body $\mathscr{B}$; corresponding to each configuration of $\mathscr{B}$ there is a distribution of material and there are 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.

3. COHERENT PHASE TRANSITIONS WITH SHARP INTERFACES

We next consider the dynamics of phase interfaces modeled as smoothly evolving surfaces. We base the discussion on fundamental laws which—when restricted to control volumes that do not intersect the interface—reduce to those introduced previously; for that reason the local results established thus far for the fields $\mathbf{u}$, $\mathbf{S}$, $\mathbf{b}$, $\mathbf{C} = \omega\mathbf{1} - (\nabla\mathbf{u})^\top\mathbf{S}$, $\mathbf{f}$, Ψ, $H^{\mathfrak{a}} = \nu^{\mathfrak{a}}$, $\mathbf{h}^{\mathfrak{a}}$, $\mu^{\mathfrak{a}}$, and $\mathsf{h}^{\mathfrak{a}}$ will be valid in **bulk** (i.e., away from the interface). Here we concentrate on deriving corresponding results for the interface, assuming throughout that the bulk fields (and their derivatives) have at most jump discontinuities across the interface.

3.1. Preliminaries

3.1.1. Surfaces and Superficial Fields. We consider a smooth **surface** $\mathscr{S}$ oriented by a choice of unit normal field $\mathbb{m}(\mathbf{x})$.

Crucial to our discussion of interfacial stress is the notion of a superficial tensor. An example of interfacial stress is surface tension described by a scalar field σ on $\mathscr{S}$. Let $\mathscr{A}$ be a subsurface of $\mathscr{S}$, and let $\mathbb{n}$, a vector field tangent to $\mathscr{S}$, denote the outward unit normal to the boundary curve $\partial\mathscr{A}$. Then $\sigma\mathbb{n}$ represents a force (per unit length) exerted on $\mathscr{A}$ across $\partial\mathscr{A}$ by the portion of $\mathscr{S}$ that lies outside of $\mathscr{A}$. Thus, as with the standard notion of stress, surface stress at a point is a linear mapping that assigns a force, here $\sigma\mathbb{n}$, to a unit normal, here a tangent vector $\mathbb{n}$. More generally, surface stress is a linear transformation $\mathbb{C}$ that maps tangent vectors $\mathbb{n}$ into vectors $\mathbb{C}\mathbb{n}$ in $\mathbb{R}^3$. (When $\mathbb{C}$ represents surface tension, $\mathbb{C}\mathbb{n}$ is also a tangent vector, but, as we shall see, there are more general situations in which $\mathbb{C}\mathbb{n}$ need not be tangent.)

Of interest here are tensor fields $\mathbb{T}$ on $\mathscr{S}$ with the property that, at each $\mathbf{x}$ on $\mathscr{S}$, $\mathbb{T}(\mathbf{x})$ is a linear transformation from the tangent space at $\mathbf{x}$ into $\mathbb{R}^3$. These two notions of a tensor field are reconciled by extending $\mathbb{T}(\mathbf{x})$ to all of $\mathbb{R}^3$ with the requirement that $\mathbb{T}(\mathbf{x})$ annihilate vectors normal to $\mathscr{S}$. Precisely, a superficial tensor-field $\mathbb{T}$ on $\mathscr{S}$ associates with each $\mathbf{x}$ in $\mathscr{S}$ a linear transformation $\mathbb{T}(\mathbf{x})$ from $\mathbb{R}^3$ into $\mathbb{R}^3$ such that

$$\mathbb{T}\mathbb{m} = \mathbf{0} \tag{3.1}$$

A superficial tensor-field $\mathbb{T}$ is *tangential* if, given any vector $\mathbb{a}$, the vector $\mathbb{T}(\mathbf{x})\,\mathbb{a}$ is tangent to $\mathscr{S}$ at each $\mathbf{x}$. Introducing the **projection**

$$\mathbb{P} = \mathbf{1} - \mathbb{m} \otimes \mathbb{m} \tag{3.2}$$

onto the surface $\mathscr{S}$, each superficial tensor-field $\mathbb{T}$ admits the decomposition

$$\mathbb{T} = \mathbb{T}_{\mathbf{tan}} + \mathbb{m} \otimes \mathbb{t}, \qquad \begin{cases} \mathbb{T}_{\mathbf{tan}} = \mathbb{P}\mathbb{T} \\ \mathbb{t} = \mathbb{T}^{\top}\mathbb{m} \end{cases} \tag{3.3}$$

with the tensor field $\mathbb{T}_{\mathbf{tan}}$ and the vector field $\mathbb{t}$ both *tangential.*

The surface gradient $\nabla_{\mathscr{S}}$ is defined through the chain rule. Let $\varphi(\mathbf{x})$ and $\mathbb{w}(\mathbf{x})$ be smooth fields on $\mathscr{S}$, with φ scalar-valued and $\mathbb{w}$ vector-valued. Then given any curve $\mathbb{l}(\tau)$ on $\mathscr{S}$, $d\varphi(\mathbb{l}(\tau))/d\tau = (\nabla_{\mathscr{S}}\varphi(\mathbb{l}(\tau)))\cdot(d\mathbb{l}(\tau)/d\tau)$ and $d\mathbb{w}(\mathbb{l}(\tau))/d\tau = (\nabla_{\mathscr{S}}\mathbb{w}(\mathbb{l}(\tau)))(d\mathbb{l}(\tau)/d\tau)$; the second relation defines $\nabla_{\mathscr{S}}\mathbb{w}$ only on vectors tangent to $\mathscr{S}$, but, in accord with (3.1), $\nabla_{\mathscr{S}}\mathbb{w}$ is extended by requiring that $(\nabla_{\mathscr{S}}\mathbb{w})\,\mathbb{m} = \mathbf{0}$. Then $\nabla_{\mathscr{S}}\varphi$ is a tangential vector-field, while $\nabla_{\mathscr{S}}\mathbb{w}$ is a **superficial tensor-field**.

The **surface divergence** of a vector field $\mathbb{w}$ on $\mathscr{S}$ is defined by $\mathrm{div}_{\mathscr{S}}\,\mathbb{w} = \mathrm{tr}(\nabla_{\mathscr{S}}\mathbb{w})$; the surface divergence $\mathrm{div}_{\mathscr{S}}\,\mathbb{T}$ of a superficial tensor-field $\mathbb{T}$ is defined via the identity $\mathbf{a}\cdot\mathrm{div}_{\mathscr{S}}\,\mathbb{T} = \mathrm{div}_{\mathscr{S}}(\mathbb{T}^{\top}\mathbf{a})$, where $\mathbf{a}$ is an arbitrary constant vector. Let $\mathscr{A}$ denote a subsurface of $\mathscr{S}$ with boundary curve $\partial\mathscr{A}$, and let $\mathbb{n}(\mathbf{x})$, a vector tangent to $\mathscr{S}$ at a point $\mathbf{x}$ on $\partial\mathscr{A}$, denote the outward unit normal to $\partial\mathscr{A}$. The **surface divergence theorem** then has the form

$$\int_{\partial\mathscr{A}} \mathbb{t}\cdot\mathbb{n}\,ds = \int_{\mathscr{A}} \mathrm{div}_{\mathscr{S}}\,\mathbb{t}\,da, \qquad \int_{\partial\mathscr{A}} \mathbb{T}\mathbb{n}\,ds = \int_{\mathscr{A}} \mathrm{div}_{\mathscr{S}}\,\mathbb{T}\,da \tag{3.4}$$

for $\mathbb{t}$ a tangential vector field and $\mathbb{T}$ a superficial tensor-field, which may or may not be tangential.

The **curvature tensor** $\mathbb{L}$ and **total curvature** $K_{\mathscr{S}}$ (twice the mean curvature) are defined by

$$\mathbb{L} = -\nabla_{\mathscr{S}}\mathbb{m}, \qquad K_{\mathscr{S}} = \mathrm{tr}\,\mathbb{L} = \mathbf{1}\cdot\mathbb{L} = \mathbb{P}\cdot\mathbb{L} = -\mathrm{div}_{\mathscr{S}}\,\mathbb{m} \tag{3.5}$$

A classical result is that $\mathbb{L}$ is symmetric and (hence) tangential. Granted this, the general relation $\mathrm{div}_{\mathscr{S}}(\mathbb{a}\otimes\mathbb{b}) = (\mathrm{div}_{\mathscr{S}}\,\mathbb{b})\,\mathbb{a} + (\nabla_{\mathscr{S}}\mathbb{a})\,\mathbb{b}$ and (3.5) yield the identities

$$\mathrm{div}_{\mathrm{S}}\,\mathbb{P} = K_{\mathscr{S}}\mathbb{m}, \qquad \mathrm{div}_{\mathscr{S}}(\mathbb{m}\otimes\mathbb{t}) = (\mathrm{div}_{\mathscr{S}}\,\mathbb{t})\,\mathbb{m} - \mathbb{L}\mathbb{t} \tag{3.6}$$

with $\mathbb{t}$ a tangential vector field.

3.1.2. Evolving Surfaces.

Let $\mathscr{S}(t)$ be a smooth surface that evolves smoothly in time, and let $V_{\mathscr{S}}(\mathbf{x}, t)$ denote the (scalar) normal velocity in the direction of the unit normal $\mathbb{m}(\mathbf{x}, t)$. Further, let $\mathbb{v}(\mathbf{x}, t)$ be a velocity field for $\mathscr{S}(t)$; i.e., a smooth superficial field that satisfies $\mathbb{v}(\mathbf{x}, t) \cdot \mathbb{m}(\mathbf{x}, t) = V_{\mathscr{S}}(\mathbf{x}, t)$ (cf. Section 2.7.2). As with migrating control volumes, $\mathbb{v}$ may be viewed as a velocity field for evolving particles constrained to $\mathscr{S}$, with the path $\boldsymbol{\zeta}(\tau)$ traversed by the particle that passes through a point $\mathbf{x}$ in $\mathscr{S}(t)$ at time t the unique solution of (2.72) with $\mathbf{q}(\boldsymbol{\zeta}(\tau), \tau)$ replaced by $\mathbb{v}(\boldsymbol{\zeta}(\tau), \tau)$. Given a field $\varphi(\mathbf{x}, t)$ on $\mathscr{S}(t)$, the **time-derivative** $\overset{\triangle}{\varphi}$ of φ **following** the motion of $\mathscr{S}$, as described by $\mathbb{v}$, is then the time derivative following such particles:

$$\overset{\triangle}{\varphi}(\mathbf{x}, t) = \frac{d\varphi}{d\tau}(\boldsymbol{\zeta}(\tau), \tau)\bigg|_{\tau = t} \tag{3.7}$$

When $\mathbb{v}$ has the intrinsic form $\mathbb{v} = V_{\mathscr{S}}\mathbb{m}$, $\overset{\triangle}{\varphi}$ represents the **normal time-derivative** of φ following $\mathscr{S}$; this derivative applied to $\mathbb{m}$ results in the identity

$$\overset{\triangle}{\mathbb{m}} = -\nabla_{\mathscr{S}} V_{\mathscr{S}} \tag{3.8}$$

Let $\mathscr{A}(t)$ denote a smoothly evolving subsurface of $\mathscr{S}(t)$ with $\mathbb{n}(\mathbf{x}, t)$ the outward unit normal to $\partial\mathscr{A}(t)$. The motion of the curve $\partial\mathscr{A}(t)$ may be characterized intrinsically by the velocity field

$$V\mathbb{m} + V_{\partial\mathscr{A}}\,\mathbb{n} \tag{3.9}$$

where $V_{\partial\mathscr{A}}$ is the velocity of $\partial\mathscr{A}$ in the direction of the normal $\mathbb{n}$. More generally, an assignment of a vector $\mathbb{w}(\mathbf{x}, t)$ to each $\mathbf{x}$ on $\partial\mathscr{A}(t)$ is a **velocity field** for $\partial\mathscr{A}$ if $\mathbb{w}$ is a smooth field that satisfies $\mathbb{w} \cdot \mathbb{m} = V_{\mathscr{S}}$ and $\mathbb{w} \cdot \mathbb{n} = V_{\partial\mathscr{A}}$, with no constraint placed on the component of $\mathbb{w}$ tangential to $\partial\mathscr{A}$.

Let $\Phi(\mathbf{x}, t)$ be continuous up to $\mathscr{S}(t)$ from either side. Then $[\![\Phi]\!]$ and $\langle\!\langle\Phi\rangle\!\rangle$ designate the **jump** and **average** of Φ across the interface, while $\Phi^{\pm}$ denote the limiting values of Φ; specifically, for $\mathbf{x}$ on $\mathscr{S}(t)$,

$$\left.\begin{aligned} [\![\Phi]\!](\mathbf{x}, t) &= \Phi^{+}(\mathbf{x}, t) - \Phi^{-}(\mathbf{x}, t), \\ \langle\!\langle\Phi\rangle\!\rangle(\mathbf{x}, t) &= \tfrac{1}{2}(\Phi^{+}(\mathbf{x}, t) + \Phi^{-}(\mathbf{x}, t)) \\ \Phi^{\pm}(\mathbf{x}, t) &= \lim_{\delta \to 0} \Phi(\mathbf{x} \pm \delta\mathbb{m}(\mathbf{x}, t), t) \end{aligned}\right\} \tag{3.10}$$

The following transport theorems are valid for $\mathscr{P}(t)$ a migrating control volume, $\mathscr{A}(t)$ the portion of $\mathscr{S}(t)$ in $\mathscr{P}(t)$, $\Phi(\mathbf{x}, t)$ a field that is smooth up to the interface from either side, and $\varphi(\mathbf{x}, t)$ a smooth superficial field:

$$\left.\begin{aligned} \overset{\centerdot}{\overline{\int_{\mathscr{P}} \Phi\, dv}} &= \int_{\mathscr{P}} \dot{\Phi}\, dv - \int_{\partial\mathscr{A}} \llbracket \Phi \rrbracket\, V_{\mathscr{S}}\, da + \int_{\partial\mathscr{P}} \Phi U_{\partial\mathscr{P}}\, da \\ \overset{\centerdot}{\overline{\int_{\mathscr{A}} \varphi\, da}} &= \int_{\mathscr{A}} (\overset{\triangle}{\varphi} - \varphi K_{\mathscr{S}} V_{\mathscr{S}})\, da + \int_{\partial\mathscr{A}} \varphi V_{\partial\mathscr{A}}\, ds \end{aligned}\right\} \tag{3.11}$$

3.2. Interface kinematics

We now consider $\mathscr{S}(t)$ as an **interface** separating phases α and β, and assume that the subregions of $\mathscr{B}$ occupied by α and β are closed regions with $\mathscr{B}$ as union and $\mathscr{S}$ as intersection.

A basic assumption of the theory is that the motion $\mathbf{u}$ and the chemical potentials $\mu^{\mathfrak{a}}$ be continuous across the interface:

$$\llbracket \mathbf{u} \rrbracket = \mathbf{0}, \qquad \llbracket \mu^{\mathfrak{a}} \rrbracket = 0 \tag{3.12}$$

The assumption $\llbracket \mathbf{u} \rrbracket = \mathbf{0}$ is the requirement that the interface be coherent;[14] it yields the **compatibility conditions**

$$\llbracket \dot{\mathbf{u}} \rrbracket + V_{\mathscr{S}} \llbracket \nabla\mathbf{u} \rrbracket\, \mathbb{m} = \mathbf{0}, \qquad \llbracket \nabla\mathbf{u} \rrbracket\, \mathbb{P} = \mathbf{0} \tag{3.13}$$

The requirement $\llbracket \mu^{\mathfrak{a}} \rrbracket = 0$, often referred to as an **assumption of local equilibrium**, allows us to consider the bulk fields $\mu^{\mathfrak{a}}$, when evaluated on $\mathscr{S}$, as appropriate *interfacial* chemical-potentials.

Let $\mathbb{v}$ be a velocity field for $\mathscr{S}$. The **motion velocity following** $\mathscr{S}$ as described by $\mathbb{v}$ is then the time derivative $\overset{\triangle}{\mathbf{u}}$ defined in (3.7); by the chain rule and (3.13),

$$\overset{\triangle}{\mathbf{u}} = \dot{\mathbf{u}}^{\pm} + (\nabla\mathbf{u}^{\pm})\, \mathbb{v} = \langle\!\langle \dot{\mathbf{u}} \rangle\!\rangle + \langle\!\langle \nabla\mathbf{u} \rangle\!\rangle \mathbb{v} \tag{3.14}$$

Let $\mathscr{A}(t)$ denote a smoothly evolving subsurface of $\mathscr{S}(t)$ and, for all sufficiently small $\varepsilon > 0$, let $\mathscr{P}_{\varepsilon}(t)$ denote the **ε-pillbox** about $\mathscr{A}(t)$ (the set of all points $\mathbf{x} \pm \delta\mathbb{m}(\mathbf{x}, t)$ with $\mathbf{x}$ in $\mathscr{A}(t)$ and $0 \leqslant \delta \leqslant \varepsilon$). Then $\mathscr{P}_{\varepsilon}(t)$ is a migrating control volume with $\mathscr{A}(t)$ the portion of $\mathscr{P}_{\varepsilon}(t)$ in $\mathscr{S}(t)$, and, for $\Phi(\mathbf{x}, t)$ any of the bulk fields,

---

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

$$\left.\begin{aligned}&\lim_{\varepsilon\to 0}\int_{\partial\mathscr{P}_\varepsilon}\Phi U_{\partial\mathscr{P}_\varepsilon}\,da=\int_{\mathscr{A}}\llbracket\Phi\rrbracket V\,da, \qquad \lim_{\varepsilon\to 0}\int_{\partial\mathscr{P}_\varepsilon}\Phi\mathbf{n}\,da=\int_{\mathscr{A}}\llbracket\Phi\rrbracket\mathbb{m}\,da,\\ &\lim_{\varepsilon\to 0}\overline{\int_{\partial\mathscr{P}_\varepsilon}\Phi\,dv}^{\,\boldsymbol{\cdot}}=0\end{aligned}\right\}\quad(3.15)$$

where $(3.15)_3$ follows from $(3.11)_1$ and $(3.15)_1$.

