Interface evolution in three-dimensions with curvature-dependent energy and surface diffusion: interface-controlled evolution, phase transitions, epitaxial growth of elastic films

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Abstract

When the interfacial energy is a nonconvex function of orientation, the anisotropic curvature flow equation becomes backward parabolic. To overcome the instability thus generated, a regularization of the equation that governs the evolution of the interface is needed. In this paper we develop a regularized theory of curvature flow in three-dimensions that incorporates surface diffusion and bulk-surface interactions. The theory is based on a superficial mass balance; configurational forces and couples consistent with superficial force and moment balances; a mechanical version of the second law that includes, via the configurational moments, work that accompanies changes in the curvature of the interface; a constitutive theory whose main ingredient is a positive-definite, isotropic, quadratic dependence of the interfacial energy on the curvature tensor. Two special cases are investigated: (i) the interface is a boundary between bulk phases or grains, and (ii) the interface separates an elastic thin film bonded to a rigid substrate from a vapor phase whose sole action is the deposition of atoms on the surface.

keywords: Regularized anisotropic curvature flow – curvature-dependent interfacial energy – surface diffusion – configurational forces and couples – interface-controlled evolution – phase transitions – epitaxial growth of elastic films.

1 Introduction

1.1 Background. Interface-controlled evolution

Mathematical theories that characterize the evolution of interfaces are of great importance in a variety of physical settings including phase transitions, epitaxial deposition and grain growth. In many situations of interest the evolution is essentially *interface-controlled*; i.e., independent of the behavior of the adjacent bulk phases. One of the earliest theories of such phenomena is due to Mullins [1956] who derived an evolution equation for a grain boundary

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in $\mathbb{R}^2$. When appropriately scaled, Mullins's equation has the simple form[1]

$$V = K, \tag{1.1}$$

with V the scalar normal velocity and K the curvature, and represents a second-order, parabolic partial differential equation.

The applicability of (1.1) is restricted by the tacit isotropy of the interface. A generalization that encompasses *anisotropy* while allowing for a jump in bulk free energy across the interface results in the evolution equation[2]

$$\beta(\mathbf{n})V = \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L} + c_0, \tag{1.2}$$

with $\mathbf{n}$ the unit normal to the interface,

$$\mathbb{L} = -\nabla_{\mathcal{S}}\mathbf{n}$$

the curvature tensor (with $\nabla_{\mathcal{S}}$ the surface gradient), $\beta(\mathbf{n}) > 0$ a modulus that describes attachment kinetics, $\psi_0(\mathbf{n})$ the interfacial free energy density, $\mathbb{P} = \mathbf{1} - \mathbf{n}\otimes\mathbf{n}$ the projection onto the surface and c_0 a (constant) difference in bulk free energies. The analogous evolution equation in $\mathbb{R}^2$ has the form

$$\beta(\theta)V = \big[\psi_0(\theta) + \psi_0''(\theta)\big]K + c_0, \tag{1.3}$$

with θ the angle from a fixed axis to $\mathbf{n}$. For $\psi_0(\mathbf{n})$ convex, (1.2) (or its two-dimensional counterpart (1.3)) is parabolic and well behaved,[3] but when $\psi_0(\mathbf{n})$ is *not convex*,[4] equation (1.2) is *backward parabolic* within nonconvex ranges of $\mathbf{n}$, and hence inherently *unstable* within such ranges.

A possible method of studying evolution governed by an interfacial energy that is not convex is to regularize the theory by allowing the energy to depend on curvature, thereby penalizing spatial oscillations as well as the tendency to form corners.[5] Such a curvature dependence, apparently first proposed on physical grounds by Herring [1951],[6] has the added advantage of providing an additional physical length scale.

A theory of curvature flow in $\mathbb{R}^2$ based on a curvature-dependent energy was developed by DiCarlo, Gurtin & Podio-Guidugli [1992].[7] When the interfacial energy has the specific form

$$\psi(\theta) + \tfrac{1}{2}\varepsilon K^2,$$

[1] Cf. also Burke & Turnbull [1952]. This equation has an extensive mathematical literature; cf., e.g., Brakke [1978], Sethian [1985], Abresch & Langer [1986], Gage & Hamilton [1986], Grayson [1987], Osher & Sethian [1988], Evans & Spruck [1991, 1992], Chen, Giga & Goto [1991], Giga & Sato [1991], Taylor, Cahn & Handwerker [1992], and Almgren, Taylor & Wang [1993].

[2] Proposed by Uwaha [1987] in $\mathbb{R}^2$ and independently by Gurtin [1988] in $\mathbb{R}^3$ (cf. also the two-dimensional treatment of Angenent & Gurtin [1989] and Gurtin [1993]). Evolution based on (1.2) has been investigated by Angenent [1991], Chen, Giga & Goto [1991], Soner [1993], and Angenent & Gurtin [1994]. The special case $V = \beta(\mathbf{n})^{-1}F$ was studied by Frank [1958]. A formulation of (1.2) based on a variational definition of the curvature term is given by Taylor [1992] and Taylor, Cahn & Handwerker [1992] who provide extensive references.

[3] Cf. Angenent [1991], Chen, Giga & Goto [1991], Barles, Soner & Souganidis [1993] and Soner [1993].

[4] Crystalline materials are often endowed with interfacial energies that are not convex. Cf. Herring [1951], Gjostein [1963], Cahn & Hoffman [1974] who, within an equilibrium framework, show that such energies lead to the possibility of corners, facets, and wrinklings.

[5] An alternative method for overcoming instabilities resulting from the nonconvexity of the interfacial energy is to allow the interface to contain corners that exclude nonconvex angle-intervals (cf. Angenent & Gurtin [1989, 1994]). This method cannot describe the formation of corners, nor can it describe the nucleation of facets.

[6] Cf. also Stewart & Goldenfeld [1992] who, for an interface $z = z(x, y, t)$ such that $\partial z/\partial x$ and $\partial z/\partial y$ are small, postulate an energy that comprises a quadratic term in Δz (essentially the curvature), justified on the grounds that an additional contribution is needed to account for the energetic cost associated with the formation of corners, and Golovin, Davis & Nepomnyashchy [1998] who argue that an energetic dependence on curvature follows from the interaction of steps on a crystal surface.

[7] Cf. Gurtin [1993], §13. This equation was proposed earlier by Angenent & Gurtin [1989], but without derivation and with θ as independent "spatial variable". The theory of Di Carlo, Gurtin & Podio-Guidugli

with $\varepsilon > 0$ constant, their theory leads to the evolution equation

$$\beta(\theta)V = \big[\psi(\theta) + \psi''(\theta)\big]K - \varepsilon\big(K_{ss} + \frac{1}{2}K^3\big) + c_0 \tag{1.4}$$

in which the subscript s denotes partial differentiation with respect to arc length; (1.4), when viewed as a partial differential equation, is *fourth-order parabolic*.

1.2 Scope

We here develop a three-dimensional theory of anisotropic interface evolution that allows for an energetic dependence on curvature. In this regard we do more than simply derive a generalization of (1.4), as we develop the theory within a thermodynamically consistent framework that allows for: (i) surface diffusion; (ii) deformation and mass transport in the bulk material; (iii) atomic deposition from a vapor reservoir. We base the theory on the notion of configurational forces[8] in conjunction with the use of "superficial control volumes" *to isolate the physical processes specific to the interface.* Such control volumes allow us to replace the adjacent bulk material by the configurational force and moment it exerts on — and the mass it supplies to — the interface, and to therefore develop interface equations once and for all, independent of the physical processes the adjacent bulk material may undergo. In fact, the interfacial force and moment balances we derive in §7 are completely general; they are independent of interfacial constitutive equations and apply in the presence of more general thermodynamic processes.

Finally, since the applications we envisage occur on a time scale that is slow compared to material sound speeds, we neglect inertia.[9]

1.3 Main results (interface conditions)

We base our study on an interfacial free energy of the form

$$\psi = \psi_0(\mathbf{n}) + \tfrac{1}{2}\varepsilon_1|\mathbb{L}|^2 + \tfrac{1}{2}\varepsilon_2 K^2,$$

with $K = \operatorname{tr}\mathbb{L}$ the total (twice the mean) curvature and ε_1 and ε_2 constant scalar moduli with $\epsilon_1 > 0$ and $\epsilon_1 + \frac{1}{2}\epsilon_2 > 0$ to ensure that the interfacial energy is positive-definite in $\mathbb{L}$. Our main result consists of a *mechanical evolution equation*

$$\begin{aligned}\beta(\mathbf{n})V = \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L} \\ - \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big] + c\end{aligned} \tag{1.5}$$

for the interfacial surface $\mathcal{S} = \mathcal{S}(t)$ supplemented by a *superficial diffusion equation*

$$\operatorname{div}_{\mathcal{S}}\big(k(\mathbf{n})\nabla_{\mathcal{S}}\mu\big) = -q \tag{1.6}$$

in which μ is the chemical potential of mobile atoms on $\mathcal{S}$ and $k(\mathbf{n}) > 0$ is a "mobility" for Fickean surface diffusion.[10] The superficial *fields* c and q represent coupling between $\mathcal{S}$ and

[1992] and that developped here are related to the work of Stewart & Goldenfeld [1992] who define the chemical potential as the variational derivative of the interfacial energy with respect to changes in the location of the surface and, starting with a mass balance that includes surface diffusion and evaporation terms, derive an evolution equation which, after linearization, yields conditions for the onset of instabilities (and the subsequent formation of facets along the surface). Cf. also Golovin, Davis & Nepomnyashchy [1998] (respectively, [1999]) who use variational arguments to obtain an evolution equation for an interface $z = h(x,t)$ (respectively, $z = h(x,y,t)$) with a curvature-dependent surface tension, assuming that dh/dx is small (respectively, $\partial h/\partial x$ and $\partial h/\partial y$ are small).

[8] Such forces and their balance are discussed by Gurtin [2000]. Here we extend the notion of configurational moments introduced by DiCarlo, Gurtin & Podio-Guidugli [1992].

[9] Inertial effects are easily included. Cf., e.g., Gurtin [2000].

[10] We neglect the terms δ° and δKV, where δ is the density of mobile surface atoms and δ° its normal time derivative following $\mathcal{S}$.

the material adjacent to it and as such depend on the specific physical processes that occur in this material: c represents the *scalar normal configurational force* exerted on[11] $\mathcal{S}$ by — and q the net mass supplied to $\mathcal{S}$ from — the adjacent material.

For the simple case of *interface-controlled evolution without surface diffusion* the evolution of $\mathcal{S}$ is determined by (1.5) with $c = c_0$ (constant); in this case (1.5) represents a three-dimensional counterpart of the evolution equation (1.4). Other important special cases are described below (cf. §§12,13).

Interface between bulk phases or grains

Suppose that $\mathcal{S}$ is an interface separating bulk material that is undergoing infinitesimal deformation and mass transport. Then for Ψ the free energy (per unit volume), ρ the atomic density, μ the chemical potential, *assumed continuous across* $\mathcal{S}$, $\boldsymbol{\jmath}$ the atomic flux, $\mathbf{E}$ the strain, and $\mathbf{T}$ the standard stress (all bulk fields), c and q are given by[12]

$$\left.\begin{aligned} c &= [\![\, \Psi - \mu\rho - \mathbf{T}\cdot\mathbf{E} \,]\!], \\ q &= [\![\rho]\!] V - [\![\boldsymbol{\jmath}]\!]\cdot\mathbf{n}, \end{aligned}\right\}$$

where $[\![f]\!]$ designates the jump in a bulk field f across $\mathcal{S}$. The basic equations consist of the interface conditions (1.5) and (1.6) with these values of c and q, the standard force balance across the interface, and the standard bulk field equations describing mass transport in an elastically strained material.

Interface-controlled evolution with surface diffusion

If we allow for surface mass transport, but neglect deformation and mass transport in bulk, then, assuming that $\beta(\mathbf{n}) \equiv 0$, while k, $[\![\rho]\!]$, and $[\![\Psi]\!]$ are constant, then (1.5) and (1.6) reduce to the single evolution equation

$$\begin{aligned} [\![\rho]\!]^2 V = -k\,\Delta_{\mathcal{S}} \Bigg\{ &\left[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\right]\cdot\mathbb{L}\Big] \\ &- \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big]\Bigg\}. \end{aligned} \tag{1.7}$$

In contast to (1.5) with c constant, this equation is sixth-order parabolic.

Interface between elastic phases without mass transport

If we neglect mass transport completely, but allow for elastic bulk phases, we arrive at the interface condition

$$\begin{aligned} [\![\, \Psi - \mathbf{T}\cdot\mathbf{E} \,]\!] = \beta(\mathbf{n})V &- \left[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\right]\cdot\mathbb{L} \\ &+ \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] + \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big]. \end{aligned} \tag{1.8}$$

The classical equilibrium condition in the absence of interfacial structure is the "Maxwell relation" $[\![\, \Psi - \mathbf{T}\cdot\mathbf{E} \,]\!] = 0$. The kinetic term $\beta(\mathbf{n})V$ was introduced by Heudug & Lehner [1985], Truskinovsky [1987], and Abeyaratne & Knowles [1990]; the term involving $\psi_0(\mathbf{n})$ was added by Gurtin & Struthers[1990] (cf. Gurtin [2000]). The condition (1.8) is supplementary to the more standard force balances in bulk and across the interface and the elastic stress-strain relations in bulk.

[11] Cf. (6.1).

[12] Cf. Gurtin & Voorhees [1993, 1996, 1998] and Gurtin [1995, 2000].

Interface between an elastic film and a vapor deposition source

We also consider an elastic film that is bonded to a rigid substrate and that has free surface $\mathcal{S}$ exposed to a vapor reservoir whose sole purpose is to supply atoms to $\mathcal{S}$.[13] We consider mass transport on $\mathcal{S}$, but neglect it in the film, and we allow for a mismatch between the lattice parameters of the film and those of the rigid substrate. We neglect all other interactions of the vapor with the film surface. Specifically, we assume that the vapor exerts neither standard nor configurational forces on the film surface. Then $\mathbf{T}^-\mathbf{n} = \mathbf{0}$ on $\mathcal{S}$ and the remaining equations on $\mathcal{S}$, (1.5) and (1.6), take the form

$$\begin{aligned}\beta(\mathbf{n})V = &\Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L}\\ &- \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big] + \mu^-\rho - \Psi^- \qquad (1.9)\end{aligned}$$

and

$$\rho V = \operatorname{div}_{\mathcal{S}}\big(k(\mathbf{n})\nabla_{\mathcal{S}}\mu^-\big) + \alpha(\mathbf{n})(\mu^+ - \mu^-), \qquad (1.10)$$

where μ^+ and μ^- are the chemical potentials in the vapor and film at $\mathcal{S}$, Ψ^- is the film strain-energy at $\mathcal{S}$, and ρ is the constant atomic density in the film. These equations are augmented by the elastic field equations (with misfit strain) in the film and the boundary condition $\mathbf{u} = \mathbf{0}$ at the interface between the film and the substrate.

If we assume that $k(\mathbf{n}) \equiv 0$, that the strain energy at the interface is negligible, and that μ^+ is constant, then these relations combine to form an equation identical in structure to the purely mechanical interface-controlled evolution equation (1.5) with c constant, but with $\beta(\mathbf{n})$ replaced by $\beta(\mathbf{n}) + \rho^2/\alpha(\mathbf{n})$ and c replaced by $\mu^+\rho$.

2 Kinematics

2.1 Surfaces

Consider a smooth surface $\mathcal{S}$ in $\mathbb{R}^3$ oriented by a choice of smooth *unit normal field* $\mathbf{n}$. In continuum mechanics, tensors are generally linear transformations from $\mathbb{R}^3$ into itself, but of interest here are tensor fields $\mathbb{B}$ on $\mathcal{S}$ with the property that, at each $\mathbf{x}$ in $\mathcal{S}$, $\mathbb{B}(\mathbf{x})$ is a linear transformation from the tangent space at $\mathbf{x}$ into $\mathbb{R}^3$. These two notions of a tensor field may be reconciled by extending $\mathbb{B}(\mathbf{x})$ to vectors normal to $\mathcal{S}$ with the requirement that $\mathbb{B}(\mathbf{x})$ annihilate such vectors. Precisely, a *superficial tensor field* $\mathbb{B}$ on $\mathcal{S}$ is a function that associates with each $\mathbf{x}$ in $\mathcal{S}$ a linear transformation $\mathbb{B}$ from $\mathbb{R}^3$ into $\mathbb{R}^3$ such that

$$\mathbb{B}\mathbf{n} = \mathbf{0}. \qquad (2.1)$$

We will refer to a superficial tensor field $\mathbb{B}$ as *tangential* if, in addition,

$$\mathbb{B}^\top\mathbf{n} = \mathbf{0}. \qquad (2.2)$$

An example of a tangential superficial tensor field is the *projection* onto $\mathcal{S}$:

$$\mathbb{P} = \mathbf{1} - \mathbf{n}\otimes\mathbf{n}. \qquad (2.3)$$

The *tangential component* $\mathbb{T}_{\tan}$ of a superficial tensor field $\mathbb{T}$ is defined by

$$\mathbb{T}_{\tan} = \mathbb{P}\mathbb{T}\mathbb{P}.$$

[13] Cf. Spencer, Voorhees & Davis [1991, 1993], Guyer & Voorhees [1996, 1998] and Spencer, Voorhees & Tersoff [2000] who investigate the morphological stability of epitaxially strained single-component and alloy thin films in the presence of surface diffusion and isotropic surface tension. See also Zhang & Bower [1999, 2001], who examine shape changes of strained islands on lattice-mismatched substrates due to surface diffusion in the presence of both isotropic and anisotropic surface energies. None of the above allow for a dependence of the interfacial free energy on curvature.

Then, for $\mathbb{B}$ a tangential tensor field, $\mathbb{B} = \mathbb{B}_{\tan}$, and hence

$$\mathbb{B} \cdot \mathbb{T} = (\mathbb{P}\mathbb{B}\mathbb{P}) \cdot \mathbb{T} = \mathbb{B} \cdot (\mathbb{P}\mathbb{T}\mathbb{P}) = \mathbb{B} \cdot \mathbb{T}_{\tan}\,. \tag{2.4}$$

The *surface gradient* $\nabla_{\mathcal{S}}$ is defined by the chain-rule; that is, for $\varphi(\mathbf{x})$ a superficial[14] scalar field, $\mathbf{g}(\mathbf{x})$ a superficial vector field, and $\mathbf{z}(\lambda)$ an arbitrary curve on $\mathcal{S}$,

$$\frac{d}{d\lambda}\varphi(\mathbf{z}(\lambda)) = \nabla_{\mathcal{S}}\varphi(\mathbf{z}(\lambda)) \cdot \frac{d\mathbf{z}(\lambda)}{d\lambda}, \qquad \frac{d}{d\lambda}\mathbf{g}(\mathbf{z}(\lambda)) = \nabla_{\mathcal{S}}\mathbf{g}(\mathbf{z}(\lambda))\frac{d\mathbf{z}(\lambda)}{d\lambda}.$$

Since $d\mathbf{z}/d\lambda$ is tangent to $\mathcal{S}$, this defines $\nabla_{\mathcal{S}}\mathbf{g}$ only on vectors tangent to $\mathcal{S}$, but in accord with (2.1), $\nabla_{\mathcal{S}}\mathbf{g}$ is extended by requiring that $(\nabla_{\mathcal{S}}\mathbf{g})\mathbf{n} = \mathbf{0}$. Thus $\nabla_{\mathcal{S}}\varphi$ is a tangential vector field, while $\nabla_{\mathcal{S}}\mathbf{g}$ is a superficial tensor field. The *surface divergence* of $\mathbf{g}$ is then defined by

$$\mathrm{div}_{\mathcal{S}}\mathbf{g} = \mathrm{tr}\,\nabla_{\mathcal{S}}\mathbf{g}, \tag{2.5}$$

while the surface divergence $\mathrm{div}_{\mathcal{S}}\mathbb{B}$ of a superficial tensor field is the superficial vector field defined through the identity

$$\mathbf{a} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{B} = \mathrm{div}_{\mathcal{S}}(\mathbb{B}^{\top}\mathbf{a}) \tag{2.6}$$

for all *constant* vectors $\mathbf{a}$. The operator $\Delta_{\mathcal{S}}$ defined on superficial scalar fields φ by

$$\Delta_{\mathcal{S}}\varphi = \mathrm{div}_{\mathcal{S}}(\nabla_{\mathcal{S}}\varphi) \tag{2.7}$$

is generally referred to as the *Laplace-Beltrami operator*.

A smooth superficial field can always be extended smoothly to a (three-dimensional) neighborhood of any given point $\mathbf{x}$ of $\mathcal{S}$. Such local extensions can be used to express $\nabla_{\mathcal{S}}$ in terms of the standard "three-dimensional gradient" ∇; e.g.,

$$\nabla_{\mathcal{S}}\varphi = \mathbb{P}\nabla\varphi, \qquad \nabla_{\mathcal{S}}\mathbf{g} = \nabla\mathbf{g}\mathbb{P}, \tag{2.8}$$

so that, in particular,

$$\mathbf{g}(\mathbf{x}) = \mathbf{x} \quad \Rightarrow \quad \nabla_{\mathcal{S}}\mathbf{g} = \mathbb{P}. \tag{2.9}$$

Surface gradients computed in this manner are independent of the choice of local extensions and are hence intrinsic to $\mathcal{S}$. In addition, they allow one to make computations using standard cartesian tensor analysis,[15] without resort to Christoffel symbols, etc.; i.e., for φ, a superficial scalar field, $\mathbf{g}$ a superficial vector field, and $\mathbb{B}$ a superficial tensor field

$$(\nabla_{\mathcal{S}}\varphi)_i = \varphi_{,j}P_{ji}, \quad (\nabla_{\mathcal{S}}\mathbf{g})_{ij} = g_{i,k}P_{kj}. \tag{2.10}$$

and

$$\mathrm{div}_{\mathcal{S}}\mathbf{g} = g_{i,k}P_{ik}, \quad (\mathrm{div}_{\mathcal{S}}\mathbb{B})_i = B_{ij,k}P_{jk}. \tag{2.11}$$

We write

$$\mathbb{L} = -\nabla_{\mathcal{S}}\mathbf{n} \tag{2.12}$$

for the *curvature tensor* and

$$K = \mathrm{tr}\,\mathbb{L} = -\mathrm{div}_{\mathcal{S}}\mathbf{n} \tag{2.13}$$

for the *total curvature* (twice the mean curvature). As is well known, $\mathbb{L}$ is *tangential* and *symmetric*.

The *identities*

$$\left.\begin{aligned} \mathrm{div}_{\mathcal{S}}\mathbb{P} &= K\mathbf{n}, \\ \mathrm{div}_{\mathcal{S}}\mathbb{L} &= \nabla_{\mathcal{S}}K + |\mathbb{L}|^2\mathbf{n}, \\ \mathrm{div}_{\mathcal{S}}\mathrm{div}_{\mathcal{S}}\mathbb{L} &= \Delta_{\mathcal{S}}K - |\mathbb{L}|^2K \end{aligned}\right\} \tag{2.14}$$

[14] A superficial field is one defined on $\mathcal{S}$.

[15] $\varphi_{,i}$ denotes $\partial\varphi/\partial x_i$, summation over repeated indices is implied, and so forth.

are useful, as is the following relation, valid for $\mathbb{B}$ a tangential tensor field,

$$\mathbf{n} \cdot \mathrm{div}_{\mathcal{S}} \mathbb{B} = \mathbb{B} \cdot \mathbb{L}. \tag{2.15}$$

The result $(2.14)_1$ follows from (2.3) and (2.13), $(2.14)_2$ is verified in Appendix B , $(2.14)_3$ follows from $(2.14)_2$, and (2.15) follows upon taking the divergence of $\mathbb{B}^{\top}\mathbf{n} = \mathbf{0}$.

Let $\mathcal{A}$ denote an arbitrary subsurface of $\mathcal{S}$, and let $\boldsymbol{\nu}$ denote the *outward unit normal* to the boundary curve $\partial\mathcal{A}$ of $\mathcal{A}$, so that $\boldsymbol{\nu}$ is *tangent* to the surface $\mathcal{S}$ and *normal* to the curve $\partial\mathcal{A}$. The surface divergence theorem, for $\mathbb{B}$ a superficial tensor field and $\mathbf{g}$ a tangential vector field, can then be stated as follows:

$$\int_{\partial\mathcal{A}} \mathbb{B}\boldsymbol{\nu}\, ds = \int_{\mathcal{A}} \mathrm{div}_{\mathcal{S}} \mathbb{B}\, da, \qquad \int_{\partial\mathcal{A}} \mathbf{g} \cdot \boldsymbol{\nu}\, ds = \int_{\mathcal{A}} \mathrm{div}_{\mathcal{S}} \mathbf{g}\, da. \tag{2.16}$$

2.2 Evolving surfaces

Assume now that $\mathcal{S} = \mathcal{S}(t)$ evolves smoothly with time t, so that the term *superficial field* now connotes a field described on $\mathcal{S}(t)$ for all t. The *intrisic* velocity of $\mathcal{S}(t)$ is its (scalar) *normal velocity* $V(\mathbf{x}, t)$ in the direction of its unit normal field $\mathbf{n}(\mathbf{x}, t)$. We refer to any superficial vector field $\mathbf{v}(\mathbf{x}, t)$ that satisfies

$$\mathbf{v} \cdot \mathbf{n} = V$$

as a *velocity field* for $\mathcal{S}$, and we refer to the field $\mathbf{v}_{\mathrm{ext}}$ defined by

$$\mathbf{v} = V\mathbf{n} + \mathbf{v}_{\mathrm{ext}}, \qquad \mathbf{n} \cdot \mathbf{v}_{\mathrm{ext}} = 0 \tag{2.17}$$

as the *extrinsic velocity* of $\mathcal{S}$ corresponding to $\mathbf{v}$.[16]

Let $\mathbf{v}$ be a velocity field for $\mathcal{S}$. Then for φ a superficial field, $\mathring{\varphi}$, the *time-derivative* of φ following $\mathcal{S}$ as described by $\mathbf{v}$, is defined as follows: given any time t_0 and any point $\mathbf{x}_0$ on $\mathcal{S}(t_0)$, let $\mathbf{y}(t)$ denote the unique solution of

$$\dot{\mathbf{y}}(t) = \mathbf{v}(\mathbf{y}(t), t), \qquad \mathbf{y}(t_0) = \mathbf{x}_0;$$

then

$$\mathring{\varphi}(\mathbf{x}_0, t_0) = \Big[\frac{d}{dt}\varphi(\mathbf{y}(t), t)\Big]_{t=t_0}. \tag{2.18}$$

The field $\mathring{\varphi}$ is referred to as the *normal time-derivative* of φ following $\mathcal{S}$ when the velocity field for $\mathcal{S}$ is its *intrinsic velocity*

$$\mathbf{v} = V\mathbf{n}.$$

The following important identities are satisfied by the normal time-derivative of $\mathbf{n}$:

$$\left.\begin{aligned} \mathring{\mathbf{n}} &= -\nabla_{\mathcal{S}} V, \\ (\nabla_{\mathcal{S}} \mathring{\mathbf{n}})_{\mathrm{tan}} &= -(\mathring{\mathbb{L}})_{\mathrm{tan}} + V\,\mathbb{L}^2. \end{aligned}\right\} \tag{2.19}$$

The first of these is standard; the second is established in Appendix B.

Let $\mathcal{A} = \mathcal{A}(t)$ denote an arbitrary evolving (bounded, connected) subsurface of $\mathcal{S}$ with $\boldsymbol{\nu}$ the outward unit normal to $\partial\mathcal{A}$. The *intrinsic velocities* for the evolution of $\partial\mathcal{A}(t)$ are its scalar velocity $U(\mathbf{x}, t)$ in the direction of $\boldsymbol{\nu}$ and the normal velocity $V(\mathbf{x}, t)$ of $\mathcal{S}(t)$; and as before, we refer to any field $\mathbf{q}(\mathbf{x}, t)$ on $\partial\mathcal{A}(t)$ of the form

$$\mathbf{q} = U\boldsymbol{\nu} + V\mathbf{n} + \mathbf{q}_{\mathrm{ext}}, \qquad \boldsymbol{\nu} \cdot \mathbf{q}_{\mathrm{ext}} = \mathbf{n} \cdot \mathbf{q}_{\mathrm{ext}} = 0, \tag{2.20}$$

[16] When the surface is parametrized by a mapping $\mathbf{x} = \mathbf{X}(\alpha_1, \alpha_2, t)$, with α_1 and α_2 scalar parameters, then $\mathbf{v}(\mathbf{x}, t) = \partial\mathbf{X}(\alpha_1, \alpha_2, t)/\partial t$ defines a velocity field with $\mathbf{v}_{\mathrm{ext}}$ generally nonzero. An analogous assertion applies to velocity fields $\mathbf{q}$ for $\partial\mathcal{A}$ (cf. (2.20)).

as a *velocity field* for $\partial\mathcal{A}$, with $\mathbf{q}_{\text{ext}}$ its corresponding *extrinsic velocity*.

Let $\mathbf{q}$ be a velocity field for $\partial\mathcal{A}$ and let φ be a field on $\partial\mathcal{A}$. Then, guided by (2.18), we define the *time-derivative* $\overset{\square}{\varphi}$ *following* $\partial\mathcal{A}$ *as described by* $\mathbf{q}$ as follows: given any t_0 and any $\mathbf{x}_0$ on $\partial\mathcal{A}(t_0)$, let $\mathbf{z}(t)$ denote the unique solution of

$$\dot{\mathbf{z}}(t) = \mathbf{q}(\mathbf{z}(t), t), \qquad \mathbf{z}(t_0) = \mathbf{x}_0;$$

then

$$\overset{\square}{\varphi}(\mathbf{x}_0, t_0) = \Big[\frac{d}{dt}\varphi(\mathbf{z}(t), t)\Big]_{t=t_0}. \tag{2.21}$$

We emphasize that the derivative $\overset{\square}{\varphi}$ depends on the choice of velocity field $\mathbf{q}$ for $\partial\mathcal{A}$. The following identities, in which $\mathring{\varphi}$ and $\mathring{\mathbf{n}}$ are *normal* time-derivatives following $\mathcal{S}$, render this dependence explicit:

$$\left.\begin{aligned} \overset{\square}{\varphi} &= \mathring{\varphi} + \mathbf{q}\cdot\nabla_{\mathcal{S}}\varphi = \mathring{\varphi} + (U\boldsymbol{\nu} + \mathbf{q}_{\text{ext}})\cdot\nabla_{\mathcal{S}}\varphi, \\ \overset{\square}{\mathbf{n}} &= \mathring{\mathbf{n}} - \mathbb{L}\mathbf{q} = \mathring{\mathbf{n}} - \mathbb{L}(U\boldsymbol{\nu} + \mathbf{q}_{\text{ext}}). \end{aligned}\right\} \tag{2.22}$$

These identities are established in Appendix B.