The velocity fields

$$\left.\begin{aligned}&\mathbb{v}=V_{\mathscr{S}}\mathbb{m}, \quad \overset{\triangle}{\mathbf{u}}=\langle\!\langle\dot{\mathbf{u}}\rangle\!\rangle+V_{\mathscr{S}}\langle\!\langle\nabla\mathbf{u}\rangle\!\rangle\mathbb{m} \quad (\text{for}\quad\mathscr{S}),\\ &\mathbf{q}=U_{\partial\mathscr{P}}\mathbf{n}, \quad \mathring{\mathbf{u}}=\dot{\mathbf{u}}+U_{\partial\mathscr{P}}(\nabla\mathbf{u})\,\mathbf{n} \quad (\text{for}\quad\partial\mathscr{P}),\end{aligned}\right\}\quad(3.16)$$

are *intrinsic* for the interface and for the boundary of a migrating control volume. For these velocity fields and $\mathscr{P}_\varepsilon(t)$ an ε-pillbox about $\mathscr{A}(t)$,

$$\left.\begin{aligned}&\lim_{\varepsilon\to 0}\int_{\partial\mathscr{P}_\varepsilon}\mathbf{Cn}\cdot\mathbf{q}\,da=\int_{\mathscr{A}}(\llbracket\mathbf{C}\rrbracket\mathbb{m})\cdot(V_{\mathscr{S}}\mathbb{m})\,da,\\ &\lim_{\varepsilon\to 0}\int_{\partial\mathscr{P}_\varepsilon}\mathbf{Sn}\cdot\mathring{\mathbf{u}}\,da=\int_{\mathscr{A}}(\llbracket\mathbf{S}\rrbracket\mathbb{m})\cdot\overset{\triangle}{\mathbf{u}}\,da\end{aligned}\right\}\quad(3.17)$$

We will localize the basic balance laws and the energy imbalance to the interface using the limit relations (3.15) and (3.17) with $\mathscr{P}(t)$ an ε-pillbox $\mathscr{P}_\varepsilon(t)$ about an arbitrary evolving subsurface $\mathscr{A}(t)$; we will refer to procedures of this type as **pillbox arguments**.

3.3. Basic Laws

3.3.1. Balance Law for Atoms.

We neglect diffusion within the interface, but, for each species $\mathfrak{a}$, allow for a supply $\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}}$ of atoms directly to the interface from the external world; we therefore write the **balance law for atoms** in the form

$$\overline{\int_{\mathscr{P}}v^{\mathfrak{a}}\,dv}^{\,\boldsymbol{\cdot}}=-\int_{\partial\mathscr{P}}\mathbf{h}^{\mathfrak{a}}\cdot\mathbf{n}\,da+\int_{\mathscr{P}}\mathsf{h}^{\mathfrak{a}}\,dv+\int_{\partial\mathscr{P}}H^{\mathfrak{a}}U_{\partial\mathscr{P}}\,da+\int_{\mathscr{A}}\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}}\,da \quad (3.18)$$

where here and in what follows, $\mathscr{A}(t)$ is the portion of $\mathscr{S}(t)$ in $\mathscr{P}(t)$,

$$\mathscr{A}=\mathscr{P}\cap\mathscr{S} \quad (3.19)$$

This balance must hold for all migrating control volumes $\mathscr{P}(t)$ and all atomic species $\mathfrak{a}$; and, since $H^{\mathfrak{a}}=v^{\mathfrak{a}}$, a pillbox argument yields the interfacial balance

$$V_{\mathscr{S}}\llbracket v^{\mathfrak{a}}\rrbracket=\llbracket\mathbf{h}^{\mathfrak{a}}\rrbracket\cdot\mathbb{m}-\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}} \quad (3.20)$$

3.3.2. Standard and Configurational Force Balances at the Interface. To the force systems discussed previously we add four fields defined on the interface for all time. Specifically, we add an **external force** $\mathbb{b}$ to the standard system, and an **interfacial stress** $\mathbb{C}$, an **internal force** $\mathbb{g}$, and an **external force** $\mathbb{e}$ to the configurational system. The fields $\mathbb{b}$, $\mathbb{g}$, and $\mathbb{e}$ have physical interpretations identical to the body forces **b**, **g**, and **e**, except that $\mathbb{b}$, $\mathbb{g}$, and $\mathbb{e}$ are concentrated on the interface. The superficial tensor field $\mathbb{C}$ represents stresses such as surface tension that act within the interface.

Let $\mathscr{P}(t)$ be an (arbitrary) migrating control volume, let $\mathscr{A}$ denote the portion of $\mathscr{S}$ in $\mathscr{P}$, and let $\mathbb{m}$ denote the outward unit normal to the boundary curve $\partial\mathscr{A}$. We introduce the **standard force** and **moment balances**

$$\left.\begin{aligned}\int_{\partial\mathscr{P}} \mathbf{Sn}\,da + \int_{\mathscr{P}} \mathbf{b}\,dv + \int_{\mathscr{A}} \mathbb{b}\,da = \mathbf{0}\\ \int_{\partial\mathscr{P}} \mathbf{x}\times\mathbf{Sn}\,da + \int_{\mathscr{P}} \mathbf{x}\times\mathbf{b}\,dv + \int_{\mathscr{A}} \mathbf{x}\times\mathbb{b}\,da = \mathbf{0}\end{aligned}\right\} \tag{3.21}$$

and the configurational force balance

$$\int_{\partial\mathscr{P}} \mathbf{Cn}\,da + \int_{\mathscr{P}} (\mathbf{g}+\mathbf{e})\,dv + \int_{\partial\mathscr{A}} \mathbb{C}\mathbb{m}\,ds + \int_{\mathscr{A}} (\mathbb{g}+\mathbb{e})\,da = \mathbf{0} \tag{3.22}$$

By the surface divergence theorem, $\int_{\partial\mathscr{A}} \mathbb{C}\mathbb{m}\,ds = \int_{\mathscr{A}} \operatorname{div}_{\mathscr{S}} \mathbb{C}\,da$; pillbox arguments applied to (3.21) and (3.22) thus yield the interfacial balances

$$[\![\mathbf{S}]\!]\,\mathbb{m} + \mathbb{b} = \mathbf{0}, \qquad [\![\mathbf{C}]\!]\,\mathbb{m} + \mathbb{g} + \mathbb{e} + \operatorname{div}_{\mathscr{S}} \mathbb{C} = \mathbf{0} \tag{3.23}$$

3.3.3. Working. Energy Imbalance. The working $\mathscr{W}(\mathscr{P})$ on a migrating control volume $\mathscr{P}(t)$ has two contributions: a contribution (2.79) associated with the bulk material and a contribution, which we now derive, that accounts for the interface $\mathscr{S}(t)$.

Let **q** be a velocity field for $\partial\mathscr{P}$ with $\mathring{\mathbf{u}}$ the corresponding motion velocity following $\partial\mathscr{P}$, let $\mathbb{v}$ be a velocity field for $\partial\mathscr{A}$ with $\overset{\triangle}{\mathbf{u}}$ the corresponding motion velocity following $\mathscr{S}$, and let $\mathbb{w}$ be a velocity field for $\partial\mathscr{A}$, where $\mathscr{A} = \mathscr{P} \cap \mathscr{S}$. The argument resulting in the terms $\mathbf{Cn}\cdot\mathbf{q}$ and $\mathbf{Sn}\cdot\mathring{\mathbf{u}}$ in (2.79) here leads us to write the working of the external forces $\mathbb{e}$ and $\mathbb{b}$ in the form $\int_{\mathscr{A}} (\mathbb{e}\cdot\mathbb{v} + \mathbb{b}\cdot\overset{\triangle}{\mathbf{u}})\,da$. Here $\overset{\triangle}{\mathbf{u}}$ rather than $\dot{\mathbf{u}}$ is the work-conjugate velocity for $\mathbb{b}$, just as $\mathring{\mathbf{u}}$ rather than $\dot{\mathbf{u}}$ is the conjugate velocity for **Sn**, and $\mathbb{v}$ is the conjugate velocity for $\mathbb{e}$, just as **q** is for **Cn**. Since $\mathbb{C}$ acts on $\mathscr{P}$ across $\partial\mathscr{A}$, it would seem appropriate to take as work-conjugate velocity for $\mathbb{C}$ the field $\mathbb{w}$, which describes the velocity of $\partial\mathscr{A}$. The field $\mathbb{g}$ represents internal forces that pin, in place, the material structure at the current location of the interface; as this structure is fixed in the reference configuration, $\mathbb{g}$ performs no work (cf. the final paragraph of Section 2.7.4). We therefore write the **working** $\mathscr{W}(\mathscr{P})$ on a migrating control volume $\mathscr{P}(t)$ in the form

$$\begin{aligned}\mathscr{W}(\mathscr{P}) = \int_{\partial\mathscr{P}} (\mathbf{Cn}\cdot\mathbf{q} + \mathbf{Sn}\cdot\mathring{\mathbf{u}})\,da + \int_{\mathscr{P}} \mathbf{b}\cdot\dot{\mathbf{u}}\,dv \\ + \int_{\mathscr{A}} (\mathbb{e}\cdot\mathbb{v} + \mathbb{b}\cdot\overset{\triangle}{\mathbf{u}})\,da + \int_{\partial\mathscr{A}} \mathbb{C}\mathbb{m}\cdot\mathbb{w}\,ds\end{aligned} \tag{3.24}$$

Finally, we generalize the energy flow $\mathscr{E}(\mathscr{P})$, defined in (2.78), to include the flow of energy corresponding to the interfacial supplies $\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}}$:

$$\mathscr{E}(\mathscr{P}) = -\int_{\partial\mathscr{P}} \mu^{\mathfrak{a}}\mathbf{h}^{\mathfrak{a}}\cdot\mathbf{n}\,da + \int_{\mathscr{P}} \mu^{\mathfrak{a}}\mathsf{h}^{\mathfrak{a}}\,dv + \int_{\partial\mathscr{P}} \mu^{\mathfrak{a}}H^{\mathfrak{a}}U_{\partial\mathscr{P}}\,da + \int_{\mathscr{A}} \mu^{\mathfrak{a}}\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}}\,da \tag{3.25}$$

In addition to the bulk energy Ψ, we allow for an **interfacial energy** ψ, per unit area, and write the **energy imbalance** for a migrating control volume $\mathscr{P}(t)$ as

$$\overline{\int_{\mathscr{P}} \Psi\,dv + \int_{\mathscr{A}} \psi\,da}^{\,\boldsymbol{\cdot}} \leqslant \mathscr{W}(\mathscr{P}) + \mathscr{E}(\mathscr{P}) \tag{3.26}$$

with $\mathscr{W}(\mathscr{P})$ and $\mathscr{E}(\mathscr{P})$ given by (3.24) and (3.25).

3.3.4. Consequences of Invariance under Changes in Velocity Field for $\mathscr{S}$ and $\partial\mathscr{A}$. Normal Configurational Balance.

We require that the theory be independent of the choice of velocity fields $\mathbb{v}$ for $\mathscr{S}$ and $\mathbb{w}$ for $\partial\mathscr{A}$, an assumption with important consequences regarding the configurational fields $\mathbb{b}$, $\mathbb{e}$, and $\mathbb{C}$.

The only term in the energy imbalance (3.26) involving the tangential component $\mathbb{t} = \mathbb{P}\mathbb{v}$ of $\mathbb{v}$, which is arbitrary, is the integral over $\mathscr{A}$ in (3.24). The corresponding integrand may be written as $V_{\mathscr{S}}(\mathbb{e} + \langle\!\langle\nabla\mathbf{u}\rangle\!\rangle^{\top}\mathbb{b})\cdot\mathbb{m} + \mathbb{b}\cdot\langle\!\langle\dot{\mathbf{u}}\rangle\!\rangle + (\mathbb{e} + \langle\!\langle\nabla\mathbf{u}\rangle\!\rangle^{\top}\mathbb{b})\cdot\mathbb{t}$, and since both $\mathscr{P}$ and $\mathbb{t}$ are arbitrary, $(\mathbb{e} + \langle\!\langle\nabla\mathbf{u}\rangle\!\rangle^{\top}\mathbb{b})$ must be normal to $\mathscr{S}$:

$$\mathbb{P}\mathbb{e} = -\mathbb{P}\langle\!\langle\nabla\mathbf{u}\rangle\!\rangle^{\top}\mathbb{b} \tag{3.27}$$

Thus (2.88), $(3.13)_2$, and $(3.23)_1$ imply that

$$\begin{aligned}\mathbb{P}[\![\mathbf{C}\mathbb{m}]\!] &= -\mathbb{P}[\![((\nabla\mathbf{u})\,\mathbb{P})^{\top}\,\mathbf{S}]\!]\,\mathbb{m} \\ &= -(\langle\!\langle\nabla\mathbf{u}\rangle\!\rangle\,\mathbb{P})^{\top}\,[\![\mathbf{S}]\!]\,\mathbb{m} = \mathbb{P}\langle\!\langle\nabla\mathbf{u}\rangle\!\rangle^{\top}\,\mathbb{b} = -\mathbb{P}\mathbb{e}\end{aligned} \tag{3.28}$$

Next, since the component of $\mathbb{w}$ tangent to $\partial\mathscr{A}$ is arbitrary, invariance under changes in $\mathbb{w}$ yields the requirement that $\int_{\partial\mathscr{A}} \mathbb{C}\mathbb{m} \cdot \mathbb{t}\, ds = 0$ for every vector field $\mathbb{t}$ tangential to $\partial\mathscr{A}$. Bearing in mind that $\mathscr{P}$ and hence $\partial\mathscr{A}$ is arbitrary, it follows that, for any $\mathbf{x}$ on $\mathscr{S}(t)$, $(\mathbb{C}(\mathbf{x}, t)\, \mathbb{a}(\mathbf{x}, t)) \cdot \mathbb{d}(\mathbf{x}, t) = 0$ for every pair of orthogonal vectors $\mathbb{a}$ and $\mathbb{d}$ tangent to $\mathscr{S}$ at $\mathbf{x}$, and this yields the conclusion that the tangential part of $\mathbb{C}$ has the form $\mathbb{C}_{\mathbf{tan}} = \sigma\mathbb{P}$; thus, by (3.3), $\mathbb{C}$ may be written as

$$\mathbb{C} = \sigma\mathbb{P} + \mathbb{m} \otimes \mathbb{c} \tag{3.29}$$

The scalar $\sigma(\mathbf{x}, t)$ represents **surface tension**. The vector $\mathbb{c}(\mathbf{x}, t)$, although tangential, represents, via the term $\mathbb{m} \otimes \mathbb{c}$, forces whose action is normal to $\mathscr{S}$; $\mathbb{c}$ is referred to as the **surface shear**.

In view of (3.6),

$$\operatorname{div}_{\mathscr{S}} \mathbb{C} = (\sigma K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbb{c})\, \mathbb{m} + \nabla_{\mathscr{S}}\sigma - \mathbb{L}\mathbb{c} \tag{3.30}$$

thus, by (3.28) and since $\nabla_{\mathscr{S}}\sigma$ and $\mathbb{L}\mathbb{c}$ are tangential, the normal and tangential configurational force balances are given by

$$\left.\begin{aligned} \mathbb{m} \cdot [\![\mathbf{C}]\!]\, \mathbb{m} + \sigma K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbb{c} + g + e = 0 \\ \nabla_{\mathscr{S}}\sigma - \mathbb{L}\mathbb{c} + \mathbb{P}\mathbb{g} = 0 \end{aligned}\right\} \tag{3.31}$$

with

$$g = \mathbb{g} \cdot \mathbb{m}, \qquad e = \mathbb{e} \cdot \mathbb{m} \tag{3.32}$$

The stress in the form (3.29) and the balance (3.31) is due to Gurtin and Struthers (1990, Eq. (7.5)) (cf. Gurtin 1988). For statical situations (with $\mathbf{C} = \Psi\mathbf{1}$ and $g = e = 0$) related results were derived earlier using variational arguments based on a constitutive equation $\psi = \hat{\psi}(\mathbb{m})$ for the interfacial energy density, with σ and $\mathbb{c}$ defined by $\sigma = \psi$ and $\mathbb{c} = -\partial\hat{\psi}(\mathbb{m})/\partial\mathbb{m}$. In particular, Herring (1951) derived the force balance implied by (3.29) at triple junctions, while Cahn and Hoffman (1972) showed variationally that the vector $\xi = \sigma\mathbb{m} - \mathbb{c}$ satisfies $\operatorname{div}_{\mathscr{S}} \xi = [\![\Psi]\!]$. Since $\mathbb{m} \cdot \operatorname{div}_{\mathscr{S}} \mathbb{C} = -\operatorname{div}_{\mathscr{S}} \xi$, this is consistent with $(3.31)_1$.[15] The "Cahn–Hoffman" vector ξ is widely used in materials science, which is not surprising, since it is only the normal component of (3.30) that generally appears in interface conditions. But the use of ξ as a basic (rather than as a derived) object masks the tensorial nature of interfacial stress, which is classical. In fact, ξ is apropos only when

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[15] See also Cahn and Hoffman (1974).

$\mathbb{C}$ has the specific form $\mathbb{C} = \sigma\mathbb{P} + \mathbb{m} \otimes \mathbb{c}$; but, in situations that allow for a standard stress $\mathbb{S}$ on the interface, neither $\mathbb{C}$ nor $\mathbb{S}$ has this form.