Also important is the following *transport theorem*:[17] for φ a smooth superficial scalar field and $\mathring{\varphi}$ its *normal* time-derivative following $\mathcal{S}$,

$$\frac{d}{dt}\int_{\mathcal{A}(t)} \varphi\, da = \int_{\mathcal{A}(t)} (\mathring{\varphi} - \varphi K V)\, da + \int_{\partial\mathcal{A}(t)} \varphi U\, ds. \tag{2.23}$$

2.3 Changes in frame

We assume that the underlying frame of reference is a *rest frame*. Consider a given time t_0 — the *observation time* — and a new frame of reference that *coincides* with the rest frame at time t_0, but is otherwise arbitrary. Then the points $\mathbf{x}^*$ of $\mathbb{R}^3$ as viewed in the *nonquiescent* frame are related to the points $\mathbf{x}$ in the rest frame through a time-dependent isometry

$$\mathbf{x}^* = \mathbf{a}(t) + \mathbf{Q}(t)\mathbf{x} \tag{2.24}$$

with $\mathbf{a}(t)$ a vector and $\mathbf{Q}(t)$ an orthogonal tensor such that

$$\mathbf{a}(t_0) = \mathbf{0}, \qquad \mathbf{Q}(t_0) = \mathbf{1}. \tag{2.25}$$

Then $\dot{\mathbf{Q}}(t_0)$ is a skew tensor and, defining vectors $\boldsymbol{\lambda}$ and $\boldsymbol{\omega}$ through

$$\boldsymbol{\lambda} = \dot{\mathbf{a}}(t_0), \qquad \dot{\mathbf{Q}}(t_0) = \boldsymbol{\omega}\times, \tag{2.26}$$

we may write the velocity of the nonquiescent frame relative to the rest frame (at the observation time) in the form

$$\mathbf{w}(\mathbf{x}) = \boldsymbol{\lambda} + \boldsymbol{\omega}\times\mathbf{x}.$$

Consider now an evolving subsurface $\mathcal{A}$ (of $\mathcal{S}$) and velocity fields $\mathbf{q}$ for $\partial\mathcal{A}$ and $\mathbf{v}$ for $\mathcal{S}$. Under the change in frame these fields transform to

$$\mathbf{q}^* = \mathbf{q} + \mathbf{w}, \qquad \mathbf{v}^* = \mathbf{v} + \mathbf{w}. \tag{2.27}$$

Consider next the time derivative $\overset{\square}{\mathbf{n}}$ following $\partial\mathcal{A}$ as described by $\mathbf{q}$. Since

$$\mathbf{n}^*(\mathbf{x}^*, t) = \mathbf{Q}(t)\mathbf{n}(\mathbf{x}, t),$$

for $\mathbf{z}(t)$ as in (2.21) and $\mathbf{z}^*(t) = \mathbf{a}(t) + \mathbf{Q}(t)\mathbf{z}(t)$,

$$\mathbf{n}^*(\mathbf{z}^*(t), t) = \mathbf{Q}(t)\mathbf{n}(\mathbf{z}(t), t),$$

and therefore, by (2.25) and (2.26),

$$\overset{\square}{\mathbf{n}}{}^* = \overset{\square}{\mathbf{n}} + \boldsymbol{\omega}\times\mathbf{n} \tag{2.28}$$

at the observation time.

[17] Cf. Gurtin, Struthers and Williams [1989].

3 Superficial control volumes

We consider an evolving surface $\mathcal{S} = \mathcal{S}(t)$ and view the ambient space on one or both sides of $\mathcal{S}$ as a fixed immobile material structure such as a macroscopic manifestation of an atomic lattice through which a species of mobile atoms is allowed to diffuse. Consider an *arbitrary* evolving subsurface $\mathcal{A} = \mathcal{A}(t)$ of $\mathcal{S}$. Our discusion of basic laws views $\mathcal{A}$ as a *superficial control volume* of infinitesimal thickness containing a portion of $\mathcal{S}$, a view that allows us to isolate $\mathcal{S}$ from the bulk material abutting it: the interaction of the bulk material with $\mathcal{S}$ manifests itself through the force exerted by the bulk material per unit area on $\mathcal{S}$ and the flux of mobile atoms per unit area that the bulk material supplies to — or removes from — $\mathcal{S}$. This view allows us to consider the physics of the surface without regard to the particular physical processes (within a large class) engaged in by the bulk material. This view also allows us to capture the physics of the interface itself, as we allow for: (i) stresses that act within $\mathcal{S}$ and exert forces and couples on $\mathcal{A}$ across its boundary curve $\partial\mathcal{A}$; (ii) internal forces and couples per unit area that serve to hold in place the material structure currently situated on $\mathcal{S}$; (iii) mobile atoms that flow through $\mathcal{S}$ and affect the mass of $\mathcal{A}$ through their flux across $\partial\mathcal{A}$.

The ambient space should be viewed as a reference configuration; if the ambient physical structure deforms, we assume that this deformation does not result in forces within the interface. *The forces associated with the interface are therefore configurational; they perform work as material structure is added to — and removed from — the superficial control volume* $\mathcal{A}$. In this regard the velocity fields $\mathbf{v}$ and $\mathbf{q}$ for $\mathcal{S}$ and $\partial\mathcal{A}$ introduced in §2.2 represent rates at which material structure is added to — and removed from — $\mathcal{A}$ as it evolves.

4 Balance of mass

We allow for a flow of mobile atoms within the surface and to the surface from the bulk material, but we assume that *the atomic density within the surface is negligible* (see footnote 10).

Consider an *arbitrary* superficial control volume $\mathcal{A} = \mathcal{A}(t)$ with U the normal velocity of $\partial\mathcal{A}$ in the direction of the outward unit normal $\boldsymbol{\nu}$ to $\partial\mathcal{A}$. *Balance of mass* for the mobile species of atoms is the requirement that

$$-\int_{\partial\mathcal{A}} \mathbf{h}\cdot\boldsymbol{\nu}\,ds + \int_{\mathcal{A}} q\,da = 0. \tag{4.1}$$

in which the underlying superficial fields[18] have the following physical interpretation:

$\mathbf{h}$	superficial atomic flux,
q	external atomic supply.

The *tangential* vector field $\mathbf{h}$ represents the flux of atoms within the surface, while q represents atoms supplied to the surface by the bulk material. The surface divergence theorem applied to (4.1) implies that

$$\int_{\mathcal{A}} (-\mathrm{div}_{\mathcal{S}}\mathbf{h} + q)\,da = 0,$$

and, since $\mathcal{A}$ was arbitrarily chosen, this yields the *local mass balance*

$$\mathrm{div}_{\mathcal{S}}\mathbf{h} = q. \tag{4.2}$$

[18]The term *superficial field* connotes a field described on $\mathcal{S}(t)$ for all t.

5 Free energy, working, and the energy imbalance

5.1 Energy imbalance

We base the theory on an energy imbalance which represents a mechanical version of the second law of thermodynamics; this imbalance asserts that, for each superficial control volume $\mathcal{A}$, the free energy of $\mathcal{A}$ increase at a rate not faster than the rate at which work is performed on $\mathcal{A}$ plus the rate at which energy is carried into $\mathcal{A}$ through mass transport. To state this imbalance precisely, let $\mathbf{v}$ be a velocity field for $\mathcal{S}$ and $\mathbf{q}$ a velocity field for $\partial\mathcal{A}$. Let $\overset{\square}{\mathbf{n}}$ denote the time derivative of the surface normal $\mathbf{n}$ following $\partial\mathcal{A}$ as described by $\mathbf{q}$. Then the *energy imbalance* expressed relative to a *rest frame* is the assertion that, for each superficial control volume $\mathcal{A}$,

$$\underbrace{\frac{d}{dt}\int_{\mathcal{A}}\psi\,da}_{\substack{\text{free energy}\\ \text{of } \mathcal{A}}} \leq \underbrace{\int_{\partial\mathcal{A}}\big(\mathbb{C}\boldsymbol{\nu}\cdot\mathbf{q}+\mathbb{M}\boldsymbol{\nu}\cdot\overset{\square}{\mathbf{n}}\big)\,ds+\int_{\mathcal{A}}(\mathbf{c}\cdot\mathbf{v}+\mathbf{f}\cdot\mathbf{0}+\mathbf{m}\cdot\mathbf{0})\,da}_{\text{rate at which work is performed on } \mathcal{A}} \underbrace{-\int_{\partial\mathcal{A}}\mu\mathbf{h}\cdot\boldsymbol{\nu}\,ds+\int_{\mathcal{A}}\mu q\,da}_{\substack{\text{energy carried into } \mathcal{A}\\ \text{by atomic transport}}}, \quad (5.1)$$

where the following physical interpretation applies to the underlying fields:

ψ	free energy density,
μ	chemical potential,
$\mathbb{C}$	configurational stress,
$\mathbb{M}$	configurational couple stress,
$\mathbf{f}$	internal configurational force,
$\mathbf{m}$	internal configurational couple,
$\mathbf{c}$	external configurational force.

Here $\mathbb{C}$ and $\mathbb{M}$ are superficial tensor fields with $\mathbb{C}\boldsymbol{\nu}$ and $\mathbb{M}\boldsymbol{\nu}$ the force and couple exerted across $\partial\mathcal{A}$. Note that $\mathbb{C}\boldsymbol{\nu}$ performs work over the velocity $\mathbf{q}$ at which $\partial\mathcal{A}$ migrates through the ambient material structure, while $\mathbb{M}\boldsymbol{\nu}$ performs work over the temporal derivative $\overset{\square}{\mathbf{n}}$ following this migration, an observation that underlines the configurational nature of $\mathbb{C}$ and $\mathbb{M}$. Similarly, $\mathbf{c}$ represents the configurational force, per unit area, exerted on $\mathcal{A}$ by the bulk material; this force performs work over the velocity $\mathbf{v}$ that describes the migration of $\mathcal{S}$. Finally, $\mathbf{f}$ and $\mathbf{m}$ represent internal forces and couples, measured per unit area, that serve to hold, in place, the material structure instantaneously situated on $\mathcal{S}$; since the structure itself is immobile (relative to a rest frame), $\mathbf{f}$ and $\mathbf{m}$ perform no work, which explains our use of $\mathbf{0}$ as a "conjugate velocity".

The quantity

$$\mathcal{W}(\mathcal{A})=\int_{\partial\mathcal{A}}\big(\mathbb{C}\boldsymbol{\nu}\cdot\mathbf{q}+\mathbb{M}\boldsymbol{\nu}\cdot\overset{\square}{\mathbf{n}}\big)\,ds+\int_{\mathcal{A}}(\mathbf{c}\cdot\mathbf{v}+\mathbf{f}\cdot\mathbf{0}+\mathbf{m}\cdot\mathbf{0})\,da, \quad (5.2)$$

which we term the *working,* represents the rate at which work is performed on superficial control volumes $\mathcal{A}$. By (2.17), (2.20), and (2.22), we can rewrite $\mathcal{W}(\mathcal{A})$ as the sum

$$\mathcal{W}(\mathcal{A})=\underbrace{\int_{\partial\mathcal{A}}\big(V\mathbf{n}\cdot\mathbb{C}\boldsymbol{\nu}+U\boldsymbol{\nu}\cdot(\mathbb{C}-\mathbb{L}\mathbb{M})\boldsymbol{\nu}+\mathbb{M}\boldsymbol{\nu}\cdot\mathring{\mathbf{n}}\big)+\int_{\mathcal{A}}V\mathbf{c}\cdot\mathbf{n}\,da}_{\text{intrinsic component of } \mathcal{W}(\mathcal{A})} + \underbrace{\int_{\partial\mathcal{A}}(\mathbb{C}-\mathbb{L}\mathbb{M})\boldsymbol{\nu}\cdot\mathbf{q}_{\text{ext}}\,ds+\int_{\mathcal{A}}\mathbf{c}\cdot\mathbf{v}_{\text{ext}}\,da}_{\text{extrinsic component of } \mathcal{W}(\mathcal{A})} \quad (5.3)$$

of an intrinsic component and an extrinsic component that depends on the choice of velocity fields $\mathbf{v}$ and $\mathbf{q}$ used to describe the evolution of $\mathcal{A}$.

Consider the change in frame described in §2.3. We assume that, at the time of observation, the fields $\mathbb{C}$, $\mathbb{M}$, $\mathbf{f}$, $\mathbf{m}$, and $\mathbf{c}$ are *invariant* (cf. (2.25)).[19] Thus in the new frame at this time, $\mathbb{C}\boldsymbol{\nu}$, $\mathbb{M}\boldsymbol{\nu}$, and $\mathbf{c}$ should perform work over the transformed fields $\mathbf{q}^*$,$\overset{\square}{\mathbf{n}}{}^*$, and $\mathbf{v}^*$. Further, since the material as observed in the new frame is both translating and rotating, the internal fields $\mathbf{f}$ and $\mathbf{m}$ now perform work: $\mathbf{f}$ over the velocity $\mathbf{w}(\mathbf{x}) = \boldsymbol{\lambda} + \boldsymbol{\omega}\times\mathbf{x}$ of the nonquiescent frame; $\mathbf{m}$ over the apparent temporal change $\boldsymbol{\omega}\times\mathbf{n}$ of $\mathbf{n}$ due to the spin of the nonquiescent frame. We therefore assume that the working as measured in the new frame is given by

$$\mathcal{W}^*(\mathcal{A}) = \int_{\partial\mathcal{A}} \big(\mathbb{C}\boldsymbol{\nu}\cdot\mathbf{q}^* + \mathbb{M}\boldsymbol{\nu}\cdot\overset{\square}{\mathbf{n}}{}^*\big)\, ds + \int_{\mathcal{A}} \big(\mathbf{c}\cdot\mathbf{v}^* + \mathbf{f}\cdot\mathbf{w} + \mathbf{m}\cdot(\boldsymbol{\omega}\times\mathbf{n})\big)\, ds, \tag{5.4}$$

or equivalently, by (2.27), (2.28), and the fact that $\boldsymbol{\lambda}$ and $\boldsymbol{\omega}$ are constant,

$$\begin{aligned}\mathcal{W}^*(\mathcal{A}) = \mathcal{W}(\mathcal{A}) &+ \boldsymbol{\lambda}\cdot\left[\int_{\partial\mathcal{A}} \mathbb{C}\boldsymbol{\nu}\, ds + \int_{\mathcal{A}} (\mathbf{c}+\mathbf{f})\, da\right] + \\ &+ \boldsymbol{\omega}\cdot\left[\int_{\partial\mathcal{A}} \big(\mathbf{x}\times\mathbb{C}\boldsymbol{\nu} + \mathbf{n}\times\mathbb{M}\boldsymbol{\nu}\big)\, ds + \int_{\mathcal{A}} \big(\mathbf{x}\times(\mathbf{c}+\mathbf{f}) + \mathbf{n}\times\mathbf{m}\big)\, da\right].\end{aligned} \tag{5.5}$$

All results concerning the couple-fields $\mathbb{M}$ and $\mathbf{m}$ derive from the basic forms (5.2) and (5.4) of the working. In these expressions, $\mathbb{M}$ is conjugate to the field $\overset{\square}{\mathbf{n}}$ (and its transform), $\mathbf{m}$ to the field $\boldsymbol{\omega}\times\mathbf{n}$; since these fields are tangential, we may assume without loss in generality that $\mathbb{M}$ is a *tangential* tensor field and $\mathbf{m}$ is a *tangential* vector field:

$$\mathbb{M}^\top\mathbf{n} = \mathbf{0}, \qquad \mathbf{m}\cdot\mathbf{n} = 0. \tag{5.6}$$

The basic mechanical relations of the theory — the configurational force and moment balances — as well as the explicit structure of the stress field $\mathbb{C}$ are consequences of two fundamental *hypotheses*:

(i) (*Frame-indifference*) Given any superficial control volume $\mathcal{A}$ and any change in frame, $\mathcal{W}^*(\mathcal{A}) = \mathcal{W}(\mathcal{A})$.