To further relate the Cahn–Hoffman vector ξ to the interfacial stress $\mathbb{C}$, let $\mathscr{A} = \mathscr{A}(t)$ be a subsurface of the interface with $\mathbb{n}$ the outward unit normal to $\partial\mathscr{A}$, and let $\mathbb{t} = \mathbb{m} \times \mathbb{n}$, so that $\mathbb{t}$ is a unit tangent field on $\partial\mathscr{A}$. Then $\mathbb{C}\mathbb{n} = \mathbb{C}(\mathbb{t} \times \mathbb{m}) = \mathbb{t} \times (\sigma\mathbb{m}) + (\mathbb{m} \otimes \mathbb{c})(\mathbb{t} \times \mathbb{m}) = \mathbb{t} \times (\sigma\mathbb{m}) - (\mathbb{m} \otimes \mathbb{m})(\mathbb{t} \times \mathbb{c})$ $= \mathbb{t} \times (\sigma\mathbb{m} - \mathbb{c}) = \mathbb{t} \times \xi$ and the *external working* of the interfacial stress is given by

$$\int_{\partial\mathscr{A}} \mathbb{C}\mathbb{n} \cdot \mathbb{w}\, ds = \int_{\partial\mathscr{A}} (\mathbb{t} \times \xi) \cdot \mathbb{w}\, ds$$

Further, the vectorial counterpart of $(3.11)_2$ yields a transport theorem for the vector-area measure $\mathbb{m}\, da$,

$$\overline{\int_{\mathscr{A}} \mathbb{m}\, da}^{\,\cdot} = \int_{\mathscr{A}} (\overset{\triangle}{\mathbb{m}} - K_{\mathscr{S}} V_{\mathscr{S}} \mathbb{m})\, da + \int_{\partial\mathscr{A}} \mathbb{m} V_{\partial\mathscr{A}}\, ds$$

which identifies the vector field $(\overset{\triangle}{\mathbb{m}} - K_{\mathscr{S}} V_{\mathscr{S}} \mathbb{m})$ as the rate at which vector-area is changing, measured pet unit area. Using this relation and the identity $\xi \cdot (\overset{\triangle}{\mathbb{m}} - K_{\mathscr{S}} V_{\mathscr{S}} \mathbb{m}) = -(\sigma K_{\mathscr{S}} V_{\mathscr{S}} + \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}})$, the *internal working* of the interfacial stress can be written in the simple form

$$-\int_{\mathscr{A}} (\sigma K_{\mathscr{S}} V_{\mathscr{S}} + \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}})\, da = \int_{\mathscr{A}} \xi \cdot (\overset{\triangle}{\mathbb{m}} - K_{\mathscr{S}} V_{\mathscr{S}} \mathbb{m})\, da$$

and, hence, represents working associated with temporal changes in the vector-area of the interface.

3.3.5. Interfacial Dissipation Inequality.

Our next step will be to localize, to the interface, the energy imbalance (3.26) with velocity fields in the intrinsic forms given by (3.16) and (3.9) (for $\mathbb{w}$). Thus let $\mathscr{A}(t)$ denote a smoothly evolving subsurface of $\mathscr{S}(t)$ and take $\mathscr{P}(t)$ to be the ε-pillbox $\mathscr{P}_\varepsilon(t)$ about $\mathscr{A}(t)$. Then, by (3.8), $\mathrm{div}_{\mathscr{S}}(V_{\mathscr{S}}\mathbb{c}) = (V_{\mathscr{S}}\, \mathrm{div}_{\mathscr{S}}\, \mathbb{c} + \mathbb{c} \cdot \nabla_{\mathscr{S}} V_{\mathscr{S}}) = (V_{\mathscr{S}}\, \mathrm{div}_{\mathscr{S}}\, \mathbb{c} - \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}})$ and therefore, appealing to (3.29),

$$\begin{aligned} \int_{\partial\mathscr{A}} \mathbb{C}\mathbb{n} \cdot \mathbb{w}\, ds &= \int_{\partial\mathscr{A}} (\sigma V_{\partial\mathscr{A}} + V_{\mathscr{S}} \mathbb{c} \cdot \mathbb{n})\, ds \\ &= \int_{\partial\mathscr{A}} \sigma V_{\partial\mathscr{A}}\, ds + \int_{\mathscr{A}} (V_{\mathscr{S}}\, \mathrm{div}_{\mathscr{S}}\, \mathbb{c} - \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}})\, da \qquad (3.33) \end{aligned}$$

Thus, by $(2.87)_2$, $(3.11)_2$, and (3.12), the pillbox argument applied to $\mathscr{P}_\varepsilon(t)$ yields

$$\begin{aligned}
&\int_{\mathscr{A}} (\overset{\triangle}{\psi} - \psi K_{\mathscr{S}} V_{\mathscr{S}})\, da + \int_{\partial\mathscr{A}} \psi V_{\partial\mathscr{A}}\, ds \\
&\quad \leqslant \int_{\mathscr{A}} (V_{\mathscr{S}} [\![\nu^{\mathfrak{a}}]\!] - [\![\mathbf{h}^{\mathfrak{a}}]\!] \cdot \mathbb{m} + \mathsf{h}^{\mathfrak{a}}_{\mathscr{S}})\, \mu^{\mathfrak{a}}\, da \\
&\qquad + \int_{\partial\mathscr{A}} \sigma V_{\partial\mathscr{A}}\, ds + \int_{\mathscr{A}} (\mathbb{m} \cdot [\![\mathbf{C}]\!]\, \mathbb{m} + \operatorname{div}_{\mathscr{S}} \mathbb{c} + e)\, V_{\mathscr{S}} da \\
&\qquad + \int_{\mathscr{A}} (([\![\mathbf{S}]\!]\, \mathbb{m} + \mathbb{b}) \cdot \overset{\triangle}{\mathbf{u}} - \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}})\, da
\end{aligned} \tag{3.34}$$

hence, using the atomic balance (3.20) and the force balances $(3.23)_1$ and $(3.31)_1$,

$$\int_{\mathscr{A}} (\overset{\triangle}{\psi} + \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}} + g V_{\mathscr{S}} - (\psi - \sigma)\, K_{\mathscr{S}} V_{\mathscr{S}})\, da + \int_{\partial\mathscr{A}} (\psi - \sigma)\, V_{\partial\mathscr{A}}\, ds \leqslant 0 \tag{3.35}$$

Given a time τ, it is possible to find a second referential control volume $\mathscr{P}'(t)$ with $\mathscr{P}'(\tau) = \mathscr{P}(\tau)$, but with $V'_{\partial\mathscr{A}}(\mathbf{x}, \tau)$, the normal velocity of the boundary curve $\partial\mathscr{A}'(\tau)$, an arbitrary scalar field; satisfaction of (3.35) for all such $\mathscr{A}'$ implies that

$$\sigma = \psi \tag{3.36}$$

and the *surface tension and surface free-energy coincide* (cf. Gurtin and Struthers 1990; Gurtin 1991). Thus, since $\mathscr{A}$ is arbitrary, (3.35) localizes to yield the interfacial dissipation inequality

$$\overset{\triangle}{\psi} + \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}} + g V_{\mathscr{S}} \leqslant 0 \tag{3.37}$$

We close by stating the resulting *Lyapunov relations*, assuming that the external forces and supplies vanish and that $\mathscr{S}(t)$ is a closed surface. For a *fixed impermeable boundary*,

$$\overset{\cdot}{\overline{\int_{\mathscr{B}} \Psi\, dv + \int_{\mathscr{S}(t)} \psi\, da}} \leqslant 0, \qquad \overset{\cdot}{\overline{\int_{\mathscr{B}} \nu^{\mathfrak{a}}\, dv}} = 0 \tag{3.38}$$

while for a *dead-loaded*, *isochemical boundary*, we have the inequalities

$$\overset{\cdot}{\overline{\int_{\mathscr{B}} (\Psi - \mathbf{S}_0 \cdot \mathbf{E} - U^{\mathfrak{a}} \nu^{\mathfrak{a}})\, dv + \int_{\mathscr{S}(t)} \psi\, da}} \leqslant 0 \tag{3.39}$$

and

$$\overset{\bullet}{\overline{\int_{\mathscr{B}} (\omega - \mathbf{S}_0 \cdot \mathbf{E} + (\mu^{\mathfrak{a}} - U^{\mathfrak{a}})\, \nu^{\mathfrak{a}})\, dv + \int_{\mathscr{S}(t)} \psi \, da}} \leqslant 0 \tag{3.40}$$

The results (3.38) and (3.39) (or its equivalent (3.40)) follow from the atomic balance (3.20) and the energy imbalance (3.26) with $\mathscr{P} = \mathscr{B}$, so that $\mathscr{A} = \mathscr{S}$ and $\partial\mathscr{A} = \varnothing$.

3.4. Constitutive Theory. Basic Equations

3.4.1. Bulk Constitutive Equations.

For the phases $\gamma = \alpha$ and $\gamma = \beta$, we consider bulk constitutive equations of the type discussed in Section 2.5, in which chemical potentials serve as independent variables. In particular, using the superscript (γ) rather than a superposed circumflex to designate the associated response functions, we consider constitutive equations requiring that, in each phase γ:

$$\boldsymbol{\nu} = -\frac{\partial \omega^{(\gamma)}}{\partial \boldsymbol{\mu}}(\boldsymbol{\mu}, \mathbf{E}), \qquad \mathbf{S} = \frac{\partial \omega^{(\gamma)}}{\partial \mathbf{E}}(\boldsymbol{\mu}, \mathbf{E}), \qquad \mathbf{h}^{\mathfrak{a}} = -\mathbf{M}^{(\gamma)\,\mathfrak{ab}}(\boldsymbol{\mu}, \mathbf{E})\, \nabla \mu^{\mathfrak{b}} \tag{3.41}$$

The local form of the second law in bulk is the inequality (2.26), and its satisfaction is ensured by (3.41) and the requirement that, in each phase γ, the matrix of mobility tensors $\mathbf{M}^{(\gamma)\,\mathfrak{ab}}$ be positive definite.

3.4.2. Constitutive Equations for the Interface.

Regarding the interface, we consider constitutive equations giving ψ, $\mathbbm{c}$, and g when $\mathbbm{m}$, $V_{\mathscr{S}}$, $\boldsymbol{\mu}$, and $(\nabla \mathbf{u})^{\pm}$ are known. Let

$$\mathbbm{s} = [\![\nabla \mathbf{u}]\!]\, \mathbbm{m} \tag{3.42}$$

A consequence of the compatibility condition $[\![\nabla \mathbf{u}]\!]\, \mathbbm{P} = \mathbf{0}$ is that $[\![\nabla \mathbf{u}]\!] = [\![\nabla \mathbf{u}]\!]\, \mathbbm{m} \otimes \mathbbm{m}$; the limits $(\nabla \mathbf{u})^{\pm}$ are therefore determined by $\mathbbm{m}$, the average $\langle\!\langle \nabla \mathbf{u} \rangle\!\rangle$, and the jump $\mathbbm{s}$ through the identity $(\nabla \mathbf{u})^{\pm} = \langle\!\langle \nabla \mathbf{u} \rangle\!\rangle \pm \frac{1}{2} \mathbbm{s} \otimes \mathbbm{m}$. We therefore consider smooth constitutive equations of the form

$$(\psi, \mathbbm{c}, g) = \hat{f}(\mathbbm{m}, \boldsymbol{\mu}, \langle\!\langle \nabla \mathbf{u} \rangle\!\rangle, \mathbbm{s}) \tag{3.43}$$

with $\hat{\psi}$, $\hat{\mathbbm{c}}$, and $\hat{g}$ the individual response functions. Then, arguing as in the paragraph concluding with (2.41), since the response must be invariant under superposed (infinitesimal) rigid displacements, (3.43) must be invariant under transformations $(\nabla \mathbf{u})^{\pm} \mapsto (\nabla \mathbf{u})^{\pm} + \mathbb{W}_0$, with $\mathbb{W}_0$ a skew tensor. Under this transformation, $\langle\!\langle \nabla\mathbf{u} \rangle\!\rangle \mapsto \langle\!\langle \nabla\mathbf{u} \rangle\!\rangle + \mathbb{W}_0$, but $\mathbb{s} \mapsto \mathbb{s}$; thus $\langle\!\langle \nabla\mathbf{u} \rangle\!\rangle$ in (3.43) may be replaced by the average strain $\langle\!\langle \mathbf{E} \rangle\!\rangle$:

$$(\psi, \mathbb{c}, g) = \hat{f}(\mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s}) \tag{3.44}$$

Consider an arbitrary constitutive process; that is, an evolution $\mathscr{S}(t)$ of the interface together with: (i) a motion $\mathbf{u}(\mathbf{x}, t)$ and a list $\boldsymbol{\mu}(\mathbf{x}, t)$ of chemical potentials defined on $\mathscr{B}$ for all t and related to $\mathscr{S}$ through the compatibility conditions (3.12); (ii) bulk fields ω, $\mathbf{v}$, $\mathbf{S}$ (and hence Ψ and $\mathbf{C}$) determined by the constitutive equations (3.41); and (iii) interfacial fields $\sigma = \psi$, $\mathbb{c}$ (and hence $\mathbb{C}$), and g determined by (3.44). Given such a constitutive process, the atomic balances (2.4) and (3.20) can be satisfied using the bulk supply h^{α} and the interfacial supply $\mathsf{h}^{\alpha}_{\mathscr{S}}$; the standard and configurational force balances $(2.12)_1$, (2.70), $(3.23)_1$, and (3.31) (subject to the invariance requirement (3.27)) can be satisfied using the bulk body forces $\mathbf{b}$ and $\mathbf{f}$, and the interfacial forces $\mathbb{b}$, $\mathbb{e}$, and $\mathbb{P}\mathbb{g}$. All of the above are arbitrarily assignable, since h^{α}, $\mathsf{h}^{\alpha}_{\mathscr{S}}$, $\mathbf{b}$, $\mathbb{b}$, and $\mathbb{e}$ are external, while $\mathbf{f}$ and $\mathbb{P}\mathbb{g}$ are indeterminate.

As before, to ensure compatibility of all constitutive processes with the second law, we require that all constitutive processes be consistent with the dissipation inequality (3.37). (The local form of the second law in bulk is (2.26), and its satisfaction is ensured by (3.41).) Letting $\mathbf{z} = (\mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s})$, this requirement yields

$$\left(\frac{\partial\hat{\psi}}{\partial\mathbb{m}}(\mathbf{z}) + \hat{\mathbb{c}}(\mathbf{z})\right) \cdot \overset{\triangle}{\mathbb{m}} + \left(\frac{\partial\hat{\psi}}{\partial\boldsymbol{\mu}}(\mathbf{z})\right) \cdot \overset{\triangle}{\boldsymbol{\mu}} + \left(\frac{\partial\hat{\psi}}{\partial\langle\!\langle \mathbf{E} \rangle\!\rangle}(\mathbf{z})\right) \cdot \overline{\overset{\triangle}{\langle\!\langle \mathbf{E} \rangle\!\rangle}}$$
$$+ \left(\frac{\partial\hat{\psi}}{\partial\mathbb{s}}(\mathbf{z})\right) \cdot \overset{\triangle}{\mathbb{s}} + \hat{g}(\mathbf{z})\, V_{\mathscr{S}} \leqslant 0 \tag{3.45}$$

One can always find an evolution of the interface together with a motion and chemical potentials (consistent with (3.12)) such that $\mathbb{m}$, $\boldsymbol{\mu}$, $\langle\!\langle \mathbf{E} \rangle\!\rangle$, $\mathbb{s}$, $V_{\mathscr{S}}$, $\overset{\triangle}{\mathbb{m}}$, $\overset{\triangle}{\boldsymbol{\mu}}$, $\overline{\overset{\triangle}{\langle\!\langle \mathbf{E} \rangle\!\rangle}}$, and $\overset{\triangle}{\mathbb{s}}$ have arbitrary values at some given point and time. Thus, since the left side of (3.45) is linear in V, $\overset{\triangle}{\mathbb{m}}$, $\overset{\triangle}{\boldsymbol{\mu}}$, $\overline{\overset{\triangle}{\langle\!\langle \mathbf{E} \rangle\!\rangle}}$, and $\overset{\triangle}{\mathbb{s}}$, the coefficients of these fields must vanish; thus $\partial\hat{\psi}/\partial\langle\!\langle \mathbf{E} \rangle\!\rangle$, $\partial\hat{\psi}/\partial\boldsymbol{\mu}$, $\partial\hat{\psi}/\partial\mathbb{s}$, and g must vanish, while $\hat{\mathbb{c}} = -\partial\hat{\psi}/\partial\mathbb{m}$.

We are therefore led to the following constitutive restrictions:

(i) the energy density and shear can depend at most on $\mathbb{m}$, with

$$\hat{\mathbb{c}}(\mathbb{m}) = -\frac{\partial\hat{\psi}}{\partial\mathbb{m}}(\mathbb{m}) \tag{3.46}$$

with $\partial/\partial\mathbb{m}$ the derivative on the unit sphere.

(*ii*) the normal internal force must vanish identically

$$g = 0 \tag{3.47}$$

Constitutive equations compatible with these restrictions are the most general relations of the form (3.44) that are consistent with the dissipation inequality (3.37).

The quantity $-(\psi + \mathbb{c} \cdot \overset{\triangle}{\mathbb{m}} + gV_{\mathscr{S}})$ represents the energy dissipated, per unit area, by propagation of the interface. Because of (3.45) and (3.46), the *interface is dissipationless*, although there is dissipation in bulk resulting from atomic diffusion.

3.4.3. Basic Equations. If we neglect the external forces $\mathbf{b}$, $\mathbb{b}$, and $\mathbb{e}$ and the atomic supplies $\mathsf{h}^{\mathfrak{a}}$ and $\mathsf{h}^{\mathfrak{a}}_{\mathscr{S}}$, then the basic equations for the bulk material are the standard balances

$$\dot{\nu}^{\mathfrak{a}} = -\operatorname{div} \mathbf{h}^{\mathfrak{a}}, \qquad \operatorname{div} \mathbf{S} = \mathbf{0} \tag{3.48}$$

supplemented by the constitutive equations (3.41) while the basic equations for the interface are the conditions of compatibility and local equilibrium (3.12) and (3.13), the atomic balance and the standard force balance

$$V_{\mathscr{S}} [\![\nu^{\mathfrak{a}}]\!] = [\![\mathbf{h}^{\mathfrak{a}}]\!] \cdot \mathbb{m}, \qquad [\![\mathbf{S}]\!] \, \mathbb{m} = \mathbf{0} \tag{3.49}$$

and the normal configurational force balance

$$[\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + \psi K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbb{c} = 0 \tag{3.50}$$

where we have employed the Eshelby relation $\mathbf{C} = \omega \mathbf{1} - (\nabla \mathbf{u})^{\top} \mathbf{S}$ together with the identity $\mathbb{m} \cdot [\![(\nabla \mathbf{u})^{\top} \mathbf{S} \mathbb{m}]\!] = [\![(\mathbf{S}\mathbb{m}) \cdot ((\nabla \mathbf{u})\, \mathbb{m})]\!] = [\![\mathbf{S} \cdot \mathbf{E}]\!]$, which follows from $(3.13)_2$, $(3.49)_2$, and the symmetry of $\mathbf{S}$. By (3.5) and (3.46), the second and third terms on the left-hand side of (3.50) can be written as $\psi K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbb{c} = (\hat{\psi}(\mathbb{m})\, \mathbf{1} + \partial^2 \hat{\psi}(\mathbb{m}) / \partial \mathbb{m}^2) \cdot \mathbb{L}$.