(ii) (*Intrinsicality*) Given any such $\mathcal{A}$, $\mathcal{W}(\mathcal{A})$ is independent of the choice of velocity fields $\mathbf{v}$ and $\mathbf{q}$ used to describe the evolution of $\mathcal{A}$ and $\partial\mathcal{A}$.

Clearly, (i) and (ii) imply the frame-indifference and intrinsicality of the energy imbalance itself. Conversely, because of the linearity of (5.3) in $\mathbf{v}_{\text{ext}}$ and $\mathbf{q}_{\text{ext}}$ and that of (5.5) in $\boldsymbol{\lambda}$ and $\boldsymbol{\omega}$, indifference and intrinsicality of the energy imbalance imply (i) and (ii).

6 Intrinsicality. Structure of the configurational stress

Intrinsicality is equivalent to the requirement that the extrinsic component of $\mathcal{W}(\mathcal{A})$ — as expessed in (5.3) — vanish. Thus, writing $\mathbf{q}_{\text{ext}}$, which is tangent to $\partial\mathcal{A}$, in the form

$$\mathbf{q}_{\text{ext}} = W\mathbf{t}, \quad \mathbf{t} = \boldsymbol{\nu}\times\mathbf{n},$$

we must have

$$\int_{\partial\mathcal{A}} W\mathbf{t}\cdot(\mathbb{C} - \mathbb{L}\mathbb{M})\boldsymbol{\nu}\, ds + \int_{\mathcal{A}} \mathbf{c}\cdot\mathbf{v}_{\text{ext}}\, da = 0,$$

[19] Recall that the frames are coincident at the time of observation. We assume, in addition, that the fields ψ, μ and $\mathbf{h}$ are invariant.

an identity that must hold for any superficial scalar field W and any vector field $\mathbf{v}_{\text{ext}}$ tangent to $\mathcal{S}$. Thus, since $\mathcal{A}$ is arbitrary: (i) the field $\mathbf{c}$ must be normal to $\mathcal{S}$ and hence of the explicit form

$$\mathbf{c} = c\mathbf{n}; \tag{6.1}$$

and (ii) the field $\mathbb{C}$ must satisfy

$$\mathbf{t} \cdot (\mathbb{C} - \mathbb{L}\mathbb{M})\boldsymbol{\nu} = 0$$

for all orthogonal unit vector fields $\boldsymbol{\nu}$ and $\mathbf{t}$ tangent to $\mathcal{S}$. It therefore follows from a theorem of Gurtin and Struthers[20] that the stress $\mathbb{C}$ must have the explicit form

$$\mathbb{C} = \sigma\mathbb{P} + \mathbf{n} \otimes \boldsymbol{\tau} + \mathbb{L}\mathbb{M} \tag{6.2}$$

in which $\boldsymbol{\tau}$ is the *tangential* vector field

$$\boldsymbol{\tau} = \mathbb{C}^{\top}\mathbf{n}. \tag{6.3}$$

Since the normal $\boldsymbol{\nu}$ to $\partial\mathcal{A}$ is tangential to $\mathcal{S}$, (6.2) implies that

$$\mathbb{C}\boldsymbol{\nu} = \sigma\boldsymbol{\nu} + \mathbb{L}\mathbb{M}\boldsymbol{\nu} + (\boldsymbol{\tau} \cdot \boldsymbol{\nu})\mathbf{n}; \tag{6.4}$$

the traction $\mathbb{C}\boldsymbol{\nu}$ across $\partial\mathcal{A}$ therefore consists of: (i) a classical uniform tension $\sigma\boldsymbol{\nu}$ supplemented by a *tangential* traction $\mathbb{L}\mathbb{M}\boldsymbol{\nu}$ arising from the couple-stess $\mathbb{M}$ and generally giving rise to a tangential shearing traction tangent to $\partial\mathcal{A}$; and (ii) a shearing traction $(\boldsymbol{\tau} \cdot \boldsymbol{\nu})\mathbf{n}$ normal to the surface. We refer to σ as the *surface tension* and to $\boldsymbol{\tau}$ as the (normal) *surface shear*.

Finally, note that, by (6.1) and (6.2), we can write the working in the *intrinsic form*

$$\mathcal{W}(\mathcal{A}) = \int_{\partial\mathcal{A}} \sigma U \, ds + \int_{\partial\mathcal{A}} \big(V\boldsymbol{\tau} \cdot \boldsymbol{\nu} + \mathbb{M}\boldsymbol{\nu} \cdot \mathring{\mathbf{n}}\big) \, ds + \int_{\mathcal{A}} cV \, da. \tag{6.5}$$

7 Frame-indifference. Configurational force and moment balances

7.1 Global balances

Frame-indifference is equivalent to the requirement that, given any superficial control volume $\mathcal{A}$, the terms involving $\boldsymbol{\lambda}$ and $\boldsymbol{\omega}$ in (5.5) must vanish for all $\boldsymbol{\lambda}$ and $\boldsymbol{\omega}$, and this leads to the *configurational force balance*

$$\int_{\partial\mathcal{A}} \mathbb{C}\boldsymbol{\nu} \, ds + \int_{\mathcal{A}} (\mathbf{c} + \mathbf{f}) \, da = \mathbf{0}, \tag{7.1}$$

and the *configurational moment balance*

$$\int_{\partial\mathcal{A}} \big(\mathbf{x} \times \mathbb{C}\boldsymbol{\nu} + \mathbf{n} \times \mathbb{M}\boldsymbol{\nu}\big) \, ds + \int_{\mathcal{A}} \big(\mathbf{x} \times (\mathbf{c} + \mathbf{f}) + \mathbf{n} \times \mathbf{m}\big) \, da = \mathbf{0}, \tag{7.2}$$

relations that must hold for all superficial control volumes $\mathcal{A}$ of $\mathcal{S}$.

7.2 Local balances

Applying the divergence theorem to (7.1) yields the local *configurational force balance*

$$\operatorname{div}_{\mathcal{S}}\mathbb{C} + \mathbf{c} + \mathbf{f} = \mathbf{0}. \tag{7.3}$$

[20] Cf. Gurtin [2000], equation (16.8).

By $(2.14)_1$ and (6.2),

$$\operatorname{div}_{\mathcal{S}}\mathbb{C} = \sigma K\mathbf{n} + \nabla_{\mathcal{S}}\sigma - \mathbb{L}\boldsymbol{\tau} + (\operatorname{div}_{\mathcal{S}}\boldsymbol{\tau})\mathbf{n} + \operatorname{div}_{\mathcal{S}}(\mathbb{L}\mathbb{M})$$

and, since $(\mathbb{L}\mathbb{M})^{\top}\mathbf{n} = \mathbb{M}^{\top}\mathbb{L}\mathbf{n} = 0$, (2.15) implies that

$$\mathbf{n}\cdot\operatorname{div}_{\mathcal{S}}(\mathbb{L}\mathbb{M}) = (\mathbb{L}\mathbb{M})\cdot\mathbb{L} = \mathbb{M}\cdot\mathbb{L}^2.$$

Thus taking the inner product of the configurational force balance (7.3) with $\mathbf{n}$ and using (6.1), we arrive at the *normal force balance*

$$\sigma K + \operatorname{div}_{\mathcal{S}}\boldsymbol{\tau} + \mathbb{M}\cdot\mathbb{L}^2 + c + \pi = 0, \tag{7.4}$$

with

$$\pi = \mathbf{f}\cdot\mathbf{n}$$

the *normal internal force*.

The localization of the moment balance, which is not so straightforward, is based on the following *identity* in which $\mathbb{B}$ is a superficial tensor field, $\mathbf{p}$ a superficial vector field, and $\mathbf{a}$ a constant vector:

$$\mathbf{a}\cdot\int_{\partial\mathcal{A}}(\mathbf{p}\times)\mathbb{B}\boldsymbol{\nu}\,ds \;=\; (\mathbf{a}\times)\cdot\int_{\mathcal{A}}\Big(-\mathbf{p}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{B} + \mathbb{B}(\nabla_{\mathcal{S}}\mathbf{p})^{\top}\Big)\,da. \tag{7.5}$$

To establish this identity assume first that $\mathbb{B}$ is *constant*. Then

$$\mathbf{a}\cdot\operatorname{div}_{\mathcal{S}}\big((\mathbf{p}\times)\mathbb{B}\big) = \operatorname{div}_{\mathcal{S}}\big(\mathbb{B}^{\top}(\mathbf{p}\times)^{\top}\mathbf{a}\big) = \operatorname{div}_{\mathcal{S}}\big(\mathbb{B}^{\top}(\mathbf{a}\times\mathbf{p})\big) = \\ \operatorname{tr}\Big(\mathbb{B}^{\top}(\mathbf{a}\times)\nabla_{\mathcal{S}}\mathbf{p}\Big) = (\mathbf{a}\times)\cdot\Big(\mathbb{B}(\nabla_{\mathcal{S}}\mathbf{p})^{\top}\Big).$$

On the other hand, for $\mathbf{p}$ *constant*,

$$\mathbf{a}\cdot\operatorname{div}_{\mathcal{S}}\big((\mathbf{p}\times)\mathbb{B}\big) = \mathbf{a}\cdot(\mathbf{p}\times\operatorname{div}_{\mathcal{S}}\mathbb{B}) = -(\mathbf{a}\times)\cdot(\mathbf{p}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{B}).$$

Applying the divergence theorem to the left side of (7.5) we conclude, using the last two identities, that (7.5) is valid.

Next, by (2.9), (2.12), (7.5), and the fact that $\mathbb{P}$ and $\mathbb{L}$ are symmetric,

$$\mathbf{a}\cdot\int_{\partial\mathcal{A}}\big(\mathbf{x}\times\mathbb{C}\boldsymbol{\nu} + \mathbf{n}\times\mathbb{M}\boldsymbol{\nu}\big)\,ds = \\ (\mathbf{a}\times)\cdot\int_{\mathcal{A}}\big(-\mathbf{x}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{C} + \mathbb{C}\mathbb{P} - \mathbf{n}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{M} - \mathbb{M}\mathbb{L}\big)\,da. \tag{7.6}$$

Thus, since $\mathbb{C}\mathbb{P} = \mathbb{C}$, we may use the moment balance (7.2) and the local force balance (7.3) to conclude that

$$(\mathbf{a}\times)\cdot\int_{\mathcal{A}}\big(\mathbb{C} - \mathbf{n}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{M} - \mathbb{M}\mathbb{L} - \mathbf{n}\otimes\mathbf{m}\big)\,da = 0,$$

or equivalently, since both $\mathbf{a}$ and $\mathcal{A}$ are arbitrary, the skew part of the integrand must vanish:

$$\mathbb{C} - \mathbb{C}^{\top} - \mathbf{n}\otimes\operatorname{div}_{\mathcal{S}}\mathbb{M} + \operatorname{div}_{\mathcal{S}}\mathbb{M}\otimes\mathbf{n} - \mathbb{M}\mathbb{L} + \mathbb{L}\mathbb{M}^{\top} - \mathbf{n}\otimes\mathbf{m} + \mathbf{m}\otimes\mathbf{n} = \mathbf{0}. \tag{7.7}$$

If we operate with the left side of (7.7) on $\mathbf{n}$ and use (5.6) and the relations $\mathbb{C}\mathbf{n} = \mathbb{L}\mathbf{n} = \mathbf{0}$ and $\boldsymbol{\tau}\cdot\mathbf{n} = 0$, we find that

$$\operatorname{div}_{\mathcal{S}}\mathbb{M} - (\mathbf{n}\cdot\operatorname{div}_{\mathcal{S}}\mathbb{M})\mathbf{n} + \mathbf{m} = \boldsymbol{\tau},$$

and, by (2.15), we have the local *configurational moment balance*

$$\operatorname{div}_{\mathcal{S}}\mathbb{M} - (\mathbb{M}\cdot\mathbb{L})\mathbf{n} + \mathbf{m} = \boldsymbol{\tau}. \tag{7.8}$$

Finally, we use (7.8), (6.2) and the symmetry of $\mathbb{L}$ to eliminate $\mathrm{div}_{\mathcal{S}}\mathbb{M}$ and $\mathbb{C}$ from (7.7); the result is

$$\mathbf{0} = \mathbb{L}\mathbb{M} - \mathbb{M}^{\top}\mathbb{L} - \mathbb{M}\mathbb{L} + \mathbb{L}\mathbb{M}^{\top} = 2\big(\mathbb{L}\,(\mathrm{sym}\mathbb{M}) - (\mathrm{sym}\mathbb{M})\mathbb{L}\big),$$

which yields the *moment constraint*

$$\mathbb{L}\,(\mathrm{sym}\mathbb{M}) = (\mathrm{sym}\mathbb{M})\,\mathbb{L}. \tag{7.9}$$

7.3 Unified normal balance

The moment balance (7.8) may be used to eliminate the term $\mathrm{div}_{\mathcal{S}}\boldsymbol{\tau}$ in (7.4). With this in mind, note that for φ a superficial scalar field, $\mathrm{div}_{\mathcal{S}}(\varphi\mathbf{n}) = -\varphi K$; thus, by (7.8)

$$\mathrm{div}_{\mathcal{S}}\boldsymbol{\tau} = \mathrm{div}_{\mathcal{S}}\mathrm{div}_{\mathcal{S}}\mathbb{M} + \mathrm{div}_{\mathcal{S}}\mathbf{m} - (\mathbb{M}\cdot\mathbb{L})K$$

and we can rewrite the normal force balance in the form

$$(\sigma + \mathbb{M}\cdot\mathbb{L})K + \mathrm{div}_{\mathcal{S}}\mathrm{div}_{\mathcal{S}}\mathbb{M} + \mathbb{M}\cdot\mathbb{L}^2 + \mathrm{div}_{\mathcal{S}}\mathbf{m} + c + \pi = 0. \tag{7.10}$$

This relation, which we refer to as the *unified normal balance*, is an amalgamation of the local configurational force and moment balances; it represents the basic mechanical balance of the theory.