If the interfacial energy density is isotropic—that is, if ψ is constant—(3.50) reduces to the balance

$$[\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + \psi K_{\mathscr{S}} = 0 \tag{3.51}$$

in which interfacial structure is reflected solely through the "capillarity" term $\psi K_{\mathscr{S}}$. Relations of the form (3.50) and (3.51) (as well as (3.56) and (3.59) given below) may be referred to as "generalized Gibbs–Thomson relations."

3.5. Generalization of the Theory to Include Dissipation at the Interface

It would seem reasonable to expect that the exchange of atoms at the interface would lead to dissipation. To accomodate this we allow for a constitutive dependence on the kinetics of the interface through a dependence on $\mathscr{V}_{\mathscr{S}}$ in the interfacial constitutive equations; specifically, we replace, (3.44) by

$$(\psi, \mathbb{c}, g) = \hat{f}(V_{\mathscr{S}}, \mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s}) \tag{3.52}$$

The argument used to derive (3.46) and (3.47) then yields the constitutive restrictions (3.46), but (3.47) is replaced by the requirement that the normal internal force obey the inequality

$$\hat{g}(V_{\mathscr{S}}, \mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s})\, V_{\mathscr{S}} \leqslant 0 \tag{3.53}$$

If the constitutive relation $g = \hat{g}(V_{\mathscr{S}}, \mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s})$ is linear in $V_{\mathscr{S}}$, then consistency with (3.53) requires that this relation have the form

$$g = -b(\mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s})\, V_{\mathscr{S}} \tag{3.54}$$

with $b(\mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s}) \geqslant 0$, the **kinetic modulus**, a constitutive quantity. In this case the interfacial motion is generally dissipative, with dissipation $gV_{\mathscr{S}} = -bV_{\mathscr{S}}^2$, per unit area.

Granted (3.46) and (3.54), the **normal configurational balance** has the form[16]

$$[\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + \psi K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbb{c} = bV_{\mathscr{S}} \tag{3.55}$$

with $b = b(\mathbb{m}, \boldsymbol{\mu}, \langle\!\langle \mathbf{E} \rangle\!\rangle, \mathbb{s})$, which reduces to

$$[\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + \psi K_{\mathscr{S}} = bV_{\mathscr{S}} \tag{3.56}$$

(with b independent of $\mathbb{m}$) when the interfacial energy density and the kinetic modulus are isotropic.

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[16] Gurtin and Struthers (1990) and Gurtin (1993b, 1995) (finite strain), Gurtin and Voorhees (1993) (infinitesimal strain). The specialization of (3.55) to statics was derived by Leo and Sekerka (1989) as an Euler–Lagrange equation for stable equilibria (cf. Alexander and Johnson 1985; Johnson and Alexander 1986; and Fonseca 1989). The analog of (3.55) appropriate to situations involving finite strain but ignoring both atomic diffusion and interfacial energy was derived by Heidug and Lehner (1985), Truskinovsky (1987, 1991), and Abeyaratne and Knowles (1990). An historical discussion of the continuum-mechanical characterization of propagating phase interfaces is given by Fried (1998).

3.6. Special Theories

One is often interested in theories appropriate to behavior near a given list $\boldsymbol{\mu}_0$ of chemical potentials. One method of generating such theories is to formally approximate the general equations under the assumption that the potential differences $\mu^{a} - \mu_0^{a}$ are small. A problem with this procedure is that the resulting approximate equations will generally not lead to conservation laws and Lyapunov functions, chiefly because the underlying thermodynamic structure is lost in the approximation. A procedure that ensures a consistent thermodynamic structure begins with bulk Gibbs functions (of a desired degree of approximation) and uses the thermodynamic relations (3.41) to define the atomic densities and stresses (cf. Gurtin 1986; Davì and Gurtin 1990).

As an example of this procedure, consider behavior in which the interface moves slowly compared to the time scale for diffusion. Restricting attention to a single mobile atomic species and assuming, without loss of generality, that $\mu_0 = 0$, such an approximation is generated as an exact theory within our framework by restricting the Gibbs function of each phase $\gamma = \alpha, \beta$ to be linear in μ (cf. Section 2.6.2), with no terms involving products of μ and $\mathbf{E}$,[17]

$$\omega^{(\gamma)}(\mu, \mathbf{E}) = -v_\gamma \mu + W^{(\gamma)}(\mathbf{E}), \qquad v_\gamma = \text{constant} \tag{3.57}$$

Then, by (3.41), $v = v_\gamma$ in each phase, so that $\dot{v} = 0$ in bulk. The basic equations are then the bulk relations

$$\operatorname{div} \mathbf{h}^{a} = 0, \qquad \operatorname{div} \mathbf{S} = \mathbf{0} \tag{3.58}$$

supplemented by the interface conditions

$$V_{\mathcal{S}} \llbracket v \rrbracket = \llbracket \mathbf{h} \rrbracket \cdot \mathbb{m}, \quad \llbracket \mathbf{S} \rrbracket \, \mathbb{m} = \mathbf{0}, \quad \llbracket v \rrbracket \, \mu = \llbracket W - \mathbf{S} \cdot \mathbf{E} \rrbracket + \psi K_{\mathcal{S}} + \operatorname{div}_{\mathcal{S}} \mathbb{c} - bV \tag{3.59}$$

Here $\llbracket v \rrbracket$ is the constant $v_\beta - v_\alpha$, $\llbracket W \rrbracket$ is the interfacial difference between $W^{(\beta)}(\mathbf{E})$ and $W^{(\alpha)}(\mathbf{E})$, and $b = 0$ in the theory of Section 3.4 but not in that of Section 3.5.

Consistent with the assumption of infinitesimal strains, one might also restrict attention to linear stress-strain relations as generated by the quadratic strain energy densities

$$W^{(\gamma)}(\mathbf{E}) = \tfrac{1}{2}(\mathbf{E} - \mathbf{E}_\gamma) \cdot \mathscr{C}^{(\gamma)}(\mathbf{E} - \mathbf{E}_\gamma) \tag{3.60}$$

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[17] Cf. Gurtin and Voorhees (1993). For computational results based on this theory see Thompson, Su and Voorhees (1994), Su and Voorhees (1996), and Thompson and Voorhees (1996).

where $\mathscr{C}^{(\gamma)}$, a *symmetric positive-definite linear transformation* from symmetric tensors into symmetric tensors, is the *elasticity tensor* of phase γ, while $\mathbf{E}_\gamma$, a constant symmetric tensor, is the stress-free strain in γ. Then, granted constant bulk mobilities $\mathbf{M}^{(\gamma)}$, the bulk constitutive equations take the form

$$\mathbf{h} = -\mathbf{M}^{(\gamma)}\,\nabla\mu, \qquad \mathbf{S} = \mathscr{C}^{(\gamma)}(\mathbf{E} - \mathbf{E}_\gamma) \tag{3.61}$$

which, with (3.59), result in linear partial differential equations in bulk.

4. COHERENT PHASE TRANSITIONS WITH INTERFACIAL LAYERS

We turn now to a theory of phase transitions in which the material is described by a single nonconvex energy density and for which the interface between phases is not a sharp surface but, instead is an interfacial layer across which the physical fields vary smoothly. As such, the theory results solely in partial differential equations; there are no free boundaries and hence no interface conditions.

As before, we consider $\mathfrak{A}$ unconstrained atomic species consistent with the atomic balance (2.4), and we allow for deformation of the body as described by a displacement field $\mathbf{u}$ and corresponding stress $\mathbf{S}$ and body force $\mathbf{b}$ consistent with the standard balances (2.12).

4.1. Microforces. Microforce Balance. Second Law

In the theory discussed thus far the microscopic state at each material point is described by the atomic densities ν^α, the atomic fluxes $\mathbf{h}^\alpha$, and the chemical potentials μ^α. But while the chemical potentials allow for an accounting of the energy transported as atoms migrate relative to the underlying lattice, there is no accounting for a corresponding expenditure of power. To rectify this, we modify the basic framework to include microforces whose working accompanies atomic diffusion. Indeed, if temporal variations in the densities ν^α are the macroscopic manifestation of atomistic kinematics, then it seems reasonable that interatomic forces be characterized macroscopically by fields that perform work when the ν^α undergo change.[18] Here it is important to focus attention not on individual atoms but on arrangements of atoms as represented by the densities.

[18] Our approach (Fried and Gurtin 1993, 1994; Fried 1996; Gurtin 1996) is based on the belief that laws involving energy should account for the working associated with each operative kinematical process. The present discussion of the Cahn–Hilliard theory is taken from Gurtin (1996). Investigations of microstructural evolution use the Cahn–Hilliard approach include Larché and Cahn (1992), Leo, Lowengrub and Jou (1998), Miyazaki, Kozakai and Mizuno (1983), Nishimori and Onuki (1990, 1991), Onuki (1989a, 1989b), Wang, Chen and Khachaturyan (1993), and Wang and Khachaturyan (1995).

Precisely, we introduce "microforces" whose working accompanies changes in the atomic densities. We describe this working through terms of the form (*force*) $\dot{v}^\alpha$, so that microforces are scalar rather than vector quantities. Specifically, the microforce system is characterized by (vector) **microstresses** $\boldsymbol{\xi}^\alpha$ together with (scalar) **body microforces** π^α and γ^α that represent, respectively, **internal** and **external** forces distributed over the volume of $\mathscr{B}$. What is most important, this system of forces is presumed consistent with the **microforce balance**

$$\int_{\partial\mathscr{P}} \boldsymbol{\xi}^\alpha \cdot \mathbf{n}\, da + \int_{\mathscr{P}} (\pi^\alpha + \gamma^\alpha)\, dv = 0 \tag{4.1}$$

for each control volume $\mathscr{P}$, or equivalently

$$\operatorname{div} \boldsymbol{\xi}^\alpha + \pi^\alpha + \gamma^\alpha = 0 \tag{4.2}$$

The following arguments, for a single atomic species, might serve as partial motivation for the microforce balance.

1. At equilibrium, if the total energy has the form $\mathscr{E}(v) = \int_{\mathscr{B}} \hat{\Psi}(v, \nabla v)\, dv$ then, for $\mathbf{p} = \nabla v$, the requirement $\delta\mathscr{E}(v)/\delta v = 0$ for all variations δv that vanish on $\partial\mathscr{B}$ yields the Euler–Lagrange equation $\operatorname{div} \boldsymbol{\xi} + \pi = 0$ with $\boldsymbol{\xi} = \partial\hat{\Psi}(v, \mathbf{p})/\partial\mathbf{p}$, $\pi = -\partial\hat{\Psi}(v, \mathbf{p})/\partial v$. This represents a statical version of the microforce balance (4.2) with $\boldsymbol{\xi}$ and π given constitutive representations and $\gamma = 0$. In dynamics with general forms of dissipation there is no such variational principle; the use of a microforce balance is an attempt to extend to dynamics an essential feature of statical theories.
2. Standard forces in continua are associated with macroscopic length scales, while microforces describe forces associated with microscopic configurations of atoms. The need for a separate microforce balance seems a necessary consequence of the disparite length scales.

The **energy imbalance** for an arbitrary part $\mathscr{P}$ consists of (2.23) with $\mathscr{W}(\mathscr{P})$ modified from the form given in (2.13) to account for the working of the microforces:

$$\begin{aligned} \overset{\cdot}{\overline{\int_{\mathscr{P}} \Psi\, dv}} \leqslant{} & \int_{\partial\mathscr{P}} \mathbf{S}\mathbf{n} \cdot \dot{\mathbf{u}}\, da + \int_{\mathscr{P}} \mathbf{b} \cdot \dot{\mathbf{u}}\, dv - \int_{\partial\mathscr{P}} \mu^\alpha \mathbf{h}^\alpha \cdot \mathbf{n}\, da \\ & + \int_{\mathscr{P}} \mu^\alpha \mathsf{h}^\alpha\, dv + \int_{\partial\mathscr{P}} (\boldsymbol{\xi} \cdot \mathbf{n})\, \dot{v}^\alpha\, da + \int_{\mathscr{P}} \gamma^\alpha \dot{v}^\alpha\, dv \end{aligned} \tag{4.3}$$

This imbalance is for the material—lattice plus atoms—and therefore does not include the working of the $\pi^{\mathfrak{a}}$, which being forces exerted by the lattice on the atoms, act internally to the material in $\mathscr{P}$; on the other hand, (4.2) represents a force balance for atomic arrangements and therefore includes the action of the $\pi^{\mathfrak{a}}$. Using the microforce balance and the identity (2.14), we arrive at the **dissipation inequality**

$$\dot{\Psi} - \mathbf{S}\cdot\dot{\mathbf{E}} + \mathbf{h}^{\mathfrak{a}}\cdot\nabla\mu^{\mathfrak{a}} + (\pi^{\mathfrak{a}} - \mu^{\mathfrak{a}})\,\dot{\nu}^{\mathfrak{a}} - \boldsymbol{\xi}^{\mathfrak{a}}\cdot\nabla\dot{\nu}^{\mathfrak{a}} \leqslant 0 \tag{4.4}$$

By (2.4) and (4.3), the Lyupunov relations (2.29), (2.31), and (3.23) are (granted their underlying assumptions) valid without change provided that $\omega = \Psi - \mu^{\mathfrak{a}}\nu^{\mathfrak{a}}$ and provided that, for each species $\mathfrak{a}$, $\gamma^{\mathfrak{a}} = 0$ on $\mathscr{B}$ and $(\boldsymbol{\xi}^{\mathfrak{a}}\cdot\mathbf{n})\,\dot{\nu}^{\mathfrak{a}} = 0$ (no sum on $\mathfrak{a}$) on $\partial\mathscr{B}$.

4.2. Constitutive Theory. Basic Equations

4.2.1. Constitutive Equations.

In the classical theory without microforces the chemical potentials are given, constitutively, as functions of densities and strain, but here we wish to consider systems sufficiently far from equilibrium that a relation of this type is no longer valid; instead we allow the chemical potentials and their gradients to join the densities and density gradients in the list of independent constitutive variables. Therefore, allowing also for constitutive descriptions of $\boldsymbol{\xi} = (\boldsymbol{\xi}^1, \boldsymbol{\xi}^2,\dots, \boldsymbol{\xi}^{\mathfrak{A}})$ and $\pi = (\pi^1, \pi^2,\dots, \pi^{\mathfrak{A}})$, we consider **constitutive equations** of the form

$$(\Psi, \mathbf{h}, \mathbf{S}, \boldsymbol{\xi}, \boldsymbol{\pi}) = \hat{F}(\boldsymbol{\nu}, \nabla\boldsymbol{\nu}, \boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}) \tag{4.5}$$

with $\hat{\Psi}$, $\hat{\mathbf{h}}$, $\hat{\mathbf{S}}$, $\hat{\boldsymbol{\xi}}$, and $\hat{\boldsymbol{\pi}}$ the individual response functions.

Given fields $\boldsymbol{\nu}$, $\boldsymbol{\mu}$, and $\mathbf{u}$, (4.5) may be used to compute the fields Ψ, $\mathbf{h}$, $\mathbf{S}$, $\boldsymbol{\xi}$, and $\boldsymbol{\pi}$; the balance laws (2.4), $(2.12)_1$, and (4.2) then determine the external fields $\mathsf{h}^{\mathfrak{a}}$, $\mathbf{b}$, and $\boldsymbol{\gamma}$ needed to support this constitutive process. As before, we require that the dissipation inequality (4.4) be satisfied in all such processes. Writing $\mathbf{p}^{\mathfrak{a}} = \nabla\nu^{\mathfrak{a}}$, $\mathbf{s}^{\mathfrak{a}} = \nabla\mu^{\mathfrak{a}}$, and $\mathbf{z} = (\boldsymbol{\nu}, \nabla\boldsymbol{\nu}, \boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E})$, this is equivalent to the requirement that the inequality

$$\begin{aligned}\left(\frac{\partial\hat{\Psi}}{\partial\nu^{\mathfrak{a}}}(\mathbf{z}) + \hat{\pi}^{\mathfrak{a}}(\mathbf{z}) - \mu^{\mathfrak{a}}\right)\dot{\nu}^{\mathfrak{a}} + \left(\frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{z}) - \boldsymbol{\xi}^{\mathfrak{a}}(\mathbf{z})\right)\cdot\dot{\mathbf{p}}^{\mathfrak{a}} + \left(\frac{\partial\hat{\Psi}}{\partial\mu^{\mathfrak{a}}}(\mathbf{z})\right)\cdot\dot{\mu}^{\mathfrak{a}}\\ + \left(\frac{\partial\hat{\Psi}}{\partial\mathbf{s}^{\mathfrak{a}}}(\mathbf{z})\right)\cdot\dot{\mathbf{s}}^{\mathfrak{a}} + \left(\frac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\mathbf{z}) - \hat{\mathbf{S}}(\mathbf{z})\right)\cdot\dot{\mathbf{E}} + \hat{\mathbf{h}}^{\mathfrak{a}}(\mathbf{z})\cdot\nabla\mu^{\mathfrak{a}} \leqslant 0\end{aligned} \tag{4.6}$$

hold for all fields $\boldsymbol{\nu}$, $\boldsymbol{\mu}$, and $\mathbf{u}$, and, arguing as before, we are led to the following constitutive restrictions:

(*i*) *the energy, the standard stress, and the microstress must be independent of the chemical potentials and their gradients, the internal microforce must be independent of the chemical potential gradients, and*

$$\left.\begin{aligned}\hat{\mathbf{S}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) &= \frac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) \\ \hat{\boldsymbol{\xi}}^{\mathfrak{a}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) &= \frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) \\ \hat{\pi}^{\mathfrak{a}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) &= \mu^{\mathfrak{a}} - \frac{\partial\hat{\Psi}}{\partial v^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\end{aligned}\right\} \tag{4.7}$$

(*ii*) *the constitutive equation for* **h** *must be consistent with the* **residual inequality**

$$\hat{\mathbf{h}}^{\mathfrak{a}}(\mathbf{v}, \nabla\mathbf{v}, \boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}) \cdot \nabla\mu^{\mathfrak{a}} \leqslant 0 \tag{4.8}$$

Combining (4.7) and the force balance (4.2), and assuming that $\boldsymbol{\gamma}$ vanishes, yields

$$\mu^{\mathfrak{a}} = \frac{\partial\hat{\Psi}}{\partial v^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) - \operatorname{div}\left(\frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\right) \tag{4.9}$$

an expression for the chemical potential that reduces to the classical relation $\mu^{\mathfrak{a}} = \partial\hat{\Psi}/\partial v^{\mathfrak{a}}$ when the energy is independent of density gradients and, more generally, reduces to Cahn's relation giving *the chemical potentials as variational derivatives of the total free energy* $\mathscr{E}(\mathbf{v}, \mathbf{u}) = \int_{\mathscr{B}} \hat{\Psi}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\, dv$ with respect to the densities:

$$\mu^{\mathfrak{a}} = \frac{\delta\mathscr{E}}{\delta v^{\mathfrak{a}}}(\mathbf{v}, \mathbf{u}) \tag{4.10}$$

We henceforth restrict attention to Fick's law in the form

$$\mathbf{h}^{\mathfrak{a}} = -\mathbf{M}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v})\, \nabla\mu^{\mathfrak{b}} \tag{4.11}$$

with the *matrix of mobility tensors* $\mathbf{M}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v})$ positive semi-definite.

4.2.2. Partial Differential Equations.

Assume that the external fields vanish: $\mathsf{h}^{\mathfrak{a}} = 0$, $\mathbf{b} = \mathbf{0}$, $\boldsymbol{\gamma} = \mathbf{0}$. Then, restricting attention to Fick's law (4.11), and combining the reduced constitutive relations with the mass and force balances leads to the general system

$$\left.\begin{array}{ll} \dot{\nu}^{\mathfrak{a}} = -\operatorname{div}\mathbf{h}^{\mathfrak{a}}, & \left\{\begin{array}{l}\mathbf{h}^{\mathfrak{a}} = -\mathsf{M}^{\mathfrak{ab}}(\boldsymbol{\nu},\mathbf{E})\,\nabla\mu^{\mathfrak{b}}\\[4pt] \mu^{\mathfrak{a}} = \dfrac{\partial\hat{\Psi}}{\partial\nu^{\mathfrak{a}}}(\boldsymbol{\nu},\nabla\boldsymbol{\nu},\mathbf{E}) - \operatorname{div}\left(\dfrac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\boldsymbol{\nu},\nabla\boldsymbol{\nu},\mathbf{E})\right)\end{array}\right. \\[16pt] \operatorname{div}\mathbf{S} = \mathbf{0}, & \mathbf{S} = \dfrac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\boldsymbol{\nu},\nabla\boldsymbol{\nu},\mathbf{E})\end{array}\right\} \tag{4.12}$$

with the strain $\mathbf{E}$ as given in (2.8).

4.2.3. Theory for Phase Transitions Involving a Single Mobile Species. We now restrict attention to a single mobile species, and, as is customary, refer to its atomic density ν as the *composition.* To describe phase transitions, we consider energy densities of the simple form

$$\Psi = \hat{\Psi}(\nu, \nabla\nu, \mathbf{E}) = f(\nu) + \frac{1}{2}\lambda(\mathbf{m})\,|\nabla\nu|^2 + W(\nu, \mathbf{E}), \qquad \mathbf{m} = \frac{\nabla\nu}{|\nabla\nu|} \tag{4.13}$$

with $\lambda(\mathbf{m})$ strictly positive, viz.

$$\lambda(\mathbf{m}) > 0 \tag{4.14}$$

The function $f(\nu)$ represents the dependence of the energy on composition when the composition gradients and strains vanish. We assume that $f(\nu)$ is a double-well potential that defines the phases. More precisely we assume that $f(\nu) \to +\infty$ as $\nu \to 0$ and as $\nu \to 1$, and that $f(\nu)$ may be convexified by a single line segment between unique compositions ν_α and ν_β, $0 < \nu_\alpha < \nu_\beta < 1$, so that

$$\mu_m(\nu_\beta - \nu_\alpha) = f(\nu_\beta) - f(\nu_\alpha), \qquad \mu_m = f'(\nu_\beta) = f'(\nu_\alpha) \tag{4.15}$$

which is the "Maxwell equal-area rule."

In a body whose average composition lies between ν_α and ν_β, the double-well structure of $f(\nu)$ makes compositional distributions consisting of regions with $\nu = \nu_\alpha$ and regions with $\nu = \nu_\beta$ energetically favorable. The *gradient energy density* $\frac{1}{2}\lambda(\mathbf{m})\,|\nabla\nu|^2$ penalizes sharp transitions between such regions and in so doing facilitates the existence of equilibria in which ν is smooth and $\mathscr{B}$ contains interfacial layers separating regions with ν close to ν_α from regions with ν close to ν_β. The dependence of the $\lambda(\mathbf{m})$ on $\mathbf{m}$ renders certain interfacial orientations energetically more favorable than others.

In accord with the assumption of infinitesimal deformations, we require that the strain energy density $W(\nu, \mathbf{E})$ be at most quadratic in $\mathbf{E}$, so that

$$W(\nu, \mathbf{E}) = \mathbf{E}\cdot\left(\tfrac{1}{2}\mathscr{C}(\nu)\,\mathbf{E} + \overline{\mathbf{S}}(\nu)\right) \tag{4.16}$$

but such an assumption is not relevant to what follows.

As consequences of (4.13) and (4.16),

$$\mu = f'(v) - \operatorname{div}\left(\lambda(\mathbf{m})\,\nabla v + \frac{1}{2}\,|\nabla v|\,\frac{\partial\lambda}{\partial\mathbf{m}}(\mathbf{m})\right) + U(v, \mathbf{E}) \tag{4.17}$$

where $\partial/\partial\mathbf{m}$ is the derivative on the unit sphere, while

$$U(v, \mathbf{E}) = \frac{\partial W}{\partial v}(v, \mathbf{E}) \tag{4.18}$$

and

$$\mathbf{S} = \frac{\partial W}{\partial \mathbf{E}}(v, \mathbf{E}) \tag{4.19}$$

For simplicity, we assume that the mobility is independent of $\mathbf{E}$, ∇v, and μ, so that

$$\mathbf{h} = -\mathbf{M}(v)\,\nabla\mu \tag{4.20}$$

The partial differential equations of the theory are then the balances

$$\dot{v} = -\operatorname{div}\mathbf{h}, \qquad \operatorname{div}\mathbf{S} = \mathbf{0} \tag{4.21}$$

augmented by (4.11) and (4.17)–(4.20).

If we define $\bar{f}(v) = f(v) - f'(v_\alpha)(v - v_\alpha)$, $\bar{\mu} = mu - \mu_m$, where μ_m is any constant, then $\mu - f'(v)$ is equal to $\bar{\mu} - \bar{f}'(v)$ plus the constant $\mu_m - f'(v_\alpha)$. Thus, since μ enters the partial differential equations through its gradient, we may, without loss in generality, replace $f(v)$ in (4.13) by $\bar{f}(v)$ and μ and $f'(v)$ in (4.17) by $\bar{\mu}$ and $f'(v)$, and this we shall do. Then, dropping the overbars, the only change we need make is to replace the Maxwell rule (4.15) by

$$f(v_\alpha) = f(v_\beta), \qquad f'(v_\alpha) = f'(v_\beta) = 0 \tag{4.22}$$

Note that, in view of the assumptions made in the paragraph containing (4.15), v_α and v_β form a strict minimum-pair for $f(v)$; i.e., $f(v) > f(v_\alpha) = f(v_\beta)$ for $v \neq v_\alpha, v_\beta$.

4.3. A More General Kinetics

In the theory discussed above atomic diffusion is the sole source of dissipation. We now sketch a generalization that allows for constitutive dependences on $\dot{v}$ and hence for a more general dissipative structure. Precisely, we replace (4.5) by constitutive equations of the form

$$(\Psi, \mathbf{h}, \mathbf{S}, \boldsymbol{\xi}, \boldsymbol{\pi}) = \hat{F}(\mathbf{v}, \nabla\mathbf{v}, \dot{\mathbf{v}}, \boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E}) \tag{4.23}$$

Compatibility with the dissipation inequality (4.4) then requires that the energy, standard stress, and microstress *be independent of atomic-density rates* and of the chemical potentials and their gradients, so that, as before,

$$\hat{\mathbf{S}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) = \frac{\partial\hat{\Psi}}{\partial\mathbf{E}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}), \qquad \boldsymbol{\xi}^{\mathfrak{a}} = \frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) \tag{4.24}$$

but now the constitutive equations for the internal microforce and atomic flux are more complicated. Specifically, introducing fields

$$\pi^{\mathfrak{a}}_{\text{dis}} = \pi^{\mathfrak{a}} + \frac{\partial\hat{\Psi}}{\partial v^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) - \mu^{\mathfrak{a}} \tag{4.25}$$

we find $\boldsymbol{\pi}_{\text{dis}}$ and $\mathbf{h}$, which, by (4.23), depend constitutively on $(\mathbf{v}, \nabla\mathbf{v}, \dot{\mathbf{v}}, \boldsymbol{\mu}, \nabla\boldsymbol{\mu}, \mathbf{E})$, must be consistent with the reduced dissipation inequality

$$\mathbf{h}^{\mathfrak{a}} \cdot \nabla\mu^{\mathfrak{a}} + \pi^{\mathfrak{a}}_{\text{dis}}\dot{v}^{\mathfrak{a}} \leqslant 0 \tag{4.26}$$

We assume that the constitutive equations for $\mathbf{h}$ and $\boldsymbol{\pi}_{\text{dis}} = (\pi^1_{\text{dis}}, \pi^2_{\text{dis}}, \ldots, \pi^{\mathfrak{A}}_{\text{dis}})$ are linear in $\dot{\mathbf{v}}$ and $\nabla\boldsymbol{\mu}$, and independent of $\boldsymbol{\mu}$:

$$\left.\begin{aligned} \mathbf{h}^{\mathfrak{a}} &= -\mathbf{M}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\,\nabla\mu^{\mathfrak{b}} - \mathbf{b}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\,\dot{v}^{\mathfrak{b}} \\ \pi^{\mathfrak{a}}_{\text{dis}} &= -\mathbf{a}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) \cdot \nabla\mu^{\mathfrak{b}} - B^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\,\dot{v}^{\mathfrak{b}} \end{aligned}\right\} \tag{4.27}$$

with overall coefficient matrix positive semi-definite. If we ignore coupling effects by setting the coefficients $\mathbf{b}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})$ and $\mathbf{a}^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})$ equal to zero, then, granted $\boldsymbol{\gamma} = \mathbf{0}$, the microforce balance (4.2) yields a relation,

$$\mu^{\mathfrak{a}} = \frac{\partial\hat{\Psi}}{\partial v^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E}) - \operatorname{div}\left(\frac{\partial\hat{\Psi}}{\partial\mathbf{p}^{\mathfrak{a}}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\right) + B^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\,\dot{v}^{\mathfrak{b}} \tag{4.28}$$

giving $\mu^{\mathfrak{a}}$ as the variational derivative $\delta\mathscr{E}/\delta v^{\mathfrak{a}}$ plus a term $B^{\mathfrak{ab}}(\mathbf{v}, \nabla\mathbf{v}, \mathbf{E})\,\dot{v}^{\mathfrak{b}}$ reflecting kinetics.

A simple extension involving a single mobile species that accounts for kinetics arises on taking (4.20) in conjunction with π_{dis} of the form

$$\pi_{\text{dis}} = |\nabla v|\; B(\mathbf{m})\; V \tag{4.29}$$

with $B(\mathbf{m}) \geqslant 0$, $\mathbf{m}$ as defined in $(4.13)_2$, and

$$V = -\frac{\dot{v}}{|\nabla v|} \tag{4.30}$$

4.4. Configurational Forces

The approach taken to configurational forces in Section 2.7 is readily adapted to the present context. On doing so, we arrive at a generalization

$$\mathbf{C} = \omega\mathbf{1} - (\nabla\mathbf{u})^{\top}\,\mathbf{S} - \nabla\nu^{\mathfrak{a}} \otimes \boldsymbol{\xi}^{\mathfrak{a}} \tag{4.31}$$

of the **Eshelby relation** (2.88). Using this expression for $\mathbf{C}$ in the configurational balance $\operatorname{div}\mathbf{C} + \mathbf{f} = \mathbf{0}$, we obtain a representation

$$\mathbf{f} = \mathbf{g} + \mathbf{e}, \qquad \begin{cases} \mathbf{g} = -\nabla\omega + \mathbf{S} : \nabla\nabla\mathbf{u} + (\nabla\nabla\nu^{\mathfrak{a}})\,\boldsymbol{\xi}^{\mathfrak{a}} - \pi^{\mathfrak{a}}\,\nabla\nu^{\mathfrak{a}} \\ \mathbf{e} = -(\nabla\mathbf{u})^{\top}\,\mathbf{b} - \gamma^{\mathfrak{a}}\,\nabla\nu^{\mathfrak{a}} \end{cases} \tag{4.32}$$

for the configurational force $\mathbf{f}$, which generalizes (2.89).

Further, granted the constitutive relations (4.24) and the definition (4.25), a direct calculation yields

$$\mathbf{g} = \nu^{\mathfrak{a}}\,\nabla\mu^{\mathfrak{a}} - \pi^{\mathfrak{a}}_{\mathrm{dis}}\,\nabla\nu^{\mathfrak{a}} \tag{4.33}$$

Consider a single mobile species, with Ψ and π_{dis} as specified in (4.13) and $(4.29)_2$, and restrict attention to a region where the gradient $\nabla\nu$ of the composition is nonvanishing. Since $\mathbf{m}$ is well-defined in such a region, we may compute the component of the configurational balance in its direction; doing so, we obtain the equation

$$\mathbf{m}\cdot(\operatorname{div}\mathbf{C}^{\mathrm{bu}} + \nu\,\nabla\mu) + \Psi^{\mathrm{xs}}K + \operatorname{div}\mathbf{c}^{\mathrm{xs}} + g + \operatorname{div}(\iota^{\mathrm{xs}}\mathbf{m}) = 0 \tag{4.34}$$

with $\mathbf{m}$ and V as defined in (4.13) and $(4.30)_3$, and

$$\left.\begin{aligned} \mathbf{C}^{\mathrm{bu}} &= (W(\nu,\mathbf{E}) - \mu\nu)\,\mathbf{1} - (\nabla\mathbf{u})^{\top}\frac{\partial W}{\partial\mathbf{E}}(\nu,\mathbf{E}) \\ \Psi^{\mathrm{xs}} &= f(\nu) + \frac{1}{2}\,\lambda(\mathbf{m})\,|\nabla\nu|^2 \\ \mathbf{c}^{\mathrm{xs}} &= -\frac{1}{2}\,|\nabla\nu|^2\,\frac{\partial\lambda}{\partial\mathbf{m}}(\mathbf{m}) \\ g^{\mathrm{xs}} &= -|\nabla\nu|^2\,B(\mathbf{m})\,V \\ \iota^{\mathrm{xs}} &= f(\nu) - \frac{1}{2}\,\lambda(\mathbf{m})\,|\nabla\nu|^2 \end{aligned}\right\} \tag{4.35}$$

and

$$K = -\operatorname{div}\mathbf{m} \tag{4.36}$$

Since, for level sets (surfaces) of v within the region in question, $\mathbf{m}$ and V define a unit normal field and a corresponding scalar normal velocity, a formal comparison of (4.34) with the normal configurational balance (3.55) suggests that, granted an appropriate scaling and averaging over the region, the terms $\mathbf{m}\cdot\operatorname{div}\mathbf{C}^{\mathrm{bu}}$, $\Psi^{\mathrm{xs}}K$, $\operatorname{div}\mathbf{c}^{\mathrm{xs}}$, and g^{xs} should correspond to $[\![\omega-\mathbf{S}\cdot\mathbf{E}]\!]$, $\psi K_{\mathscr{S}}$, $\operatorname{div}_{\mathscr{S}}\mathbb{c}$, and $-bV_{\mathscr{S}}$, respectively. This being the case, complete correspondence of (4.34) to (3.55) would require that the terms $\mathbf{m}\cdot(v\nabla\mu)$ and $\operatorname{div}(\iota^{\mathrm{xs}}\mathbf{m})$ be negligible when scaled and averaged appropriately over the region in question.

5. SHARP-INTERFACE LIMIT OF THE THEORY INVOLVING A SINGLE MOBILE SPECIES

We now examine the correspondence between the theory with nonsharp interfaces and the more standard sharp-interface theory,[19] restricting attention to the case of a single mobile species and leaving until the end any discussion of kinetic effects, as introduced in Section 4.3. In particular, we will show that the equations of the sharp-interface theory discussed in Section 3.6 may be considered as the formal asymptotic limit of the equations of Section 4.2.3, granted the additional assumption

$$U(v_\gamma,\mathbf{E})=0,\qquad \gamma=\alpha,\beta \tag{5.1}$$

5.1. Scaling

We let ς and $\varkappa$ denote scale factors associated with the constitutive functions W and λ. Then, letting L denote a characteristic length and T a characteristic time, we assume that ς and $\varkappa$ yield a small dimensionless modulus

$$0<\varepsilon=\frac{\varkappa}{\varsigma L^2}\ll 1 \tag{5.2}$$

and, labeling the dimensional (unscaled) fields with asterisks, introduce the dimensionless independent variables

$$\mathbf{x}=\frac{\mathbf{x}^*}{L},\qquad t=\frac{t^*}{T} \tag{5.3}$$

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[19] Similar results are derived by Leo, Lowengrub and Jou (1997). Our analysis, which was carried out independently of the work of Leo, Lowengrub and Jou, uses a scaling proposed by Fried and Vedantam (1994; unpublished) and is based on Pego's (1989) analysis of the Cahn–Hilliard equation; but, in contrast to Pego, we use the configurational balance (4.34) to derive the "generalized Gibbs–Thomson relation."

dependent variables

$$\left.\begin{aligned} \mathbf{u}_\varepsilon(\mathbf{x},t) = \frac{\mathbf{u}^*(\mathbf{x}^*,t^*)}{L}, \quad \mathbf{S}_\varepsilon(\mathbf{x},t) = \frac{\mathbf{S}^*(\mathbf{x}^*,t^*)}{\varsigma} \\ v_\varepsilon(\mathbf{x},t) = v^*(\mathbf{x}^*,t^*), \quad \mu_\varepsilon(\mathbf{x},t) = \frac{\mu^*(\mathbf{x}^*,t^*)}{\varsigma}, \quad \mathbf{h}_\varepsilon(\mathbf{x},t) = \frac{T\mathbf{h}^*(\mathbf{x}^*,t^*)}{L} \end{aligned}\right\} \tag{5.4}$$

and constitutive functions

$$\left.\begin{aligned} W(v_\varepsilon,\mathbf{E}_\varepsilon) = \frac{W^*(v^*,\mathbf{E}^*)}{\varsigma}, \quad U(v_\varepsilon,\mathbf{E}_\varepsilon) = \frac{U^*(v^*,\mathbf{E}^*)}{\varsigma}, \quad f(v_\varepsilon) = \frac{\varkappa f^*(v^*)}{\varsigma^2 L^2} \\ \lambda(\mathbf{m}_\varepsilon) = \frac{\lambda^*(\mathbf{m}^*)}{\varkappa}, \quad \mathbf{M}(v_\varepsilon) = \frac{L^2\varsigma\mathbf{M}^*(v^*)}{T} \end{aligned}\right\} \tag{5.5}$$

where the dependence of the fields on the parameter ε has been made explicit and the quantities without asterisks in (5.5) are assumed to be of $O(1)$ in ε.