8 Internal working. Local dissipation inequality

Consider the intrinsic form of the working as expressed in (6.5). Since $\mathring{\mathbf{n}} = -\nabla_{\mathcal{S}}V$,

$$\int_{\partial\mathcal{A}} V\boldsymbol{\tau}\cdot\boldsymbol{\nu}\,ds = \int_{\mathcal{A}}(V\mathrm{div}_{\mathcal{S}}\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\nabla_{\mathcal{S}}V)\,da = \int_{\mathcal{A}}(V\mathrm{div}_{\mathcal{S}}\boldsymbol{\tau} - \boldsymbol{\tau}\cdot\mathring{\mathbf{n}})\,da.$$

Further, since $\mathbb{M}$ is tangential, we may use (2.4) and $(2.19)_2$ to conclude that

$$\mathbb{M}\cdot\nabla_{\mathcal{S}}\mathring{\mathbf{n}} = \mathbb{M}\cdot(\nabla_{\mathcal{S}}\mathring{\mathbf{n}})_{\tan} = \mathbb{M}\cdot\big(-(\mathring{\mathbb{L}})_{\tan} + V\,\mathbb{L}^2\big); \tag{8.1}$$

therefore

$$\begin{aligned}\int_{\partial\mathcal{A}}\mathbb{M}\boldsymbol{\nu}\cdot\mathring{\mathbf{n}}\,ds &= \int_{\partial\mathcal{A}}(\mathring{\mathbf{n}}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{M} + \mathbb{M}\cdot\nabla_{\mathcal{S}}\mathring{\mathbf{n}})\,da\\ &= \int_{\mathcal{A}}\big[\mathring{\mathbf{n}}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{M} - \mathbb{M}\cdot\big((\mathring{\mathbb{L}})_{\tan} - V\,\mathbb{L}^2\big)\big]\,da.\end{aligned}$$

Thus (6.5) takes the form

$$\mathcal{W}(\mathcal{A}) = \int_{\partial\mathcal{A}}\sigma U\,ds + \int_{\mathcal{A}}\big[(c + \mathrm{div}_{\mathcal{S}}\boldsymbol{\tau} + \mathbb{M}\cdot\mathbb{L}^2)V + (\mathrm{div}_{\mathcal{S}}\mathbb{M} - \boldsymbol{\tau})\cdot\mathring{\mathbf{n}} - \mathbb{M}\cdot(\mathring{\mathbb{L}})_{\tan}\big]\,da,$$

and, appealing to the normal force balance (7.4) and the moment balance (7.8),

$$\mathcal{W}(\mathcal{A}) = \int_{\partial\mathcal{A}}\sigma U\,ds - \int_{\mathcal{A}}\big[(\sigma K + \pi)V + \mathbf{m}\cdot\mathring{\mathbf{n}} + \mathbb{M}\cdot(\mathring{\mathbb{L}})_{\tan}\big]\,da. \tag{8.2}$$

The relation (8.2) represents the *internal working*, that is, the rate at which work is performed within the control volume $\mathcal{A}$.

Next, in view of (8.2), we may use (2.23) to rewrite the energy imbalance (5.1) in the form

$$\int_{\mathcal{A}}(\mathring{\psi}-\psi KV)\,da\le\int_{\partial\mathcal{A}}(\sigma-\psi)U\,ds-\int_{\mathcal{A}}\big[(\sigma K+\pi)V+\mathbf{m}\cdot\mathring{\mathbf{n}}+\mathbb{M}\cdot(\mathring{\mathbb{L}})_{\tan}\big]\,da \\ -\int_{\partial\mathcal{A}}\mu\mathbf{h}\cdot\boldsymbol{\nu}\,ds+\int_{\mathcal{A}}\mu q\,da. \quad (8.3)$$

Given any time t and any fixed subsurface $\mathcal{A}'$ of $\mathcal{S}$, it is possible to construct an superficial control volume $\mathcal{A}$ such that, at t, $\mathcal{A}$ coincides with $\mathcal{A}'$, but the scalar velocity U of $\mathcal{A}$ in the direction $\boldsymbol{\nu}$ is, at time t, an arbitrarily prescribed field on $\partial\mathcal{A}'$. The requirement that (8.3) hold for all such t, $\mathcal{A}'$, and U implies that

$$\sigma=\psi, \quad (8.4)$$

which is the classical identification of surface tension with surface free energy. Finally, if we apply the divergence theorem to the term in (8.3) involving the mass flux we find, using (8.4) and the local mass balance (4.2),

$$\int_{\mathcal{A}}\big[\mathring{\psi}+\mathbf{m}\cdot\mathring{\mathbf{n}}+\mathbb{M}\cdot(\mathring{\mathbb{L}})_{\tan}+\pi V+\mathbf{h}\cdot\nabla_{\mathcal{S}}\mu\big]\,da\le 0, \quad (8.5)$$

and, since this inequality must hold for all $\mathcal{A}$,

$$\mathring{\psi}+\mathbf{m}\cdot\mathring{\mathbf{n}}+\mathbb{M}\cdot(\mathring{\mathbb{L}})_{\tan}+\pi V+\mathbf{h}\cdot\nabla_{\mathcal{S}}\mu\le 0, \quad (8.6)$$

a *local dissipation inequality* essential to our development of a suitable constitutive theory.

9 Digression: Standard theory

Within the framework developed here the standard theory, which does not account for a superficial couple-stress, has

$$\mathbb{M}\equiv\mathbf{0}, \quad (9.1)$$

so that, by (7.8),

$$\boldsymbol{\tau}=\mathbf{m}.$$

In this theory the constitutive equation for the free energy has the form

$$\psi=\psi_0(\mathbf{n}) \quad (9.2)$$

and determines the internal couple through the relation

$$\mathbf{m}=-\frac{\partial\psi_0(\mathbf{n})}{\partial\mathbf{n}} \quad (9.3)$$

(where $\partial/\partial\mathbf{n}$ denotes the derivative on the unit sphere). The internal force π represents the kinetics of atomic exchanges associated with the evolution of $\mathcal{S}$; its constitutive relation has the form

$$\pi=-\beta(\mathbf{n})V, \quad (9.4)$$

with $\beta(\mathbf{n})\ge 0$ a *kinetic modulus*.

Since $K=\mathbb{P}\cdot\mathbb{L}$ and

$$\mathrm{div}_{\mathcal{S}}\mathbf{m}=-\frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\cdot\nabla_{\mathcal{S}}\mathbf{n}=\frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\cdot\mathbb{L}, \quad (9.5)$$

the unified normal balance (7.10) with $\sigma=\psi$, when augmented by the relations (9.1)-(9.4), takes the form

$$\beta(\mathbf{n})V=\Big[\psi_0(\mathbf{n})\mathbb{P}+\frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L}+c. \quad (9.6)$$

The normal external configurational force c represents the mechanical coupling between the surface $\mathcal{S}$ and the bulk material. When $c = 0$, (9.6) represents a partial differential equation for the evolution of the the surface; this equation is usually referred to as the *curvature flow equation*.

The standard constitutive equation for the diffusive flux is *Fick's law*

$$\mathbf{h} = -k(\mathbf{n})\,\nabla_{\mathcal{S}}\mu, \tag{9.7}$$

with $k \geq 0$ a scalar *mobility*.[21] This equation with local mass balance (4.2) yields

$$\mathrm{div}_{\mathcal{S}}\big(k(\mathbf{n})\nabla_{\mathcal{S}}\mu\big) = -q. \tag{9.8}$$

As with the field c, the mass supply q represents coupling between the surface $\mathcal{S}$ and the bulk material. These fields depend on the mechanical and mass transport processes taking place in the bulk material. Coupling of these bulk processes generally results in a coupling of the superficial equations (9.6) and (9.8) via the fields c and q.

Note that, by (9.2) and (9.3), $\mathring{\psi} = -\mathbf{m}\cdot\mathring{\mathbf{n}}$; thus, by (9.4) and (9.7), the local dissipation inequality (8.6) reduces to

$$\Gamma \stackrel{\text{def}}{=} -\pi V - \mathbf{h}\cdot\nabla_{\mathcal{S}}\mu = \beta(\mathbf{n})V^2 + k(\mathbf{n})\,|\nabla_{\mathcal{S}}\mu|^2 \geq 0 \tag{9.9}$$

and is automatically satisfied, since $\beta(\mathbf{n})$ and $k(\mathbf{n})$ are positive. The quantity Γ represents the *dissipation* per unit area due to kinetics and surface diffusion.

10 Constitutive theory

When the response function $\psi_0(\mathbf{n})$ for the surface energy is *nonconvex* the equation (9.6) — viewed as a partial differential equation for the evolution of $\mathcal{S}$, given c — is backward parabolic and hence unstable for certain ranges of the orientation $\mathbf{n}$. To remedy this we regularize the theory by allowing for an energetic dependence on curvature within a constitutive framework that preserves much of the basic structure of the standard theory. But, since temporal changes in the curvature are work-conjugate to the couple stress $\mathbb{M}$ (cf. (8.6)), in contrast to the standard theory $\mathbb{M}$ should play an essential role in a thermodynamically consistent theory.

Specifically, we base the theory on the following set of constitutive equations:[22]

(i) The free energy ψ is a function $\psi_0(\mathbf{n})$ augmented by a positive-definite, quadratic, isotropic function of $\mathbb{L}$. Thus, since the isotropic invariants of $\mathbb{L}$ are K and $|\mathbb{L}|^2$, we consider a constitutive equation of the form

$$\psi = \psi_0(\mathbf{n}) + \tfrac{1}{2}\varepsilon_1|\mathbb{L}|^2 + \tfrac{1}{2}\varepsilon_2 K^2 \tag{10.1}$$

with ε_1 and ε_2 scalar moduli.

(ii) The couple stress and internal couple are given by constitutive equations of the form

$$\mathbb{M} = \hat{\mathbb{M}}(\mathbf{n},\mathbb{L}), \qquad \mathbf{m} = \hat{\mathbf{m}}(\mathbf{n},\mathbb{L}). \tag{10.2}$$

[21] More generally, one might take $\mathbf{h} = -\mathbb{K}(\mathbf{n})\,\nabla_{\mathcal{S}}\mu$, with $\mathbb{K}(\mathbf{n})$ a symmetric tensor that satisfies $\mathbb{K}(\mathbf{n})\mathbf{n} = \mathbf{0}$ and $\mathbf{u}\cdot\mathbb{K}(\mathbf{n})\mathbf{u} > 0$ for all $\mathbf{u} \neq \mathbf{0}$ orthogonal to $\mathbf{n}$. The simpler relation (9.7) (with appropriate $k(\mathbf{n})$) would then ensue under cubic symmetry.

[22] More generally, one can show that constitutive equations giving ψ, $\mathbf{h}$, $\mathbb{M}$, $\mathbf{m}$, and π as functions of $\aleph = (\mathbf{n},\mathbb{L},V,\mu,\nabla_{\mathcal{S}}\mu)$ are consistent with the local dissipation inequality (8.6) for all evolving surfaces $\mathcal{S}$ and all superficial fields μ for $\mathcal{S}$ if and only if: (i) ψ, $\mathbb{M}$, and $\mathbf{m}$ are independent of $(V,\mu,\nabla_{\mathcal{S}}\mu)$; (ii) denoting by a "hat" the associated constitutive response functions, $\mathbb{M} = -\partial\hat{\psi}/\partial\mathbb{L}$ and $\mathbf{m} = -\partial\hat{\psi}/\partial\mathbf{n}$ (with the "partial derivatives" consistent with the manifold constraint $\mathbb{L}\mathbf{n} = \mathbf{0}$); (iii) the response functions $\hat{\pi}$ and $\hat{\mathbf{h}}$ must satisfy $\hat{\pi}(\aleph)V + \hat{\mathbf{h}}(\aleph)\cdot\nabla_{\mathcal{S}}\mu \leq 0$.

(iii) The constitutive equations for the internal force π and the diffusive flux $\mathbf{h}$ have the standard form

$$\pi = -\beta(\mathbf{n})V, \qquad \mathbf{h} = -k(\mathbf{n})\,\nabla_{\mathcal{S}}\mu, \tag{10.3}$$

with $\beta(\mathbf{n})$ and $k(\mathbf{n})$ nonnegative.

Let $\mathbb{L}_0$ denote the traceless part of $\mathbb{L}$:

$$\mathbb{L} = \mathbb{L}_0 + \tfrac{1}{2}K\mathbb{P}, \qquad \operatorname{tr}\mathbb{L}_0 = \mathbb{P}\cdot\mathbb{L}_0 = 0.$$

Then $|\mathbb{L}|^2 = |\mathbb{L}_0|^2 + \frac{1}{2}K^2$ and $\mathbb{L}_0\cdot\mathbb{P} = 0$, so that

$$\psi = \psi_0(\mathbf{n}) + \tfrac{1}{2}\varepsilon_1|\mathbb{L}_0|^2 + \tfrac{1}{2}\left(\varepsilon_2 + \tfrac{1}{2}\varepsilon_1\right)K^2.$$

Because $\mathbb{L}_0$ and K can be specified independently, it follows that

$$\varepsilon_1 > 0 \quad \text{and} \quad \varepsilon_2 + \frac{1}{2}\varepsilon_1 > 0$$

are together necessary and sufficient that the dependence on $\mathbb{L}$ be positive definite.

Returning to (10.1), consider an arbitrary evolution of $\mathcal{S}$. Since $\overset{\circ}{\mathbb{P}} = -\overset{\circ}{\mathbf{n}}\otimes\mathbf{n} - \mathbf{n}\otimes\overset{\circ}{\mathbf{n}}$ (cf. (2.3)) and $\mathbb{L}\mathbf{n} = \mathbf{0}$,

$$\overset{\circ}{K} = \overset{\circ}{\overline{\mathbb{P}\cdot\mathbb{L}}} = \mathbb{P}\cdot\overset{\circ}{\mathbb{L}} + \overset{\circ}{\mathbb{P}}\cdot\mathbb{L} = \mathbb{P}\cdot\overset{\circ}{\mathbb{L}}.$$

Thus, appealing to the constitutive equations,

$$\begin{aligned}\overset{\circ}{\psi} &= \frac{\partial\psi_0(\mathbf{n})}{\partial\mathbf{n}}\cdot\overset{\circ}{\mathbf{n}} + (\varepsilon_1\mathbb{L} + \varepsilon_2 K\,\mathbb{P})\cdot\overset{\circ}{\mathbb{L}}\\ &= \frac{\partial\psi_0(\mathbf{n})}{\partial\mathbf{n}}\cdot\overset{\circ}{\mathbf{n}} + (\varepsilon_1\mathbb{L} + \varepsilon_2 K\,\mathbb{P})\cdot(\overset{\circ}{\mathbb{L}})_{\tan},\end{aligned}$$

and the local dissipation inequality (8.6) takes the form

$$\Big[\frac{\partial\psi_0(\mathbf{n})}{\partial\mathbf{n}} + \hat{\mathbf{m}}(\mathbf{n},\mathbb{L})\Big]\cdot\overset{\circ}{\mathbf{n}} + \Big[(\varepsilon_1\mathbb{L} + \varepsilon_2 K\,\mathbb{P}) + \hat{\mathbb{M}}(\mathbf{n},\mathbb{L})\Big]\cdot(\overset{\circ}{\mathbb{L}})_{\tan} - \Gamma \le 0, \tag{10.4}$$

with $\Gamma = \Gamma(\mathbf{n},\mathbb{L},V,\mu,\nabla_{\mathcal{S}}\mu)$ given by (9.9). For *any* prescribed choice of the *values* of $\mathbf{n}$, $\mathbb{L}$, V, μ, $\nabla_{\mathcal{S}}\mu$, $\overset{\circ}{\mathbf{n}}$ and $(\overset{\circ}{\mathbb{L}})_{\tan}$, it is possible to find an evolving surface $\mathcal{S}$ and an associated chemical potential such that the underlying fields are consistent with this prescribed choice at some particular point and time, say $(\mathbf{x}_0,t_0)$ (cf. Appendix C). Writing $\mathbf{a}(\mathbf{n},\mathbb{L})$ and $\mathbb{A}(\mathbf{n},\mathbb{L})$ for the terms "dotted" with $\overset{\circ}{\mathbf{n}}$ and $(\overset{\circ}{\mathbb{L}})_{\tan}$, respectively, then $\mathbf{a}(\mathbf{n},\mathbb{L})$ and $\overset{\circ}{\mathbf{n}}$ are each orthogonal to $\mathbf{n}$, while $\mathbb{A}(\mathbf{n},\mathbb{L})$ and $(\overset{\circ}{\mathbb{L}})_{\tan}$ are each symmetric and annihilate $\mathbf{n}$. Moreover, within these constraints $\overset{\circ}{\mathbf{n}}$ and $(\overset{\circ}{\mathbb{L}})_{\tan}$ may be arbitrarily chosen at $(\mathbf{x}_0,t_0)$; thus $\mathbf{a}(\mathbf{n},\mathbb{L})$ and $\mathbb{A}(\mathbf{n},\mathbb{L})$ must vanish. The constitutive equations for the internal couple and the couple stress must therefore have the specific form:[23]

$$\left.\begin{aligned}\mathbf{m} &= -\frac{\partial\psi_0(\mathbf{n})}{\partial\mathbf{n}},\\ \mathbb{M} &= -\varepsilon_1\mathbb{L} - \varepsilon_2 K\,\mathbb{P}.\end{aligned}\right\} \tag{10.5}$$

Remark. We have provided constitutive descriptions only for those fields which appear in the local dissipation inequality (8.6). The tangential component of the internal force $\mathbf{f}$ and the surface shear $\boldsymbol{\tau}$ do not appear in (8.6), and consequently, do not enter the theory in a manner relevant to the underlying thermodynamics. More intuitively: (i) the intrinsic

[23] By $(10.5)_2$, the moment constraint (7.9) is automatically satisfied. In fact, it can be shown that (7.9) is satisfied for any *isotropic* interfacial energy.

motion of $\mathcal{S}$ is normal to itself; for that reason, the tangential component of $\mathbf{f}$ does not perform work; and (ii) the surface shear typically performs work internally over $\mathring{\mathbf{n}}$,[24] a form of working here accounted for by the couple $\mathbf{m}$. The fields $\mathbb{P}\mathbf{f}$ and $\boldsymbol{\tau}$ are therefore considered as *indeterminate*, that is, not specified constitutively but instead considered as defined by the moment balance (7.8) and the tangential component of the force balance (7.3).