With this scaling, the free energy density is given by

$$\Psi = \varepsilon^{-1} f(v_\varepsilon) + \tfrac{1}{2}\varepsilon\lambda(\mathbf{m}_\varepsilon)\,|\nabla v_\varepsilon|^2 + W(v_\varepsilon,\mathbf{E}_\varepsilon) \tag{5.6}$$

and the governing field equations are

$$\dot{v}_\varepsilon = -\operatorname{div}\mathbf{h}_\varepsilon, \qquad \operatorname{div}\mathbf{S}_\varepsilon = \mathbf{0} \tag{5.7}$$

with $\mathbf{h}_\varepsilon$ and $\mathbf{S}_\varepsilon$ as determined by

$$\left.\begin{aligned} &\mathbf{h}_\varepsilon = -\mathbf{M}(v_\varepsilon)\,\nabla\mu_\varepsilon \\ &\mu_\varepsilon = \varepsilon^{-1} f'(v_\varepsilon) - \varepsilon\operatorname{div}\left(\lambda(\mathbf{m}_\varepsilon)\,\nabla v_\varepsilon + \frac{1}{2}\,|\nabla v_\varepsilon|\,\frac{\partial\lambda}{\partial\mathbf{m}_\varepsilon}(\mathbf{m}_\varepsilon)\right) + U(v_\varepsilon,\mathbf{E}_\varepsilon) \\ &\mathbf{S}_\varepsilon = \frac{\partial W}{\partial\mathbf{E}}(v_\varepsilon,\mathbf{E}_\varepsilon) \end{aligned}\right\} \tag{5.8}$$

5.2. Constitutive Connections

We now show that the formal asymptotic limit, as $\varepsilon \to 0$, of the partial differential equations defined by (5.6) and (5.7) is the sharp interface theory of Section 3.6 with

$$\mathbf{M}^{(\gamma)} = \mathbf{M}(v_\gamma), \qquad W^{(\gamma)}(\mathbf{E}) = W(v_\gamma,\mathbf{E}) \tag{5.9}$$

for $\gamma = \alpha, \beta$, so that, in bulk,

$$\left.\begin{aligned} \omega = \omega^{(\gamma)}(\mu, \mathbf{E}) = -v_\gamma \mu + W^{(\gamma)}(\mathbf{E}), \qquad \mathbf{h} = -\mathbf{M}^{(\gamma)}\, \nabla\mu \\ \mathbf{S} = \mathbf{S}^{(\gamma)}(\mathbf{E}) = \frac{\partial W^{(\gamma)}}{\partial \mathbf{E}}\,(\mathbf{E}) \end{aligned}\right\} \tag{5.10}$$

Here it is tacit that the theory of Section 3.6 has been rendered dimensionless by an approach analogous to that taken in Section 5.1.

Regarding the interface, we assume that the response function $\hat{\psi}$ delivering the interfacial energy density in the sharp-interface theory is related to the gradient energy modulus λ through

$$\hat{\psi}(\mathbb{m}) = \sqrt{\lambda(\mathbb{m})} \int_{v_\alpha}^{v_\beta} \sqrt{2f(v)}\, dv \tag{5.11}$$

Given a particular choice of constitutive equations within the sharp-interface theory developed in Section 3, the analysis that we present in the sequel will show that the constitutive connections (5.9)–(5.11) imply that the partial differential equations of the theory at hand are formally asymptotic, in the limit as $\varepsilon \to 0$, to the bulk and interfacial partial differential equations of the sharp-interface theory. While we do not do so here, it can also be shown that these constitutive connections also imply consonance of the integral statements of balance of the two theories and of the local and global expressions for dissipation imbalance (cf. Fried and Gurtin 1996; Fried 1997; Fried and Grach 1997).

5.3. Expansions

Hereafter, we focus on a fixed portion $\mathscr{R}$ of $\mathscr{B}$ that, over some time interval, consists of three evolving subregions: $\mathscr{R}_\varepsilon^\alpha$, $\mathscr{S}_\varepsilon$, and $\mathscr{R}_\varepsilon^\beta$. At each time t, $\mathscr{S}_\varepsilon(t)$ is a transition layer comprised of points $\mathbf{x}$ in $\mathscr{B}$ with $v_\alpha < v_\varepsilon(\mathbf{x}, t) < v_\beta$, while $\mathscr{R}_\varepsilon^\alpha(t)$ and $\mathscr{R}_\varepsilon^\beta(t)$ consist of points $\mathbf{x}$ with $v_\varepsilon(\mathbf{x}, t) \approx v_\alpha$ and $v_\varepsilon(\mathbf{x}, t) \approx v_\beta$, respectively. We assume that the limit

$$\mathscr{S} = \lim_{\varepsilon \to 0+} \mathscr{S}_\varepsilon \tag{5.12}$$

exists, with $\mathscr{S}(t)$ a smoothly evolving surface and with

$$\mathscr{R} = \mathscr{R}^\alpha(t) \cup \mathscr{S}(t) \cup \mathscr{R}^\beta(t) \tag{5.13}$$

with $\mathscr{R}^\gamma(t) = \lim_{\varepsilon \to 0} \mathscr{R}_\varepsilon^\gamma(t)$ for $\gamma = \alpha, \beta$.

We insist that the chemical potential $\mu_\varepsilon(\mathbf{x}, t)$ and the motion $\mathbf{u}_\varepsilon(\mathbf{x}, t)$ have limits as $\varepsilon \to 0$,

$$\lim_{\varepsilon \to 0} \mu_\varepsilon(\mathbf{x}, t) = \mu(\mathbf{x}, t), \qquad \lim_{\varepsilon \to 0} \mathbf{u}_\varepsilon(\mathbf{x}, t) = \mathbf{u}(\mathbf{x}, t) \tag{5.14}$$

except possibly on $\mathscr{S}(t)$. Further, we require that the chemical potential μ_ε, its gradient $\nabla\mu_\varepsilon$, and the strain $\mathbf{E}_\varepsilon$ be bounded as $\varepsilon \to 0$.

Granted constitutive equations under which the atomic flux tends to infinity with the chemical-potential gradient and the stress with the strain, these hypotheses are actually consequences of the inner expansions for v_ε and $\mathbf{u}_\varepsilon$ in conjunction with with the balances (5.7) applied within the layer.

We write $d(\mathbf{x}, t)$ for the **signed distance** between a point $\mathbf{x}$ in $\mathscr{R}$ and the surface $\mathscr{S}(t)$, with $d(\mathbf{x}, t) < 0$ in $\mathscr{R}^\alpha_\varepsilon(t)$ and $d(\mathbf{x}, t) > 0$ in $\mathscr{R}^\beta_\varepsilon(t)$. Then

$$\mathbb{m}(\mathbf{x}, t) = \nabla d(\mathbf{x}, t) \qquad \text{and} \qquad V_{\mathscr{S}}(\mathbf{x}, t) = -\dot{d}(\mathbf{x}, t) \tag{5.15}$$

represent a unit normal-field and corresponding scalar normal-velocity-field for $\mathscr{S}(t)$. We also assume that $d(\mathbf{x}, t)$ is smooth within $\mathscr{S}_\varepsilon(t)$ and that given any $\mathbf{x}$ on $\mathscr{S}_\varepsilon(t)$, there is a unique $\mathbb{z}$ on $\mathscr{S}(t)$ with $\mathbb{z} = \mathbf{x} - d(\mathbf{x}, t)\, \mathbb{m}(\mathbf{x}, t)$. The mapping $\mathbf{x} \mapsto (d(\mathbf{x}, t), \mathbb{z}(\mathbf{x}, t))$ is then one-to-one on $\mathscr{S}_\varepsilon(t)$; further, $\mathbb{m}(\mathbf{x}, t)$ and $V_{\mathscr{S}}(\mathbf{x}, t)$ are well-defined and independent of $d(\mathbf{x}, t)$ at each $\mathbf{x}$ in $\mathscr{S}_\varepsilon(t)$: $\mathbb{m}(\mathbf{x}, t) = \mathbb{m}(\mathbb{z}, t)$, $V_{\mathscr{S}}(\mathbf{x}, t) = V_{\mathscr{S}}(\mathbb{z}, t)$. Thus, writing $\nabla_{\mathscr{S}}$ and $\mathrm{div}_{\mathscr{S}}$ for the surface gradient and surface divergence on $\mathscr{S}$, the curvature tensor $\mathbb{L}$ and the total curvature $K_{\mathscr{S}}$ for $\mathscr{S}$,

$$\mathbb{L} = -\nabla_{\mathscr{S}} \mathbb{m}, \qquad K_{\mathscr{S}} = \mathrm{tr}\, \mathbb{L} = -\mathrm{div}_{\mathscr{S}}\, \mathbb{m} \tag{5.16}$$

$\mathbb{L}(\mathbf{x}, t) = \mathbb{L}(\mathbb{z}, t)$, $K_{\mathscr{S}}(\mathbf{x}, t) = K_{\mathscr{S}}(\mathbb{z}, t)$.

Within $\mathscr{S}_\varepsilon(t)$, we stretch the coordinate normal to $\mathscr{S}(t)$ by letting

$$r(\mathbf{x}, t) = \varepsilon^{-1} d(\mathbf{x}, t) \tag{5.17}$$

and, in accord with this, we assume that the thickness $h_\varepsilon(t)$ of $\mathscr{S}_\varepsilon(t)$ tends to zero with ε, but at slightly slower rate, viz.

$$\lim_{\varepsilon \to 0} h_\varepsilon = 0, \qquad \lim_{\varepsilon \to 0} (\varepsilon^{-1} h_\varepsilon) = +\infty, \qquad \lim_{\varepsilon \to 0} (\varepsilon^{-1} h_\varepsilon^2) = 0 \tag{5.18}$$

For the fields $\eta_\varepsilon = \mathbf{u}_\varepsilon$ and $\eta_\varepsilon = v_\varepsilon$, we introduce an **outer expansion**

$$\eta_\varepsilon(\mathbf{x}, t) = \eta_0^{\mathrm{out}}(\mathbf{x}, t) + \varepsilon \eta_1^{\mathrm{out}}(\mathbf{x}, t) + O(\varepsilon^2) \tag{5.19}$$

assumed valid within the regions $\mathscr{R}^\alpha_\varepsilon$ and $\mathscr{R}^\beta_\varepsilon$, and an **inner expansion**

$$\eta_\varepsilon(\mathbf{x}, t) = \eta_0^{\mathrm{in}}(r(\mathbf{x}, t), \mathbb{z}(\mathbf{x}, t), t) + \varepsilon \eta_1^{\mathrm{in}}(r(\mathbf{x}, t), \mathbb{z}(\mathbf{x}, t), t) + O(\varepsilon^2) \tag{5.20}$$

assumed valid within the layer; here, $\eta_0^{\mathrm{out}}(\mathbf{x}, t)$, $\eta_1^{\mathrm{out}}(\mathbf{x}, t)$ and $\eta_0^{\mathrm{in}}(r, \mathbb{z}, t)$, $\eta_1^{\mathrm{in}}(r, \mathbb{z}, t)$ are smooth, bounded functions of their arguments. We further assume that these expansions are twice formally differentiable in their arguments in the sense that $\nabla\eta_\varepsilon = \nabla\eta_0^{\mathrm{out}} + \varepsilon\nabla\eta_1^{\mathrm{out}} + O(\varepsilon^2)$ for the outer expansion and, on letting $\acute{\eta}_\varepsilon$ denote the partial derivative of η_ε with respect to r, $\acute{\eta}_\varepsilon = \acute{\eta}_0^{\mathrm{in}} + \varepsilon\acute{\eta}_1^{\mathrm{in}} + O(\varepsilon^2)$ for the inner expansion, and so forth.

Hence, we do not presume that $\mathscr{S}_\varepsilon(t)$ is disjoint from $\mathscr{R}_\varepsilon^\gamma(t)$: the regions $\mathscr{S}_\varepsilon(t) \cap (\mathscr{R}_\varepsilon^\alpha(t) \cup \mathscr{R}_\varepsilon^\beta(t))$ of overlap represent sets where the outer and inner expansions agree. In particular, we have the matching condition

$$(\eta_0^{\mathrm{out}})^\pm (\mathbf{x}, t) = \lim_{d(\mathbf{x}, t) \to 0\pm} \eta_0^{\mathrm{out}}(\mathbf{x}, t) = \lim_{r \to \pm\infty} \eta_0^{\mathrm{in}}(r, \mathbb{z}, t) = (\eta_0^{\mathrm{in}})^\pm (r, \mathbb{z}, t) \tag{5.21}$$

relating the $O(1)$ terms of the inner and outer expansions for η_ε within the overlap region.

In terms of the variables $(r, \mathbb{z})$, the derivative with respect to $\mathbb{z}$ holding r fixed may be identified with the gradient $\nabla_{\mathscr{S}}$ on $\mathscr{S}$. Let

$$\mathbb{P} = \mathbf{1} - \mathbb{m} \otimes \mathbb{m}, \qquad \mathbb{M}_\varepsilon = -\nabla\mathbb{m} \tag{5.22}$$

(The dependence of $\mathbb{M}_\varepsilon$ on ε will become clear.) Then, since $\mathbb{z}(\mathbf{x}, t) = \mathbf{x} - d(\mathbf{x}, t)\, \mathbb{m}(\mathbf{x}, t)$,

$$\nabla\mathbb{z} = \mathbb{P} + d\mathbb{M}_\varepsilon \tag{5.23}$$

Since $|d| \leqslant h_\varepsilon = o(1)$ and $\acute{d} = \varepsilon$, differentiating $\mathbb{m}(\mathbb{z}(\mathbf{x}, t), t)$ with respect to $\mathbf{x}$ results in the conclusions

$$\mathbb{M}_\varepsilon = (\mathbf{1} - d\mathbb{L})^{-1}\, \mathbb{L} = \mathbb{L} + o(1), \qquad \acute{\mathbb{M}}_\varepsilon = \varepsilon(\mathbf{1} - d\mathbb{L})^{-1}\, \mathbb{L}\mathbb{M}_\varepsilon = O(\varepsilon) \tag{5.24}$$

Thus, for Φ and $\mathbf{v}$ scalar- and vector-valued fields,

$$\left.\begin{aligned} \nabla\Phi &= \varepsilon^{-1}\acute{\Phi}\mathbb{m} + (\mathbf{1} + d\mathbb{m}_\varepsilon)\, \nabla_{\mathscr{S}}\Phi = \varepsilon^{-1}\acute{\Phi}\mathbb{m} + (1 + o(1))\, \nabla_{\mathscr{S}}\Phi \\ \nabla\mathbf{v} &= \varepsilon^{-1}\acute{\mathbf{v}} \otimes \mathbb{m} + (\nabla_{\mathscr{S}}\mathbf{v})(\mathbf{1} + d\mathbb{m}_\varepsilon) = \varepsilon^{-1}\acute{\mathbf{v}} \otimes \mathbb{m} + (1 + o(1))\, \nabla_{\mathscr{S}}\mathbf{v} \end{aligned}\right\} \tag{5.25}$$

so that

$$\begin{aligned} \nabla\nabla\Phi = {} & \varepsilon^{-2}\acute{\acute{\Phi}}\mathbb{m} \otimes \mathbb{m} + \varepsilon^{-1}(1 + o(1))(\nabla_{\mathscr{S}}\acute{\Phi} \otimes \mathbb{m} + \mathbb{m} \otimes \nabla_{\mathscr{S}}\acute{\Phi} - \acute{\Phi}\mathbb{L}) \\ & + (\nabla_{\mathscr{S}}\nabla_{\mathscr{S}}\Phi)\, O(1) + O(1)\, \nabla_{\mathscr{S}}\Phi \end{aligned} \tag{5.26}$$

with the $O(1)$ and $o(1)$ estimates in (5.25) and (5.26) being of appropriate tensorial order and independent of Φ and $\mathbf{v}$.

5.4. Asymptotic Results

5.4.1. Coherency, Compatability, Local Equilibrium. By (5.25), $\mathbf{E}_\varepsilon = \varepsilon^{-1}\mathbf{E}^{\text{in}}_{-1} + O(1)$, $2\mathbf{E}^{\text{in}}_{-1} = \acute{\mathbf{u}}^{\text{in}}_0 \otimes \mathbb{m} + \mathbb{m} \otimes \acute{\mathbf{u}}^{\text{in}}_0$, and the assumption that $\mathbf{E}_\varepsilon$ be bounded as $\varepsilon \to 0$ yields the conclusion that $\mathbf{u}^{\text{in}}_0$ must be independent of r. Thus, the matching requirement (5.21) implies that $[\![\mathbf{u}^{\text{out}}_0]\!] = [\![\mathbf{u}^{\text{in}}_0]\!] = \mathbf{0}$, where $[\![\eta]\!] = \eta^+ - \eta^-$, and, by $(5.14)_2$, we arrive at the coherency condition

$$[\![\mathbf{u}]\!] = 0 \tag{5.27}$$

Further, since $\acute{\mathbf{u}}^{\text{in}}_0 = \mathbf{0}$, $(5.25)_2$ and $(5.15)_2$ yield

$$\nabla \mathbf{u}_\varepsilon = \nabla_{\mathscr{S}} \mathbf{u}^{\text{in}}_1 + \acute{\mathbf{u}}^{\text{in}}_1 \otimes \mathbb{m} + O(\varepsilon), \qquad \dot{\mathbf{u}}_\varepsilon = \dot{\mathbf{u}}^{\text{in}}_0 - V_{\mathscr{S}} \acute{\mathbf{u}}^{\text{in}}_1 + O(\varepsilon) \tag{5.28}$$

and we have the compatibility conditions

$$[\![\dot{\mathbf{u}}]\!] + V_{\mathscr{S}} [\![\nabla \mathbf{u}]\!]\, \mathbb{m} = \mathbf{0}, \qquad [\![\nabla \mathbf{u}]\!]\, \mathbb{P} = \mathbf{0} \tag{5.29}$$

Some care is needed in establishing the estimate for $\dot{\mathbf{u}}(r, \mathbb{z}, t)$, which is the derivative of $\mathbf{u}_\varepsilon(r, \mathbb{z}, t)$ with respect to t holding $\mathbf{x}$ fixed. Indeed, while the partial derivative of $\mathbf{u}_\varepsilon(r, \mathbb{z}, t)$ with respect to r is well-defined, the partial derivative of $\mathbf{u}_\varepsilon(r, \mathbb{z}, t)$ with respect to $\mathbb{z}$ (holding t fixed) is not, since $\mathbb{z} \in \mathscr{S}(t)$, but we can write $\dot{\mathbf{u}}_\varepsilon(r, \mathbb{z}, t)$ as $\varepsilon^{-1}\acute{\mathbf{u}}(r, \mathbb{z}, t)\, \dot{d}(\mathbf{x}, t)$ plus an $O(1)$ term; namely, the derivative of $\mathbf{u}_\varepsilon(r, \mathbb{z}(\mathbf{x}, t), t)$ with respect to t holding r and $\mathbf{x}$ fixed.

As an additional consequence of the r-independence of $\mathbf{u}^{\text{in}}_0$, we obtain

$$\mathbf{E}_\varepsilon = \mathbf{E}^{\text{in}}_0 + O(\varepsilon), \qquad \mathbf{E}^{\text{in}}_0 = \tfrac{1}{2}(\nabla_{\mathscr{S}} \mathbf{u}^{\text{in}}_0 + (\nabla_{\mathscr{S}} \mathbf{u}^{\text{in}}_0)^\top) + \tfrac{1}{2}(\acute{\mathbf{u}}^{\text{in}}_1 \otimes \mathbb{m} + \mathbb{m} \otimes \acute{\mathbf{u}}^{\text{in}}_1) \tag{5.30}$$

Consider, now, the form of the chemical potential μ_ε away from the layer. Inserting the outer expansions of v_ε and $\mathbf{u}_\varepsilon$ in $(5.8)_2$, we find that

$$\mu_\varepsilon = \varepsilon^{-1}\mu^{\text{out}}_{-1} + O(1), \qquad \mu^{\text{out}}_{-1} = f'(v^{\text{out}}_0) \tag{5.31}$$

The assumed boundedness of μ_ε therefore requires that $\mu^{\text{out}}_{-1} = f'(v^{\text{out}}_0) = 0$, so that, since $f(v)$ is a double-well potential with equal minima at v_α and v_β,

$$v^{\text{out}}_0 = \begin{cases} v_\alpha & \text{on } \mathscr{R}^\alpha_\varepsilon \\ v_\beta & \text{on } \mathscr{R}^\beta_\varepsilon \end{cases} \tag{5.32}$$

Thus, by (5.1), the outer expansion for μ_ε becomes

$$\mu_\varepsilon = \mu_0^{\mathrm{out}} + O(\varepsilon), \qquad \mu_0^{\mathrm{out}} = f''(v_0^{\mathrm{out}})\, v_1^{\mathrm{out}} \tag{5.33}$$

Next, to determine the form of the chemical potential μ_ε within the layer, we note that, from $(5.25)_1$,

$$\nabla v_\varepsilon = \varepsilon^{-1} \acute{v}_0^{\mathrm{in}} \mathbbm{m} + \nabla_{\mathscr{S}} v_0^{\mathrm{in}} + \acute{v}_1^{\mathrm{in}} \mathbbm{m} + O(\varepsilon) \tag{5.34}$$

whence $|\nabla v_\varepsilon| = \varepsilon^{-1} \acute{v}_0^{\mathrm{in}} + \acute{v}_1^{\mathrm{in}} + O(\varepsilon)$, and, granted that $\acute{v}_0^{\mathrm{in}}$ is nonvanishing,

$$\mathbf{m}_\varepsilon = \frac{\nabla v_\varepsilon}{|\nabla v_\varepsilon|} = \mathbbm{m} + O(\varepsilon) \tag{5.35}$$

and

$$\mathbf{P}_\varepsilon = \mathbf{1} - \mathbf{m}_\varepsilon \otimes \mathbf{m}_\varepsilon = \mathbb{P} + O(\varepsilon) \tag{5.36}$$

Thus, employing 05.30), (5.34), and (5.35) in $(5.8)_2$, we find that μ_ε has an inner expansion of the form

$$\mu_\varepsilon = \varepsilon^{-1} \mu_{-1}^{\mathrm{in}} + O(1), \qquad \mu_{-1}^{\mathrm{in}} = f'(v_0^{\mathrm{in}}) - \lambda(\mathbbm{m})\, \acute{\acute{v}}_0^{\mathrm{in}} \tag{5.37}$$

But μ_ε must be bounded as $\varepsilon \to 0$. Hence, bearing in mind the matching condition (5.21) and the result (5.32), v_0^{in} must satisfy the boundary-value problem

$$\lambda(\mathbbm{m})\, \acute{\acute{v}}_0^{\mathrm{in}} = f'(v_0^{\mathrm{in}}), \qquad \begin{cases} \lim\limits_{r \to -\infty} v_0^{\mathrm{in}}(r, \cdot, \cdot) = v_\alpha \\ \lim\limits_{r \to +\infty} v_0^{\mathrm{in}}(r, \cdot, \cdot) = v_\beta \end{cases} \tag{5.38}$$

and the far-field conditions $\acute{v}_0^{\mathrm{in}}(\pm\infty, \cdot, \cdot) = \acute{\acute{v}}_0^{\mathrm{in}}(\pm\infty, \cdot, \cdot) = 0$. The assumed properties of λ and f guarantee that (5.38) possesses a unique solution v_0^{in} that increases monotonically from the value v_α at $r = -\infty$ to the value v_β at $r = +\infty$.

Now, since $\mu_{-1}^{\mathrm{in}} = 0$, the inner expansion for μ_ε becomes

$$\mu_\varepsilon = \mu_0^{\mathrm{in}} + O(\varepsilon) \tag{5.39}$$

where, by (5.30), (5.34), (5.35), $(4.14)_2$, and $(5.8)_2$,

$$\begin{aligned} \mu_0^{\mathrm{in}} = f''(v_0^{\mathrm{in}})\, v_1^{\mathrm{in}} - \lambda(\mathbbm{m})\, \acute{\acute{v}}_1^{\mathrm{in}} - \mathrm{div}_{\mathscr{S}} \left(\acute{v}_0^{\mathrm{in}} \left(\lambda(\mathbbm{m})\, \mathbbm{m} + \frac{1}{2} \frac{\partial \lambda}{\partial \mathbbm{m}}(\mathbbm{m}) \right) \right) \\ - (\nabla_{\mathscr{S}} \acute{v}_0^{\mathrm{in}}) \cdot \left(\frac{\partial \lambda}{\partial \mathbbm{m}}(\mathbbm{m}) \right) \end{aligned} \tag{5.40}$$

Finally, arguing as in the proof of (5.27), the presumed boundedness of $\nabla\mu_\varepsilon$ yields the condition of local equilibrium

$$[\![\mu]\!]=0 \tag{5.41}$$

for the limiting value of the chemical potential.

5.4.2. Implications of the Bulk Constitutive Connections.

Granted the provisions of Section 5.2, the results (5.32) and (5.33) guarantee that, in the the bulk regions $\mathscr{R}^{\gamma}_{\varepsilon}$ $(\gamma=\alpha,\beta)$,

$$v_\varepsilon=v_\gamma+O(\varepsilon),\qquad \mu_\varepsilon=\mu_0^{\mathrm{out}}+O(\varepsilon),\qquad \mathbf{E}=\mathbf{E}_0^{\mathrm{out}}+O(\varepsilon) \tag{5.42}$$

and hence

$$\left.\begin{aligned} W(v_\varepsilon,\mathbf{E}_\varepsilon)&=W(v_\gamma,\mathbf{E}_0^{\mathrm{out}})+O(\varepsilon)=W^{(\gamma)}(\mathbf{E})+O(\varepsilon)\\ W(v_\varepsilon,\mathbf{E}_\varepsilon)-\mu_\varepsilon v_\varepsilon&=W(v_\gamma,\mathbf{E}_0^{\mathrm{out}})-\mu_0^{\mathrm{out}}v_\gamma+O(\varepsilon)=\omega^{(\gamma)}(\mu,\mathbf{E})+O(\varepsilon)\\ \mathbf{M}(v_\varepsilon)&=\mathbf{M}(v_\gamma)+O(\varepsilon)=\mathbf{M}^{(\gamma)}+O(\varepsilon)\end{aligned}\right\} \tag{5.43}$$

5.4.3. Energy Partition Within the Layer.

Granted the boundary conditions $(5.38)_{2,3}$, the differential equation $(5.38)_1$ possesses a first integral

$$\tfrac{1}{2}\lambda(\mathbb{m})\,|\acute{v}_0^{\mathrm{in}}|^2=f(v_0^{\mathrm{in}}) \tag{5.44}$$

which we interpret as an expression of energy partition (to most significant order in ε), between the double-well potential $f(v_\varepsilon)$ and the gradient energy density $\frac{1}{2}\lambda(\mathbf{m}_\varepsilon)\,|\nabla v_\varepsilon|^2$, within the layer. Since $f(v)$ and $f'(v)$ vanish at $v=v_\alpha$, v_β, v_0^{in} must decay according to

$$\acute{v}_0^{\mathrm{in}}(r,\cdot,\cdot)=O(e^{-c|r|})\qquad\text{as}\quad |r|\to\infty \tag{5.45}$$

with $c>0$ independent of r. Hence, $\acute{v}_0^{\mathrm{in}}$ is, as a function of r, square-integrable on $(-\infty,+\infty)$, and, drawing upon (5.44) and (5.38),

$$\int_{-\infty}^{+\infty}\sqrt{\lambda(\mathbb{m})}|\,\acute{v}_0^{\mathrm{in}}(r,\cdot,\cdot)|^2\,dr=\int_{v_\alpha}^{v_\beta}\sqrt{2f(v)}\,dv \tag{5.46}$$

a result that, granted (5.11), implies the identities

$$\left.\begin{aligned}\int_{-\infty}^{+\infty}\lambda(\mathbb{m})\,|\acute{v}_0^{\rm in}(r,\cdot,\cdot)|^2\,dr&=\hat{\psi}(\mathbb{m})\\ \frac{1}{2}\int_{-\infty}^{+\infty}\frac{\partial\lambda}{\partial\mathbb{m}}(\mathbb{m})\,|\acute{v}_0^{\rm in}(r,\cdot,\cdot)|^2\,dr&=\frac{\partial\hat{\psi}}{\partial\mathbb{m}}(\mathbb{m})\end{aligned}\right\}\tag{5.47}$$

Next, since, $\mathbf{m}_\varepsilon=\nabla v_\varepsilon/|\nabla v_\varepsilon|$, a straightforward calculation shows that $|\nabla v_\varepsilon|\,\nabla\mathbf{m}_\varepsilon=\mathbf{P}_\varepsilon\nabla\nabla v_\varepsilon$. This identity and (5.26) have two useful consequences. Firstly, since $\mathbf{P}_\varepsilon\mathbb{m}=O(\varepsilon)$,

$$\nabla\mathbf{m}_\varepsilon=O(1),\qquad \acute{\mathbf{m}}_\varepsilon=O(\varepsilon)\tag{5.48}$$

Secondly, $(\nabla\mathbf{m}_\varepsilon)\,\mathbf{P}_\varepsilon=\nabla_{\mathscr{S}}\mathbb{m}+o(1)$; therefore, since $\operatorname{div}\mathbf{m}_\varepsilon=\operatorname{tr}\nabla\mathbf{m}_\varepsilon=\operatorname{tr}((\nabla\mathbf{m}_\varepsilon)\,\mathbf{P}_\varepsilon)$,

$$\operatorname{div}\mathbf{m}_\varepsilon=-K_{\mathscr{S}}+o(1)\tag{5.49}$$

5.4.4. Atomic Balance. Standard Force Balance. From (5.32), (5.33), $(5.8)_1$, and $(5.43)_3$, the terms of the atomic balance $(5.7)_1$ admit the bulk estimates

$$\dot{v}_\varepsilon=O(\varepsilon),\qquad \operatorname{div}\mathbf{h}_\varepsilon=-\operatorname{div}(\mathbf{M}(v_\gamma)\,\nabla\mu_0^{\rm out})+O(\varepsilon)\tag{5.50}$$

on $\mathscr{R}_\varepsilon^\gamma$ $(\gamma=\alpha,\beta)$; hence, by $(5.43)_3$, in the region occupied by phase γ, $\mathbf{h}=\lim_{\varepsilon\to 0}\mathbf{h}_\varepsilon$ satisfies

$$\operatorname{div}\mathbf{h}=0\tag{5.51}$$

with

$$\mathbf{h}=-\mathbf{M}^{(\gamma)}\,\nabla\mu\tag{5.52}$$

Next, since $\acute{\mu}_0^{\rm in}=0$, $(5.15)_2$, (5.39), $(5.8)_1$, and $(5.43)_3$ yield estimates

$$\dot{v}_\varepsilon=-\varepsilon^{-1}\overset{\prime}{\overline{V_{\mathscr{S}}v_0^{\rm in}}}+O(1),\quad \operatorname{div}\mathbf{h}_\varepsilon=-\varepsilon^{-1}\overset{\prime}{\overline{(\mathbf{M}(v_0^{\rm in})(\nabla_{\mathscr{S}}\mu_0^{\rm in}+\acute{\mu}_1^{\rm in}\mathbb{m}))\cdot\mathbb{m}}}+O(1)\tag{5.53}$$

within the layer. Thus, by (5.18)

$$\left.\begin{aligned}\int_{-h_\varepsilon}^{+h_\varepsilon}\dot{v}_\varepsilon d(\varepsilon r)&=-V_{\mathscr{S}}[\![v_0^{\rm in}]\!]+o(1)=-V_{\mathscr{S}}[\![v]\!]+o(1)\\ \int_{-h_\varepsilon}^{+h_\varepsilon}\operatorname{div}\mathbf{h}_\varepsilon d(\varepsilon r)&=-[\![\mathbf{M}(v_0^{\rm in})(\nabla_{\mathscr{S}}\mu_0^{\rm in}+\acute{\mu}_1^{\rm in}\mathbb{m})]\!]\cdot\mathbb{m}+o(1)\\ &=[\![\mathbf{h}]\!]\cdot\mathbb{m}+o(1)\end{aligned}\right\}\tag{5.54}$$

hence, bearing in mind $(5.7)_1$, the limiting fields must satisfy

$$V_{\mathscr{S}}[\![v]\!] = [\![\mathbf{h}]\!] \cdot \mathbb{m} \tag{5.55}$$

on $\mathscr{S}$.

A similar argument shows that the limiting stress field $\mathbf{S} = \lim_{\varepsilon \to 0} \mathbf{S}_\varepsilon$ satisfies

$$\operatorname{div} \mathbf{S} = \mathbf{0}, \qquad \mathbf{S} = \frac{\partial W^{(\gamma)}}{\partial \mathbf{E}}(\mathbf{E}), \qquad \mathbf{E} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^\top) \tag{5.56}$$

in the region occupied by phase γ and

$$[\![\mathbf{S}]\!]\, \mathbb{m} = \mathbf{0} \tag{5.57}$$

on $\mathscr{S}$.