11 Superficial evolution equations

Using the identities (Appendix B)

$$\left.\begin{aligned} \mathrm{div}_{\mathcal{S}}(K^2\mathbf{n}) &= -K^3, \\ \mathrm{div}_{\mathcal{S}}(K\mathbb{P}) &= K^2\mathbf{n} + \nabla_{\mathcal{S}}K \end{aligned}\right\} \tag{11.1}$$

in conjunction with $(2.14)_2$ and $(10.5)_2$, we obtain

$$\mathrm{div}_{\mathcal{S}}\mathrm{div}_{\mathcal{S}}\mathbf{M} = -\varepsilon_1(\Delta_{\mathcal{S}}K - |\mathbb{L}|^2K) - \varepsilon_2(\Delta_{\mathcal{S}}K - K^3). \tag{11.2}$$

Substitution of (9.5), $(10.3)_2$, and (11.2) into the unified normal balance (7.10) yields the *superficial unified configurational balance*:

$$\begin{aligned} \beta(\mathbf{n})V = \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L} + \\ - \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \mathrm{tr}\,(\mathbb{L}^3)\Big] - \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big] + c. \end{aligned} \tag{11.3}$$

This equation and the *superficial diffusion equation*

$$\mathrm{div}_{\mathcal{S}}\big(k(\mathbf{n})\nabla_{\mathcal{S}}\mu\big) = -q \tag{9.8 \textit{bis}}$$

represent the basic evolution equations for the surface.

The fields c and q depend on the physical processes taking place in the material adjacent to $\mathcal{S}$. In the next two sections we discuss the behavior of the bulk material in two special cases of interest:

(i) $\mathcal{S}$ represents an interface between bulk phases or grains.

(ii) $\mathcal{S}$ represents an interface between an elastic film and an agency whose sole action is the deposition of atoms over this interface.

In each case we derive specific forms for the fields c and q in terms of the underlying bulk fields.

12 Interface between bulk phases or grain boundaries

In this section we allow for the possibility of bulk elasticity, but we *neglect inertia and restrict attention to infinitesimal deformations.*

The bulk material on the two sides of $\mathcal{S}$ is described by the fields

Ψ	free energy density,
μ	chemical potential,
ρ	bulk atomic density,
$\boldsymbol{\jmath}$	bulk atomic flux,
$\mathbf{T}$	stress,
$\mathbf{u}$	displacement,

[24] Cf., Gurtin [1995].

with each presumed to be smooth away from $\mathcal{S}$ and up to $\mathcal{S}$ from either side. For Φ any such field we write Φ^+ for the limit of Φ, at $\mathcal{S}$, from the phase into which $\mathbf{n}$ points, Φ^- for the corresponding limit from the other phase, and

$$[\![\Phi]\!] = \Phi^+ - \Phi^-$$

for the *jump in* Φ *across* $\mathcal{S}$. We assume that *the jump in chemical potential vanishes* and that the common value

$$\mu^+ = \mu^- = \mu \tag{12.1}$$

represents the chemical potential of the interface. We assume also that the interface is *coherent*,

$$\mathbf{u}^+ = \mathbf{u}^-,$$

a condition that renders the tangential derivative of $\mathbf{u}$ continuous across $\mathcal{S}$:

$$[\![\nabla \mathbf{u}]\!]\mathbb{P} = \mathbf{0}. \tag{12.2}$$

Since we neglect inertia, balance of forces requires that

$$\operatorname{div} \mathbf{T} = \mathbf{0} \tag{12.3}$$

in bulk and

$$[\![\mathbf{T}]\!]\mathbf{n} = \mathbf{0} \tag{12.4}$$

on $\mathcal{S}$, and balance of moments is the requirement that $\mathbf{T} = \mathbf{T}^\top$. The relation (12.4) represents the standard (Newtonian) force balance for the interface. Configurational forces are distinct from such standard forces, and their balance, as represented by the configurational force balance (7.3), *should not be confused with the standard balance* (12.4).

Associated with the bulk material is a configurational stress tensor[25]

$$\mathbf{C} = (\Psi - \mu\rho)\mathbf{1} - (\nabla \mathbf{u})^\top \mathbf{T} \tag{12.5}$$

whose resulting traction on the two sides of $\mathcal{S}$ gives the external configurational force $\mathbf{c}$ on $\mathcal{S}$:

$$\mathbf{c} = \mathbf{C}^+\mathbf{n} + \mathbf{C}^-(-\mathbf{n}) = [\![\mathbf{C}]\!]\mathbf{n}.$$

Note that, by (12.2) and (12.4), given any vector $\mathbf{t}$ tangent to $\mathcal{S}$,

$$\mathbf{t} \cdot \mathbf{c} = \mathbf{t} \cdot [\![\mathbf{C}]\!]\mathbf{n} = \mathbf{t} \cdot [\![(\nabla \mathbf{u})^\top \mathbf{T}]\!]\mathbf{n} = [\![(\nabla \mathbf{u})\mathbf{t}]\!] \cdot \mathbf{T}^\pm \mathbf{n} = 0,$$

so that $\mathbf{c} = c\mathbf{n}$, in accord with (6.1). Thus, by (12.5),

$$c = [\![\Psi]\!] - \mu[\![\rho]\!] - \mathbf{n} \cdot [\![(\nabla \mathbf{u})^\top \mathbf{T}]\!]\mathbf{n}. \tag{12.6}$$

Moreover, (12.2), (12.4), and the symmetry of $\mathbf{T}$ imply that

$$\mathbf{n} \cdot [\![(\nabla \mathbf{u})^\top \mathbf{T}]\!]\mathbf{n} = [\![\mathbf{T} \cdot \mathbf{E}\,]\!]$$

with

$$\mathbf{E} = \tfrac{1}{2}\big(\nabla \mathbf{u} + \nabla \mathbf{u}^\top\big) \tag{12.7}$$

the *strain tensor;* (12.6) therefore has the alternative form

$$c = [\![\,\Psi - \mu\rho - \mathbf{T} \cdot \mathbf{E}\,]\!]. \tag{12.8}$$

Balance of mass in bulk is the requirement that

$$\frac{\partial \rho}{\partial t} = -\operatorname{div} \boldsymbol{\jmath} \tag{12.9}$$

[25] Cf. Fried and Gurtin [1999] and the references therein. See also Gurtin & Voorhees [1993] and Gurtin [2000].

away from the interface. Moreover, the net mass flow into $\mathcal{S}$, per unit area, from the bulk material gives the mass supply q:

$$\begin{aligned} q &= \rho^+ V - \boldsymbol{\jmath}^+ \cdot \mathbf{n} - \rho^- V + \boldsymbol{\jmath}^- \cdot \mathbf{n} \\ &= [\![\rho]\!] V - [\![\boldsymbol{\jmath}]\!] \cdot \mathbf{n}. \end{aligned} \tag{12.10}$$

The general theory with deformation and mass transport is complicated: the basic interface equations are the configurational balance (11.3) and the superficial diffusion equation (9.8) with c and q given by (12.8) and (12.10), and the standard force balance (12.4). These are coupled to the bulk force and mass balances, (12.3) and (12.9), supplemented by bulk constitutive equations which, for elastic phases, consist of equations giving the bulk Gibbs function $\Psi - \mu\rho$ as a phase-dependent function of $(\mathbf{E}, \mu)$, giving $\mathbf{T}$ and $-\rho$, respectively, as partial derivatives of this Gibbs function with respect to $\mathbf{E}$ and μ, and giving $\boldsymbol{\jmath}$ as a linear function of $\nabla\mu$ (Fick's law).[26]

We now consider in detail special cases of the general theory, *neglecting mass transport in bulk*.

12.1 Interface-controlled evolution without surface diffusion

We neglect deformation and mass transport in bulk; specifically, $\mathbf{u} \equiv \mathbf{0}$, $\mathbf{T} \equiv \mathbf{0}$, $[\![\rho]\!] \equiv 0$, $[\![\Psi]\!] \equiv$ constant, $\mathbf{h} \equiv 0$, and $\boldsymbol{\jmath} \equiv 0$, so that

$$c = [\![\Psi]\!], \qquad q = 0.$$

We then have a single evolution equation for the interface:

$$\begin{aligned} \beta(\mathbf{n})V = &\Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2 \psi_0(\mathbf{n})}{\partial \mathbf{n}^2}\Big] \cdot \mathbb{L} \\ &- \varepsilon_1 \Big[\Delta_{\mathcal{S}} K - \tfrac{1}{2} K |\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2 \Big[\Delta_{\mathcal{S}} K + K|\mathbb{L}|^2 - \tfrac{1}{2} K^3\Big] + [\![\Psi]\!]. \end{aligned} \tag{12.11}$$

For $\beta(\mathbf{n}) > 0$, (12.11) represents a fourth-order, parabolic partial differential equation for the evolution of $\mathcal{S}$.

12.2 Interface-controlled evolution with surface diffusion

Here both deformation and mass transport in bulk are neglected; specifically, $\mathbf{u} \equiv \mathbf{0}$, $\mathbf{T} \equiv \mathbf{0}$, and $\boldsymbol{\jmath} \equiv \mathbf{0}$, while Ψ and ρ are *constant* in each phase. Then

$$c = [\![\Psi]\!] - \mu [\![\rho]\!], \qquad q = [\![\rho]\!] V,$$

and the basic equations have the form

$$\begin{aligned} \beta(\mathbf{n})V = &\Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2 \psi_0(\mathbf{n})}{\partial \mathbf{n}^2}\Big] \cdot \mathbb{L} + \\ &- \varepsilon_1 \Big[\Delta_{\mathcal{S}} K - \tfrac{1}{2} K |\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2 \Big[\Delta_{\mathcal{S}} K + K|\mathbb{L}|^2 - \tfrac{1}{2} K^3\Big] + [\![\Psi]\!] - \mu [\![\rho]\!] \end{aligned} \tag{12.12}$$

and

$$[\![\rho]\!] V = -\operatorname{div}_{\mathcal{S}}\big(k(\mathbf{n}) \nabla_{\mathcal{S}} \mu\big). \tag{12.13}$$

[26] Such bulk constitutive equations are discussed in detail by Gurtin & Voorhees [1993] and Fried and Gurtin [1999].

If we assume that $\beta(\mathbf{n}) \equiv 0$ and k is constant, then (12.12) and (12.13) combine to give a single equation for the evolution of the interface:

$$[\![\rho]\!]^2 V = -k\,\Delta_{\mathcal{S}} \Bigg\{ \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2 \psi_0(\mathbf{n})}{\partial \mathbf{n}^2}\Big] \cdot \mathbb{L} \Big] - \varepsilon_1 \Big[\Delta_{\mathcal{S}} K - \tfrac{1}{2} K |\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2 \Big[\Delta_{\mathcal{S}} K + K|\mathbb{L}|^2 - \tfrac{1}{2} K^3\Big] \Bigg\}. \quad (12.14)$$

For $[\![\rho]\!] \neq 0$ and $k > 0$, and modulo a rescaling, this equation has the abstract form

$$V = \Delta_{\mathcal{S}} \Delta_{\mathcal{S}} K + \Phi(\mathbf{n}, \mathbb{L})$$

and hence represents a sixth-order parabolic partial-differential equation for the evolution of the interface.

12.3 Theory with elastic phases, but without mass transport

Here $[\![\rho]\!] \equiv 0$, $\mathbf{h} \equiv 0$, and $\boldsymbol{\jmath} \equiv 0$, so that $q \equiv 0$. In this case the interface conditions consist of the standard balance

$$[\![\mathbf{T}]\!]\mathbf{n} = \mathbf{0} \quad (12.4\,bis)$$

and the configurational balance

$$[\![\,\Psi - \mathbf{T}\cdot\mathbf{E}\,]\!] = \beta(\mathbf{n})V - \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2 \psi_0(\mathbf{n})}{\partial \mathbf{n}^2}\Big] \cdot \mathbb{L} + \varepsilon_1 \Big[\Delta_{\mathcal{S}} K - \tfrac{1}{2} K |\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] + \varepsilon_2 \Big[\Delta_{\mathcal{S}} K + K|\mathbb{L}|^2 - \tfrac{1}{2} K^3\Big]. \quad (12.15)$$

To discuss the bulk constitutive equations, we label the phases by the integers 1 and 2 (with phase 2 lying on the side of $\mathcal{S}$ into which $\mathbf{n}$ points). We consider linearly elastic phases whose natural states are separated by a *misfit strain* $\mathbf{E}_0$ that arises from a mismatch between the lattice parameters of the two phases. Precisely, we assume that the bulk free energy is given by constitutive equations

$$\Psi = \begin{cases} \frac{1}{2}\mathbf{E}\cdot\mathcal{L}_1\mathbf{E} & \text{in phase 1} \\ \frac{1}{2}(\mathbf{E}-\mathbf{E}_0)\cdot\mathcal{L}_2(\mathbf{E}-\mathbf{E}_0) & \text{in phase 2,} \end{cases} \quad (12.16)$$

where $\mathbf{E}_0$ is a constant symmetric tensor and $\mathcal{L}_1$ and $\mathcal{L}_2$, the elasticity tensors, are constant (symmetric, positive-definite) linear transformations of symmetric tensors into symmetric tensors. Consistent with this we assume that the stress is given by the linear relations

$$\mathbf{T} = \begin{cases} \mathcal{L}_1\mathbf{E} & \text{in phase 1} \\ \mathcal{L}_2(\mathbf{E}-\mathbf{E}_0) & \text{in phase 2.} \end{cases} \quad (12.17)$$

The bulk equations then consist of the standard balance $\operatorname{div}\mathbf{T} = \mathbf{0}$ supplemented by the constitutive equations (12.16) and (12.17) and the strain-displacement relation (12.7); these yield a system of strongly elliptic partial differential equations for the displacement $\mathbf{u}$.