5.4.5. Normal Configurational Force Balance.

To derive the normal configurational balance of the sharp-interface theory, we consider the normal component (4.34) of the configurational balance of the theory at hand, modified appropriately so as to reflect the scaling in Section 5.1 and the present absence of kinetics, viz.

$$\mathbf{m}_\varepsilon \cdot (\operatorname{div} \mathbf{C}^{\mathrm{bu}}_\varepsilon + v_\varepsilon \nabla \mu_\varepsilon) + \Psi^{\mathrm{xs}}_\varepsilon K_\varepsilon + \operatorname{div} \mathbf{c}^{\mathrm{xs}}_\varepsilon + \operatorname{div}(\imath^{\mathrm{xs}}_\varepsilon \mathbf{m}_\varepsilon) = 0 \tag{5.58}$$

with

$$\left.\begin{aligned}
\mathbf{C}^{\mathrm{bu}}_\varepsilon &= (W(v_\varepsilon, \mathbf{E}_\varepsilon) - \mu_\varepsilon v_\varepsilon)\,\mathbf{1} - (\nabla \mathbf{u}_\varepsilon)^\top \frac{\partial W}{\partial \mathbf{E}}(v_\varepsilon, \mathbf{E}_\varepsilon) \\
\Psi^{\mathrm{xs}}_\varepsilon &= \varepsilon^{-1} f(v_\varepsilon) + \frac{1}{2}\varepsilon \lambda(\mathbf{m}_\varepsilon)\, |\nabla v_\varepsilon|^2 \\
K_\varepsilon &= -\operatorname{div} \mathbf{m}_\varepsilon \\
\mathbf{c}^{\mathrm{xs}}_\varepsilon &= -\frac{1}{2}\varepsilon\, |\nabla v_\varepsilon|^2 \frac{\partial \lambda}{\partial \mathbf{m}_\varepsilon}(\mathbf{m}_\varepsilon) \\
\imath^{\mathrm{xs}}_\varepsilon &= \varepsilon^{-1} f(v_\varepsilon) - \frac{1}{2}\varepsilon \lambda(\mathbf{m}_\varepsilon)\, |\nabla v_\varepsilon|^2
\end{aligned}\right\} \tag{5.59}$$

We consider each term of (5.58) separately. First, from the inner expansion of v_ε, (5.30), (5.39), (5.40), (5.44), $(5.8)_{2,3}$, and $(5.43)_{1,2}$, we have the estimate

$$\mathbf{m}_\varepsilon \cdot (\operatorname{div} \mathbf{C}_\varepsilon^{\text{bu}} + v_\varepsilon \nabla \mu_\varepsilon)$$

$$= \varepsilon^{-1} \overset{\prime}{\overline{\mathbb{m} \cdot (\omega^{(\gamma)}(\mu_0^{\text{in}}, \mathbf{E}_0^{\text{in}})\, \mathbf{1} - (\nabla \mathbf{u}_0^{\text{in}})^\top\, \mathbf{S}^{(\gamma)}(\mathbf{E}_0^{\text{in}}))\, \mathbb{m}}} + O(1) \tag{5.60}$$

so that

$$\begin{aligned} &\int_{-h_\varepsilon}^{+h_\varepsilon} \mathbf{m}_\varepsilon \cdot (\operatorname{div} \mathbf{C}_\varepsilon^{\text{bu}} + v_\varepsilon\, \nabla \mu_\varepsilon)\, d(\varepsilon r) \\ &\qquad = \mathbb{m} \cdot [\![\omega^{(\gamma)}(\mu_0^{\text{in}}, \mathbf{E}_0^{\text{in}})\, \mathbf{1} - (\nabla \mathbf{u}_0^{\text{in}})^\top\, \mathbf{S}^{(\gamma)}(\mathbf{E}_0^{\text{in}})]\!]\, \mathbb{m} + o(1) \\ &\qquad = \mathbb{m} \cdot [\![\omega \mathbf{1} - (\nabla \mathbf{u})^\top\, \mathbf{S}]\!]\, \mathbb{m} + o(1) \\ &\qquad = [\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + o(1) \end{aligned} \tag{5.61}$$

Next, since $\acute{v}_0^{\text{in}}$, as in function of r square-integrable on $(-\infty, \infty)$, for $\Phi = o(1)$,

$$\varepsilon^{-1} \int_{-h_\varepsilon}^{h_\varepsilon} |\acute{v}_0^{\text{in}}|^2\, \Phi\, dr = o(1) \tag{5.62}$$

By (5.34), (5.35), and (5.44),

$$\Psi_\varepsilon^{\text{xs}} = \varepsilon^{-1} \lambda(\mathbb{m})\, |\acute{v}_0^{\text{in}}|^2 + O(1) \tag{5.63}$$

so that, appealing to $(5.47)_1$, (5.49), and (5.62),

$$\int_{-h_\varepsilon}^{+h_\varepsilon} \Psi_\varepsilon^{\text{xs}} K_\varepsilon\, d(\varepsilon r) = \hat{\psi}(\mathbb{m})\, K_{\mathscr{S}} + o(1) \tag{5.64}$$

Further, since $\partial \lambda(\mathbf{m}_\varepsilon)/\partial \mathbf{m}_\varepsilon \in \mathbf{m}_\varepsilon^\perp$, while $\partial^2 \lambda(\mathbf{m}_\varepsilon)/\partial \mathbf{m}_\varepsilon^2$ is a linear transformation of $\mathbf{m}_\varepsilon^\perp$ into itself, (5.25), (5.39), and (5.48) yield

$$\begin{aligned} \operatorname{div} \mathbf{c}_\varepsilon^{\text{xs}} &= -\frac{1}{2}\, \varepsilon\, |\nabla v_\varepsilon|^2 \left(\frac{\partial^2 \lambda}{\partial \mathbf{m}_\varepsilon^2} (\mathbf{m}_\varepsilon) \right) \cdot ((\nabla \mathbf{m}_\varepsilon)\, \mathbf{P}_\varepsilon) - \varepsilon((\mathbf{P}_\varepsilon \nabla\nabla v_\varepsilon)\, \nabla v_\varepsilon) \cdot \frac{\partial \lambda}{\partial \mathbf{m}_\varepsilon} (\mathbf{m}_\varepsilon) \\ &= \frac{1}{2}\, \varepsilon^{-1}\, |v_0^{\text{in}}|^2 \left(\nabla_{\mathscr{S}} \mathbb{m} \cdot \left(\frac{\partial^2 \lambda}{\partial \mathbf{m}_\varepsilon^2} (\mathbb{m}) \right) + o(1) \right) + O(1) \end{aligned} \tag{5.65}$$

thus, since $\operatorname{div}_{\mathscr{S}} (\partial \lambda(\mathbb{m})/\partial \mathbb{m}) = \nabla_{\mathscr{S}} \mathbb{m} \cdot (\partial^2 \lambda(\mathbb{m})/\partial \mathbb{m}^2)$ is independent of r, we may use (5.62) and $(5.47)_2$ to conclude that

$$\int_{-h_\varepsilon}^{+h_\varepsilon} \operatorname{div} \mathbf{c}_\varepsilon^{\text{xs}}\, d(\varepsilon r) = \operatorname{div}_{\mathscr{S}}\, \mathbb{c} + o(1) \tag{5.66}$$

As our final estimate, we will prove that

$$\int_{-h_\varepsilon}^{+h_\varepsilon} \operatorname{div}(\imath_\varepsilon^{\mathrm{xs}} \mathbf{m}_\varepsilon)\, d(\varepsilon r) = o(1) \tag{5.67}$$

By $(5.25)_1$,

$$\overset{\prime}{\overline{\nabla v_\varepsilon}} = \varepsilon^{-1} \acute{\acute{v}}_0^{\mathrm{in}} \mathbbm{m} + O(1), \qquad \nabla_{\mathscr{S}}(|\nabla v_\varepsilon|^2) = O(\varepsilon^{-1}) \tag{5.68}$$

Thus, since $f(v_0^{\mathrm{in}}) = \frac{1}{2}\lambda(\mathbbm{m})\, |\acute{v}_0^{\mathrm{in}}|^2$, $f'(v_0^{\mathrm{in}}) = \lambda(\mathbbm{m})\, \acute{\acute{v}}_0^{\mathrm{in}}$, $\mathbf{m}_\varepsilon = \mathbbm{m} + O(\varepsilon)$, and $\acute{\mathbf{m}}_\varepsilon = O(\varepsilon)$,

$$\left.\begin{aligned} \imath_\varepsilon^{\mathrm{xs}} = f'(v_0^{\mathrm{in}})\, v_1^{\mathrm{in}} - O(1)\, |\acute{v}_0^{\mathrm{in}}|^2 - \lambda(\mathbbm{m})\, \acute{v}_0^{\mathrm{in}} \acute{v}_1^{\mathrm{in}} + O(\varepsilon) = O(1) \\ \overset{\prime}{\overline{\imath_\varepsilon^{\mathrm{xs}}}} = O(1), \qquad \mathbf{m}_\varepsilon \cdot (\nabla_{\mathscr{S}} \imath_\varepsilon^{\mathrm{xs}}) = O(1) \end{aligned}\right\} \tag{5.69}$$

Therefore, using $(5.25)_2$,

$$\operatorname{div}(\imath_\varepsilon^{\mathrm{xs}} \mathbf{m}_\varepsilon) = \varepsilon^{-1} \overset{\prime}{\overline{\mathbbm{m} \cdot (\imath_\varepsilon^{\mathrm{xs}} \mathbf{m}_\varepsilon)}} + (1 + o(1))\, \operatorname{div}_{\mathscr{S}}(\imath_\varepsilon^{\mathrm{xs}} \mathbf{m}_\varepsilon) = \varepsilon^{-1} \overset{\prime}{\overline{\imath_\varepsilon^{\mathrm{xs}}}} + O(1) \tag{5.70}$$

so that

$$\int_{-h_\varepsilon}^{+h_\varepsilon} \operatorname{div}(\imath_\varepsilon^{\mathrm{xs}} \mathbf{m}_\varepsilon)\, d(\varepsilon r) = \imath_\varepsilon^{\mathrm{xs}} \big|_{r=-\infty}^{r=+\infty} + o(1) \tag{5.71}$$

and, since $f'(v_0^{\mathrm{in}})$ and $\acute{v}_0^{\mathrm{in}}$ approach zero as $r \to \pm\infty$, (5.67) follows.

Finally, integrating (5.58) from $\varepsilon r = -h_\varepsilon$ to $\varepsilon r = +h_\varepsilon$, we find, with the aid of the estimates (5.61), (5.64), (5.66), and (5.67), that

$$[\![\omega - \mathbf{S} \cdot \mathbf{E}]\!] + \psi K_{\mathscr{S}} + \operatorname{div}_{\mathscr{S}} \mathbbm{c} = 0 \tag{5.72}$$

on $\mathscr{S}$, with

$$\omega = -v_\gamma \mu + W^{(\gamma)}(\mathbf{E}), \qquad \mathbf{S} = \frac{\partial W^{(\gamma)}}{\partial \mathbf{E}}(\mathbf{E}), \qquad \psi = \hat{\psi}(\mathbbm{m}), \qquad \mathbbm{c} = -\frac{\partial \hat{\psi}}{\partial \mathbbm{m}}(\mathbbm{m}) \tag{5.73}$$

A more conventional approach to deriving the generalized Gibbs–Thomson relation (5.72) involves using the Fredholm alternative. Specifically, rewriting (5.39) in the form

$$\lambda(\mathbb{m})\,\acute{\acute{v}}_1^{\mathrm{in}} - f''(v_0^{\mathrm{in}})\,v_1^{\mathrm{in}} = \rho - \mu_0^{\mathrm{in}},$$

$$\rho = -\mathrm{div}_{\mathscr{S}}\left(\acute{v}_0^{\mathrm{in}}\left(\lambda(\mathbb{m})\,\mathbb{m} + \frac{1}{2}\frac{\partial\lambda}{\partial\mathbb{m}}(\mathbb{m})\right)\right) - (\nabla_{\mathscr{S}}\acute{v}_0^{\mathrm{in}})\cdot\left(\frac{\partial\lambda}{\partial\mathbb{m}}(\mathbb{m})\right)$$

and recognizing that $\acute{v}_0^{\mathrm{in}}$ satisfies the homogeneous equation $\lambda(\mathbb{m})\,\acute{v}_0^{\mathrm{in}} - f''(v_0^{\mathrm{in}})\,v_0^{\mathrm{in}} = 0$, which results on differentiating $(5.38)_1$ with respect to r, we see that ρ and $\acute{v}_0^{\mathrm{in}}$ must be orthogonal:

$$\int_{-\infty}^{+\infty} \rho\,\acute{v}_0^{\mathrm{in}}\,dr = 0$$

Evaluating this integral then yields (5.72). Our derivation seems more intuitive and closer to the underlying physics, as it establishes the normal configurational force balance of the sharp-interface theory by integrating, across the layer, the counterpart of that balance for the diffuse-interface theory.

5.5. Modification to Account for Dissipation at the Interface

To account for dissipation at the interface, we merely consider the more general theory with transition kinetics as developed in Section 4.3 and supplement the constitutive scaling relations (5.4) with

$$B(\mathbf{m}_\varepsilon) = \frac{L^2}{\varkappa T}\,B^*(\mathbf{m}^*) \tag{5.74}$$

in which case, the balance (5.58) is modified to read

$$\mathbf{m}_\varepsilon\cdot(\mathrm{div}\,\mathbf{C}_\varepsilon^{\mathrm{bu}} + v_\varepsilon\nabla\mu_\varepsilon) + \Psi_\varepsilon^{\mathrm{xs}}K_\varepsilon + \mathrm{div}\,\mathbf{c}_\varepsilon^{\mathrm{xs}} + g_\varepsilon^{\mathrm{xs}} + \mathrm{div}(\imath_\varepsilon^{\mathrm{xs}}\mathbf{m}_\varepsilon) = 0 \tag{5.75}$$

with $\mathbf{C}_\varepsilon^{\mathrm{bu}}$, $\Psi_\varepsilon^{\mathrm{xs}}$, $\mathbf{c}_\varepsilon^{\mathrm{xs}}$, and $\imath_\varepsilon^{\mathrm{xs}}$ as defined in (5.59) and

$$g_\varepsilon^{\mathrm{xs}} = -\varepsilon\,|\nabla v_\varepsilon|^2\,B(\mathbf{m}_\varepsilon)\,V_\varepsilon \tag{5.76}$$

Then, introducing the constitutive connection

$$b(\mathbb{m}) = \frac{B(\mathbb{m})}{\sqrt{\lambda(\mathbb{m})}}\int_{v_\alpha}^{v_\beta}\sqrt{f(v)}\,dv \tag{5.77}$$

and arguing as above yields results of Section 5.4.3, with (5.72) replaced by

$$[\![\omega - \mathbf{S}\cdot\mathbf{E}]\!] + \psi K_{\mathscr{S}} + \mathrm{div}_{\mathscr{S}}\,\mathbb{c} + g = 0, \qquad g = -b(\mathbb{m})\,V_{\mathscr{S}} \tag{5.78}$$

on $\mathscr{S}$.

APPENDIX A. SOME LEMMAS

Let $\mathscr{W}$ and $\mathscr{V}$ be vector spaces. Further, let H and L be mappings from $\mathscr{W}$ into $\mathscr{V}$ with H continuous and L linear, and assume that H and L are consistent with the generalized flux inequality

$$H(w) \cdot Lw \leqslant 0 \qquad \text{for all } w \text{ in } \mathscr{W} \tag{A.1}$$

The following Lemmas, which are included here for completeness, appear also in Gurtin (1989).

Lemma 1. Let L be onto (i.e., assume that $\mathscr{V} = \mathrm{Rg}(L) =$ range of L). Then, given any element w of $\mathscr{W}$,

$$Lw = 0 \qquad \text{implies} \qquad H(w) = 0 \tag{A.2}$$

Proof. Assume that $Lw = 0$. Then, since L is linear, if we expand $\zeta(q) = H(q) \cdot Lq$ with $q = w + \lambda z$, $\lambda > 0$, divide by λ, and let $\lambda \to 0$, we find that $H(w) \cdot Lz \leqslant 0$ for every z in $\mathscr{W}$. Since L is onto, there is a z such that $Lz = H(w)$, which yields $H(w) = 0$. ▮

Lemma 2. Assume that H is linear and that (A.2) holds. Then there is a positive semi-definite linear transformation M from $\mathrm{Rg}(L)$ into $\mathrm{Rg}(L)$ such that

$$Hw = -Mv \qquad \text{whenever} \qquad v = Lw \tag{A.3}$$

Proof. Choose v of $\mathrm{Rg}(L)$. Assume that w_1 and w_2 are such that $v = Lw_1 = Lw_2$. Let $w_{12} = w_1 - w_2$. Then $Lw_{12} = 0$, so that, by (A.2), $Hw_{12} = 0$; thus, since H is linear, $Hw_1 = Hw_2$. It is therefore meaningful to define M: $\mathrm{Rg}(L) \to \mathrm{Rg}(L)$ as follows: for any v in $\mathrm{Rg}(L)$ choose some (the choice is immaterial) w in $\mathscr{W}$ such that $v = Lw$ and define $M(v) = -Hw$. It is then a simple matter to verify that M is linear and positive semi-definite. ▮

We now apply these results to establish generalizations of Fick's law.

1. Paragraph following (2.53). Fix $(\mathbf{v}, \mathbf{E})$ and suppress it in what follows; (2.45) and (2.53) then take the form

$$\hat{\mathbf{h}}^{\mathfrak{a}}(\mathbf{p}, \mathbf{G}) \cdot \mathbf{s}^{\mathfrak{a}} \leqslant 0, \qquad \mathbf{s}^{\mathfrak{a}} = \lambda^{\mathfrak{a}\mathfrak{b}} \mathbf{p}^{\mathfrak{b}} + \mathbf{A}^{\mathfrak{a}} : \mathbf{G}, \qquad \mathbf{s} = \nabla \boldsymbol{\mu}, \quad \mathbf{p} = \nabla \mathbf{v} \tag{A.4}$$

   To apply the lemmas, let $\mathscr{W}$ be the space of all pairs $w = (\mathbf{p}, \mathbf{G})$, let $\mathscr{V}$ be the space of all lists $\mathbf{s} = (\mathbf{s}^1, \mathbf{s}^2, \ldots, \mathbf{s}^{\mathfrak{A}})$ (and hence all lists $\mathbf{h} = (\mathbf{h}^1, \mathbf{h}^2, \ldots, \mathbf{h}^{\mathfrak{A}})$), take $H = \hat{\mathbf{h}}$ (so that H maps $\mathscr{W}$ continuously into $\mathscr{V}$, and take L: $\mathscr{W} \to \mathscr{V}$ to be the linear mapping of $(\mathbf{p}, \mathbf{G})$ into $\mathbf{s}$ specified in (A.4). Then the flux inequality reduces to (A.1). Further, L is onto if the matrix with entries $\kappa^{\mathfrak{a}\mathfrak{b}}$ is invertible or more generally, if, given any $\mathbf{m}$ in $\mathscr{V}$, there is a pair $(\mathbf{p}, \mathbf{G})$ that delivers $\mathbf{m}$ through the second of (A.4). We now show that this will be so if the stress-composition moduli are nontrivial. Thus choose $\mathbf{s}$, choose an arbitrary species α (and suppress it where convenient), let $\mathbf{v} = \mathbf{s}^\alpha$ and take $\mathbf{p} = \mathbf{0}$. Then we must show that there exists a $\mathbf{G}$ such that $\mathbf{A} : \mathbf{G} = \mathbf{v}$, or in components $A_{ij} G_{ijk} = v_k$, bearing in mind that $\mathbf{G}$ should satisfy $G_{ijk} = G_{ikj}$. Since $\mathbf{A}$ is symmetric and $\mathbf{A} \neq \mathbf{0}$, we may assume, without loss in generality, that $\mathbf{A}$ is diagonal with $A_{11} \neq 0$. Then $\mathbf{G}$ with all components zero except $G_{11k} = G_{1k1} = v_k / A_{11}$ $(k = 1, 2, 3)$ is a solution of $\mathbf{A} : \mathbf{G} = \mathbf{v}$. Thus, given any of the hypotheses of the paragraph following (2.53), L is onto, so that, by Lemma 1, (A.2) is satisfied. Granted this, if the atomic flux is quasi-linear, then H is linear. Then the hypotheses of Lemma 2 are satisfied, so that the conclusion of (A.3) holds; but this is just Fick's law (2.52).

2. Paragraph containing (2.61). The mapping L is defined by $(\mathbf{s}, \mathbf{G}) \to \mathbf{s}$.

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