13 Interface between an elastic film and a vapor deposition source

We consider an elastic film that is bonded to a rigid substrate and that has free surface $\mathcal{S}$ exposed to a vapor reservoir whose sole purpose is to supply atoms to $\mathcal{S}$. We consider

mass transport on $\mathcal{S}$, but neglect it in the film, so that the fields relevant to the film are as specified at the beginning of §12, but with

$$\boldsymbol{\jmath} \equiv 0, \quad \rho \equiv \text{constant}.$$

Then μ is indeterminate within the film, but not on $\mathcal{S}$.

We suppose that the film lies on the side of $\mathcal{S}$ from which $\mathbf{n}$ points, so that, using the notation specified in §12, Φ^- denotes the limit of a field Φ, at $\mathcal{S}$, from the film. Consistent with this, we use the superscript "$+$" to describe fields associated with the vapor at $\mathcal{S}$; the values of such fields away from $\mathcal{S}$ are not considered. We do not require that the chemical potential be continuous across $\mathcal{S}$; in fact, the jump $\mu^+ - \mu^-$ is an essential ingredient of the theory.

We assume that there is a mismatch between the lattice parameters of the film and those of the rigid substrate and therefore take the free energy of the film in the form

$$\Psi = \tfrac{1}{2}(\mathbf{E} - \mathbf{E}_0) \cdot \mathcal{L}(\mathbf{E} - \mathbf{E}_0), \tag{13.1}$$

with $\mathbf{E}$ the strain given by (12.7), $\mathbf{E}_0$ the (symmetric) misfit strain, and $\mathcal{L}$ the (symmetric, positive definite) elasticity tensor. The stress $\mathbf{T}$ is then given by

$$\mathbf{T} = \mathcal{L}(\mathbf{E} - \mathbf{E}_0), \tag{13.2}$$

and the equation to be satisfied in the film is the standard balance

$$\operatorname{div} \mathbf{T} = \mathbf{0}. \tag{13.3}$$

As before, these equations with (12.7) form a system of strongly elliptic partial differential equations for the displacement $\mathbf{u}$. We require that $\mathbf{u}$ satisfy the boundary condition $\mathbf{u} = \mathbf{0}$ at the interface between the film and the substrate.

The vapor reservoir is assumed to supply mass to $\mathcal{S}$ at a rate[27]

$$q^+ = \alpha(\mathbf{n})(\mu^+ - \mu^-), \tag{13.4}$$

per unit area, with μ^+ the chemical potential of the vapor at $\mathcal{S}$ and $\alpha(\mathbf{n}) > 0$ a scalar constitutive modulus.[28] The net mass supply to $\mathcal{S}$ is then q^+ supplemented by the supply $-\rho V$ from the film:

$$q = \alpha(\mathbf{n})(\mu^+ - \mu^-) - \rho V. \tag{13.5}$$

We neglect all other interactions of the vapor with the $\mathcal{S}$. Specifically, we assume that the vapor exerts neither standard nor configurational forces on $\mathcal{S}$. Thus the net standard force exerted on $\mathcal{S}$ is due to the traction exerted by the film:

$$\mathbf{T}^- \mathbf{n} = \mathbf{0}. \tag{13.6}$$

This result and (12.5) yield

$$\mathbf{C}^- \mathbf{n} = (\Psi^- - \mu^- \rho)\mathbf{n}$$

and, consequently, the conclusion that

$$c = \mu^- \rho - \Psi^-. \tag{13.7}$$

In view of (13.5) and (13.7), the interface equations (12.11) and (9.8) take the form

$$\begin{aligned} \beta(\mathbf{n})V = &\Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2 \psi_0(\mathbf{n})}{\partial \mathbf{n}^2}\Big] \cdot \mathbb{L} \\ &- \varepsilon_1 \Big[\Delta_{\mathcal{S}} K - \tfrac{1}{2} K |\mathbb{L}|^2 + \operatorname{tr}(\mathbb{L}^3)\Big] - \varepsilon_2 \Big[\Delta_{\mathcal{S}} K + K|\mathbb{L}|^2 - \tfrac{1}{2} K^3\Big] + \mu^- \rho - \Psi^- \end{aligned} \tag{13.8}$$

[27] Cf. Zhang & Bower [2001], who posit a relation of the form (13.4) for $\mu^+ \geq \mu^-$, but require that $q^+ = 0$ for $\mu^+ < \mu^-$.

[28] See Zhang & Bower [2001] in $\mathbb{R}^3$ with surface diffusion and an interfacial energy that depends on $\mathbf{n}$. For the two-dimensional regularized case with the surface energy a quadratic function of curvature, cf. Bower & Gurtin [2001].

and

$$\rho V = \mathrm{div}_{\mathcal{S}}\big(k(\mathbf{n})\nabla_{\mathcal{S}}\mu^-\big) + \alpha(\mathbf{n})(\mu^+ - \mu^-). \tag{13.9}$$

The resulting system of equations consists of the interface conditions (13.6), (13.8), and (13.9) coupled to the field equations for $\mathbf{u}$ as described in the paragraph containing (13.3).

The foregoing system is complicated. If we *neglect surface diffusion*,

$$k(\mathbf{n}) \equiv 0, \tag{13.10}$$

then (13.8) and (13.9) combine to give

$$\begin{aligned}\Big[\beta(\mathbf{n}) + \frac{\rho^2}{\alpha(\mathbf{n})}\Big]V = \Big[\psi_0(\mathbf{n})\mathbb{P} + \frac{\partial^2\psi_0(\mathbf{n})}{\partial\mathbf{n}^2}\Big]\cdot\mathbb{L} \\ - \varepsilon_1\Big[\Delta_{\mathcal{S}}K - \tfrac{1}{2}K|\mathbb{L}|^2 + \mathrm{tr}\,(\mathbb{L}^3)\Big] - \varepsilon_2\Big[\Delta_{\mathcal{S}}K + K|\mathbb{L}|^2 - \tfrac{1}{2}K^3\Big] + \mu^+\rho - \Psi^-.\end{aligned} \tag{13.11}$$

Interestingly, when the strain energy Ψ^- at the interface is negligible and μ^+ is constant, then (13.11) is identical in form to the purely mechanical interface-controlled evolution equation (12.11), but with $\beta(\mathbf{n})$ replaced by $\beta(\mathbf{n}) + \rho^2/\alpha(\mathbf{n})$ and $[\![\Psi]\!]$ replaced by $\mu^+\rho$.

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Appendices

A Derivation of the unified normal balance via the principle of virtual work

Our use of configurational forces and moments is nonstandard and for that reason we present an alternative verification of the unified normal balance using the principle of virtual power.

We consider a virtual motion of the surface $\mathcal{S}$ at a fixed time t; that is, we presume that $\mathcal{S}$ (and hence $\mathbf{n}$ and $\mathbb{L}$) are known at t and consider the fields V, $\mathring{\mathbf{n}}$ and $\mathring{\mathbb{L}}$ as *virtual velocities* to be specified independently in a manner consistent with (2.19) and the constraint $\mathring{\mathbb{L}}\mathbf{n} = -\mathbb{L}\mathring{\mathbf{n}}$. More specifically, denoting the virtual fields by $\tilde{V}$ (for V), $\tilde{\mathbf{n}}$ (for $\mathring{\mathbf{n}}$), and $\tilde{\mathbb{L}}$ (for $\mathring{\mathbb{L}}$) to differentiate them from fields associated with the actual motion of the interface, we require that

$$\left.\begin{aligned}\tilde{\mathbf{n}} &= -\nabla_{\mathcal{S}}\tilde{V},\\ (\tilde{\mathbb{L}})_{\tan} &= -(\nabla_{\mathcal{S}}\tilde{\mathbf{n}})_{\tan} + \tilde{V}\,\mathbb{L}^2,\\ \tilde{\mathbb{L}}\mathbf{n} &= -\mathbb{L}\tilde{\mathbf{n}}, \qquad \tilde{\mathbb{L}} = \tilde{\mathbb{L}}^{\top},\end{aligned}\right\} \tag{A.1}$$

and that $\tilde{V}$, $\tilde{\mathbf{n}}$, and $\tilde{\mathbb{L}}$ vanish in a neighborhood of the relative boundary $\partial\mathcal{S}$ of $\mathcal{S}$ (a restriction that allows for a discussion of virtual power without regard to contributions on $\partial\mathcal{S}$). For convenience, we refer to the list

$$\mathcal{V} = (\tilde{V}, \tilde{\mathbf{n}}, \tilde{\mathbb{L}})$$

as a *generalized virtual velocity*.

The principle of virtual power asserts that in any virtual motion the power expended on $\mathcal{S}$ by material (or bodies) external to $\mathcal{S}$ be balanced by the power expended within $\mathcal{S}$. The

external expenditure of power is presumed to arise from the external (scalar) force c whose working accompanies the normal motion of $\mathcal{S}$:

$$\mathcal{W}_{\rm ext}(\mathcal{V}) = \int_{\mathcal{S}} c\tilde{V}\, da \tag{A.2}$$

(cf. (6.5)). The power expended *internally* results from the actions of (i) the couple $\mathbf{m}$ whose working accompanies the rotation of $\mathcal{S}$, (ii) the couple-stress $\mathbb{M}$ whose working accounts for temporal changes in the curvature of $\mathcal{S}$, (iii) the internal force π whose working accompanies the normal motion of $\mathcal{S}$, and (iv) the surface tension σ whose working accompanies temporal changes in the area of $\mathcal{S}$. We therefore write the internal power in the form

$$\mathcal{W}_{\rm int}(\mathcal{V}) = -\int_{\mathcal{S}} \big[(\sigma K + \pi)\tilde{V} + \mathbf{m}\cdot\tilde{\mathbf{n}} + \mathbb{M}\cdot(\tilde{\mathbb{L}})_{\rm tan}\big]\, da \tag{A.3}$$

(cf. (8.2)). The principle of virtual power then requires that

$$\mathcal{W}_{\rm ext}(\mathcal{V}) = \mathcal{W}_{\rm int}(\mathcal{V}) \tag{A.4}$$

for all generalized virtual velocities $\mathcal{V}$.

By $(\text{A.1})_2$,

$$\mathbf{m}\cdot\tilde{\mathbf{n}} = -\nabla_{\mathcal{S}}\tilde{V}\cdot\mathbf{m} = -{\rm div}_{\mathcal{S}}(\tilde{V}\mathbf{m}) + \tilde{V}{\rm div}_{\mathcal{S}}\mathbf{m},$$

and, by $(\text{A.1})_3$,

$$\begin{aligned}\mathbb{M}\cdot(\tilde{\mathbb{L}})_{\rm tan} &= \mathbb{M}\cdot(-\nabla_{\mathcal{S}}\tilde{\mathbf{n}} + \tilde{V}\,\mathbb{L}^2)\\ &= \tilde{V}\mathbb{M}\cdot\mathbb{L}^2 - {\rm div}_{\mathcal{S}}(\mathbb{M}\tilde{\mathbf{n}}) + \tilde{\mathbf{n}}\cdot{\rm div}_{\mathcal{S}}\mathbb{M},\end{aligned}$$

where

$$\begin{aligned}\tilde{\mathbf{n}}\cdot{\rm div}_{\mathcal{S}}\mathbb{M} &= -\nabla_{\mathcal{S}}\tilde{V}\cdot{\rm div}_{\mathcal{S}}\mathbb{M} \;=\; -\nabla_{\mathcal{S}}\tilde{V}\cdot\mathbb{P}{\rm div}_{\mathcal{S}}\mathbb{M}\\ &= -{\rm div}_{\mathcal{S}}(\tilde{V}\mathbb{P}{\rm div}_{\mathcal{S}}\mathbb{M}) + \tilde{V}{\rm div}_{\mathcal{S}}(\mathbb{P}{\rm div}_{\mathcal{S}}\mathbb{M}),\end{aligned}$$

and, by (2.3),

$$\begin{aligned}{\rm div}_{\mathcal{S}}(\mathbb{P}{\rm div}_{\mathcal{S}}\mathbb{M}) &= {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} - {\rm div}_{\mathcal{S}}\big((\mathbf{n}\cdot{\rm div}_{\mathcal{S}}\mathbb{M})\mathbf{n}\big)\\ &= {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} - {\rm div}_{\mathcal{S}}\big((\mathbb{L}\cdot\mathbb{M})\mathbf{n}\big)\\ &= {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} + (\mathbb{L}\cdot\mathbb{M})K.\end{aligned}$$

Thus the internal power can be rewritten as

$$\mathcal{W}_{\rm int}(\mathcal{V}) = -\int_{\mathcal{S}}\big(\sigma K + \pi + {\rm div}_{\mathcal{S}}\mathbf{m} + {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} + \mathbb{M}\cdot(\mathbb{L}^2 + K\mathbb{L})\big)\tilde{V}\, da. \tag{A.5}$$

By (A.2) and (A.5), (A.4) reduces to

$$\int_{\mathcal{S}}\big(\sigma K + \pi + {\rm div}_{\mathcal{S}}\mathbf{m} + {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} + \mathbb{M}\cdot(\mathbb{L}^2 + K\mathbb{L}) + c\big)\tilde{V}\, da = 0.$$

Since this relation must hold for all smooth fields $\tilde{V}$ that vanish in a neighborhood of $\partial\mathcal{S}$, the fundamental lemma of the calculus of variations yields the unified normal balance at the interface (7.10):

$$\sigma K + \pi + {\rm div}_{\mathcal{S}}\mathbf{m} + {\rm div}_{\mathcal{S}}{\rm div}_{\mathcal{S}}\mathbb{M} + \mathbb{M}\cdot(\mathbb{L}^2 + K\mathbb{L}) + c = 0.$$

The converse assertion — that (7.10) implies the principle of virtual power — follows from reversing the foregoing argument.

B Surface identities

Here, we derive the identities $(2.14)_2$, (2.19), (2.22) and (11.1).

In verifying $(2.14)_2$, we recall that, at any time t, $\mathbf{n}$ can be extended smoothly to a *three-dimensional* neighborhood of any given point $\mathbf{x}$ of the evolving surface $\mathcal{S}$. By (2.12) and $(2.8)_2$,

$$L_{ik} = -n_{i,j}P_{jk}, \tag{B.1}$$

where $(\ )_{,i}$ denotes differentiation with respect to the i-th cartesian coordinate, and summation over repeated indices is implied. The symmetry of $\mathbb{L}$ then yields

$$n_{i,j}P_{jk} = n_{k,j}P_{ji}, \tag{B.2}$$

and, by (2.13) and (B.1),

$$K = -n_{i,j}P_{ji}. \tag{B.3}$$

Moreover, the identity (verified below)

$$(\mathrm{div}_{\mathcal{S}}L)_i = -(n_{i,j}P_{jk})_{,r}P_{rk}, \tag{B.4}$$

when combined with (B.2), yields

$$(\mathrm{div}_{\mathcal{S}}L)_i = -n_{k,jr}P_{ji}P_{rk} - n_{k,j}P_{rk,j}P_{rk}. \tag{B.5}$$

Consider the first term on the right hand side of (B.5):

$$-n_{k,jr}P_{ji}P_{rk} = -(n_{k,r}P_{rk})_{,j}P_{ji} + n_{k,r}P_{rk,j}P_{ij}.$$

By (B.3) and (2.3),

$$\begin{aligned}-n_{k,jr}P_{ji}P_{rk} &= (\nabla K)_j P_{ji} - P_{ji}n_{k,r}(n_{r,j}n_k + n_r n_{k,j})\\ &= (\nabla_{\mathcal{S}}K)_i - (\nabla_{\mathcal{S}}n)_{ri}[(\nabla n)^{\top}n]_r - (\nabla_{\mathcal{S}}n)_{ki}[(\nabla n)n]_k,\end{aligned}$$

and, $\mathbb{L}$ being tangential,

$$\mathbb{L}^{\top}\mathbf{n} = \mathbb{P}(\nabla\mathbf{n})^{\top}\mathbf{n} = (\nabla\mathbf{n})^{\top} - (\mathbf{n}\otimes\mathbf{n})(\nabla\mathbf{n})^{\top}\mathbf{n} = 0,$$

from which it follows that

$$(\nabla_{\mathcal{S}}\mathbf{n})[(\nabla\mathbf{n})^{\top}\mathbf{n}] = (\nabla_{\mathcal{S}}\mathbf{n})(\mathbf{n}\otimes\mathbf{n})(\nabla\mathbf{n})^{\top}\mathbf{n} = -(\mathbf{n}\cdot(\nabla\mathbf{n})\mathbf{n})\mathbb{L}\mathbf{n} = 0.$$

Thus,

$$-n_{k,jr}P_{ji}P_{rk} = (\nabla_{\mathcal{S}}K)_i - (L(\nabla n)n)_i. \tag{B.6}$$

As for the second term on the right hand side of (B.5), we have

$$\begin{aligned}-n_{k,j}P_{ji,r}P_{rk} &= n_{k,j}(n_{j,r}n_i + n_j n_{i,r})P_{rk}\\ &= n_{k,j}(n_{j,r}P_{rk})n_i + (n_{i,r}P_{rk})n_{k,j}n_j\\ &= -n_{k,j}L_{jk}n_i - L_{ik}(\nabla n)_{kj}n_j,\end{aligned}$$

and, $\mathbb{L}$ being tangential and symmetric,

$$\begin{aligned}-n_{k,j}P_{ji,r}P_{rk} &= -n_{k,j}P_{jr}L_{rk}n_i - (L(\nabla n)n)_i\\ &= L_{rk}L_{rk}n_i - (L(\nabla n)n)_i\\ &= (\mathbb{L}\cdot\mathbb{L})n_i - (L(\nabla n)n)_i.\end{aligned} \tag{B.7}$$

Finally, combining (B.6) and (B.7), we arrive at $(2.14)_2$:

$$\mathrm{div}_{\mathcal{S}}\mathbb{L} = \nabla_{\mathcal{S}}K + (\mathbb{L}\cdot\mathbb{L})\mathbf{n}. \tag{B.8}$$

For this derivation to be complete, it suffices to establish (B.4). First, note that the right hand side of (B.4) can be rewritten as

$$\begin{aligned} -(n_{i,j}P_{jk})_{,r}P_{rk} &= -n_{i,jr}P_{jr} + n_{i,j}(n_j n_{k,r} + n_{j,r}n_k)P_{rk} \\ &= -P_{jr}n_{i,jr} + n_{i,j}n_{j,r}(P_{rk}n_k) + (n_{k,r}P_{rk})n_{i,j}n_j \\ &= -P_{jk}n_{i,jk} + (n_{l,j}P_{jl})n_{i,k}n_k. \end{aligned} \tag{B.9}$$

Next, by (2.6) and (2.12),

$$\mathbf{a}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{L} = -\mathrm{div}_{\mathcal{S}}(\mathbb{P}^{\top}(\nabla\mathbf{n})^{\top}\mathbf{a}) \tag{B.10}$$

$$= -\mathbf{a}\cdot(\nabla\mathbf{n})\mathrm{div}_{\mathcal{S}}\mathbb{P} - \mathbb{P}\cdot\nabla((\nabla\mathbf{n})^{\top}\mathbf{a})\mathbb{P}, \tag{B.11}$$

which, by $(2.14)_1$, reduces as

$$\mathbf{a}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{L} = \mathbf{a}\cdot[\mathrm{tr}\,(\nabla\mathbf{n})\mathbb{P})](\nabla\mathbf{n})\mathbf{n} - \mathbf{b}\cdot\mathbf{a}, \tag{B.12}$$

with

$$b_k = P_{ji}n_{k,ji}. \tag{B.13}$$

Since $\mathbf{a}$ is arbitrary, (B.12) reduces to

$$(\mathrm{div}_{\mathcal{S}}L)_i = (n_{l,j}P_{jl})n_{i,k}n_k - P_{jk}n_{i,jk}. \tag{B.14}$$

Comparison of (B.14) and (B.9) yields the desired identity.

Next, we establish the identity $(2.19)_2$. By $(2.8)_2$, (2.18) and the chain rule,

$$\begin{aligned} \nabla_{\mathcal{S}}\mathring{\mathbf{n}} &= \nabla[\dot{\mathbf{n}} + V(\nabla\mathbf{n})\mathbf{n}]\mathbb{P} \\ &= \left[\dot{\overline{\nabla\mathbf{n}}} + V(\nabla\nabla\mathbf{n})\mathbf{n} + \nabla\mathbf{n}\nabla(V\mathbf{n})\right]\mathbb{P} \\ &= \left[\mathring{\overline{\nabla\mathbf{n}}} + \nabla\mathbf{n}(V\nabla\mathbf{n} + \mathbf{n}\otimes\nabla V)\right]\mathbb{P}. \end{aligned} \tag{B.15}$$

Thus, by (2.12),

$$\nabla_{\mathcal{S}}\mathring{\mathbf{n}} = -\mathring{\mathbb{L}} - \nabla\mathbf{n}\mathring{\mathbb{P}} + V(\nabla\mathbf{n})^2\mathbb{P} + \nabla\mathbf{n}(\mathbf{n}\otimes\nabla V)\mathbb{P}, \tag{B.16}$$

where

$$\mathring{\mathbb{P}} = -\mathring{\mathbf{n}}\otimes\mathbf{n} - \mathbf{n}\otimes\mathring{\mathbf{n}}. \tag{B.17}$$

Also, by $(2.19)_1$,

$$\nabla\mathbf{n}(\mathbf{n}\otimes\nabla V)\mathbb{P} = -(\nabla\mathbf{n})\mathbf{n}\otimes\mathring{\mathbf{n}}. \tag{B.18}$$

Moreover, from (2.12) and $(2.8)_2$, it follows that

$$(\nabla\mathbf{n})^2\mathbb{P} = \mathbb{L}^2. \tag{B.19}$$

Finally, substitution of (B.17), (B.18) and (B.19) into (B.16) yields $(2.19)_2$.

We now establish the identities (2.22). By (2.21), (2.20) and the chain rule,

$$\overset{\square}{\mathbf{n}} = \mathbf{n}_t + (\nabla\mathbf{n})\mathbf{q} = \mathbf{n}_t + U(\nabla\mathbf{n})\boldsymbol{\nu} + V(\nabla\mathbf{n})\mathbf{n} + (\nabla\mathbf{n})\mathbf{q}_{\mathrm{ext}}, \tag{B.20}$$

which, by (2.18) and the chain rule, reduces to

$$\overset{\square}{\mathbf{n}} = \mathring{\mathbf{n}} + U(\nabla\mathbf{n})\boldsymbol{\nu} + (\nabla\mathbf{n})\mathbf{q}_{\mathrm{ext}}. \tag{B.21}$$

The identity $(2.22)_2$ then follows from (B.21), (2.12) and the fact that $\boldsymbol{\nu}$ and $\mathbf{q}_{\mathrm{ext}}$ are tangential. The derivation of $(2.22)_1$ proceeds along identical lines and is thus omitted.

We conclude by verifying (11.1). The first of these identities is a trivial consequence of (2.13). As for the second, by (2.6), (2.3) and (2.13),

$$\begin{aligned} \mathbf{a}\cdot\mathrm{div}_{\mathcal{S}}(K\mathbb{P}) &= \mathrm{div}_{\mathcal{S}}(K(\mathbf{a} - (\mathbf{a}\cdot\mathbf{n})\mathbf{n}) \\ &= \mathbf{a}\cdot\nabla_{\mathcal{S}}K - K(\mathbf{a}\cdot\mathbf{n})\mathrm{div}_{\mathcal{S}}\mathbf{n} \qquad \text{(B.22)} \\ &= \mathbf{a}\cdot\nabla_{\mathcal{S}}K + K^2\mathbf{a}\cdot\mathbf{n}, \qquad \text{(B.23)} \end{aligned}$$

where $\mathbf{a}$ is a constant vector. The requirement that this relation holds for any such $\mathbf{a}$ yields $(11.1)_2$.

C Construction of the evolving surface used in obtaining thermodynamical restrictions

We here construct an evolving surface and an associated chemical potential such that, at $\mathbf{x}_0 = 0$ and $t_0 = 0$, the superficial fields

$$V,\ \mathbf{n},\ \mathring{\mathbf{n}},\ \mathbb{L},\ (\mathring{\mathbb{L}})_{\rm tan},\ \mu,\ \nabla_{\mathcal{S}}\mu$$

have arbitrarily prescribed values.[29] This result is used in our derivation of the thermodynamically restricted constitutive relations (10.5).

Consider the quadratic surface $\mathcal{S} = \mathcal{S}(t)$ corresponding to the zero level set of the function

$$\varphi(\mathbf{x},t) = \frac{1}{2}\mathbf{x}\cdot\mathbb{K}(t)\mathbf{x} + \mathbf{k}(t)\cdot\mathbf{x} + a(t), \tag{C.1}$$

where $\mathbb{K}(t)$ is a symmetric tensor, $\mathbf{k}(t)$ is a unit vector and $a(t)$ a scalar satisfying $a(0) = 0$, so that $\mathbf{x}_0 = \mathbf{0}$ belongs to $\mathcal{S}(0)$.[30] Then, for $\mathbf{x} \in \mathcal{S}(t)$, the unit normal $\mathbf{n}(\mathbf{x},t)$, the (scalar) normal velocity $V(\mathbf{x},t)$ and the curvature tensor $\mathbb{L}(\mathbf{x},t)$ are given by

$$\left.\begin{aligned} \mathbf{n}(\mathbf{x},t) &= \frac{\nabla\varphi(\mathbf{x},t)}{\ell(\mathbf{x},t)}, \quad \ell(\mathbf{x},t) = |\nabla\varphi(\mathbf{x},t)| \\ V(\mathbf{x},t) &= -\frac{\dot\varphi(\mathbf{x},t)}{\ell(\mathbf{x},t)}, \\ \mathbb{L}(\mathbf{x},t) &= -\frac{1}{\ell(\mathbf{x},t)}\mathbb{P}(\mathbf{x},t)(\nabla\nabla\varphi(\mathbf{x},t))\mathbb{P}(\mathbf{x},t), \end{aligned}\right\} \tag{C.2}$$

with

$$\mathbb{P}(\mathbf{x},t) = \mathbf{1} - \frac{1}{\ell^2(\mathbf{x},t)}\nabla\varphi(\mathbf{x},t)\otimes\nabla\varphi(\mathbf{x},t).$$

(Note that the fields in (C.2) are well defined on all of $\mathbb{R}^3$.)

From (C.2) and (C.1), it follows that

$$V_0 = -\dot a(0), \qquad \mathbf{n}_0 = \mathbf{k}(0), \qquad \mathbb{L}_0 = -\mathbb{P}_0\mathbb{K}(0)\mathbb{P}_0, \tag{C.3}$$

where Φ_0 denotes the value of a scalar, vector or tensor field Φ at $\mathbf{x}_0 = 0$ and $t_0 = 0$ (e.g., $\mathbb{P}_0 = \mathbf{1} - \mathbf{k}(0)\otimes\mathbf{k}(0)$). Moreover, by $(\text{C.2})_{1,2}$, (C.1) and the chain rule,

$$\mathring{\mathbf{n}}_0 = \dot{\mathbf{k}}(0) - \dot a(0)\mathbb{P}_0\mathbb{K}(0)\mathbf{n}_0(0). \tag{C.4}$$

In addition, $(\text{C.2})_3$ yields

$$(\mathring{\mathbb{L}})_{\rm tan} = -\frac{1}{\ell}\Big\{\mathbb{P}\Big(\dot{\mathbb{K}} - \frac{\mathring{\ell}}{\ell}\mathbb{K}\Big)\mathbb{P} - (\mathring{\mathbf{n}}\otimes\mathbf{n})\mathbb{K}\mathbb{P} - \mathbb{P}\mathbb{K}(\mathbf{n}\otimes\mathring{\mathbf{n}})\Big\}. \tag{C.5}$$

Next, given any two orthogonal vectors $\mathbf{a}$ and $\mathbf{b}$ with $|\mathbf{a}| = 1$, and an arbitrary function $\delta(t)$ satisfying $\delta(0) = 0$ and $\dot\delta(0) = 1$, let

$$\mathbf{k}(t) = \frac{\mathbf{a} + \delta(t)\mathbf{b}}{|\mathbf{a} + \delta(t)\mathbf{b}|}. \tag{C.6}$$

Similarly, given any scalar α, any pair of symmetric tensors $\mathbf{A}$ and $\mathbf{B}$ with $\mathbf{A} = \mathbb{P}_0\mathbf{A}\mathbb{P}_0$ and $\mathbf{B} = \mathbb{P}_0\mathbf{B}\mathbb{P}_0$, and any function $\varepsilon(t)$ satisfying $\varepsilon(0) = 0$ and $\dot\varepsilon(0) = 1$, let

$$a(t) = \alpha t, \qquad \mathbb{K}(t) = \mathbf{A} + \varepsilon(t)\mathbf{B}. \tag{C.7}$$

[29] It can then easily be shown that the constraints $\mathbf{n}\mathring{\mathbf{n}} = 0$ and $\mathring{\mathbb{L}}\mathbf{n} = -\mathbb{L}\mathring{\mathbf{n}}$ are satisfied by this construction.

[30] Trivially, $\nabla\varphi(\mathbf{x},t)$ never vanishes on $\mathcal{S}$.

Then, by (C.3)-(C.7),

$$V_0 = -\alpha, \qquad \mathbf{n}_0 = \mathbf{a}, \qquad \mathring{\mathbf{n}}_0 = \mathbf{b}, \tag{C.8}$$

so that, by $(C.3)_3$ and (C.5),

$$\mathbb{L}_0 = -\mathbf{A}, \qquad \big((\mathring{\mathbb{L}})_{\tan}\big)_0 = -\mathbf{B}.$$

To complete the construction, consider a chemical potential of the form

$$\mu(\mathbf{x}) = \boldsymbol{\beta}_0 \cdot \mathbf{x} + \beta_1$$

with $\boldsymbol{\beta}_0$ a constant vector such that $\boldsymbol{\beta}_0 \cdot \mathbf{n}_0 = 0$ and β_1 a constant scalar. Then

$$\mu_0 = \beta_1, \qquad (\nabla_{\mathcal{S}}\mu)_0 = \boldsymbol{\beta}_0.$$

Thus appropriate choices of α, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{A}$, $\mathbf{B}$, β_1 and $\boldsymbol{\beta}_0$ allow for the arbitrary specification of V, $\mathbf{n}$, $\mathring{\mathbf{n}}$, $\mathbb{L}$, $(\mathring{\mathbb{L}})_{\tan}$, μ and $\nabla_{\mathcal{S}}\mu$ at $\mathbf{x}_0 = 0$ and $t_0 = 0$.

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